

Separation and Recovery of Monomers in Industrial Streams by Adsorption

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by

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Abstract

In this work, the focus was given to the development of adsorption-based separation processes to recover unreacted monomers in nitrogen-rich gas vent streams from the poly(vinyl chloride), polyethylene, and polypropylene industries. According to the supplied specifications and the emission standards present in the literature, the designed systems aim to produce a nitrogen stream with monomer contamination lower than the established limit for free air release and a monomer stream with a purity high enough to be recycled into the polymerization process.

Using a magnetic suspension microbalance, adsorption equilibrium data for vinyl chloride and nitrogen were obtained on samples of Maxsorb, Carbotech DGK, and on MIL-100(Fe) material. Adsorption equilibrium isotherms for ethylene and propylene were also obtained on MIL-100(Fe). All equilibrium measurements were performed at a pressure range of 0 to 5 bar and at 303, 323, 373 K, except for vinyl chloride, measured only up to 2.5 bar. A brief characterization of the new adsorbent materials is given, and the variation of the isosteric heat is calculated for the measured equilibrium isotherms.

The dynamic adsorption behavior of ethylene, propylene, and nitrogen was measured by single, binary, and pseudo-binary breakthrough curves on a bench scale single column PSA unit. In turn, the breakthrough experiments were used to validate the single and multicomponent equilibrium isotherms and the developed fixed bed model.

Based on equilibrium data obtained from the literature, preliminary work was developed to capture and recover vinyl chloride on Pittsburgh PCB activated carbon. The viability and performance of the separation were tested in this work, and the multitubular temperature and pressure swing adsorption process was developed and validated using a 2D and an equivalent 1D fixed bed mathematical model. Together with the obtained experimental equilibrium data, a total of 6 adsorption separation cycles were successfully designed for the separation and recovery of a vinyl chloride/nitrogen mixture, producing a vinyl chloride stream with 95 %(v/v) purity and a nitrogen stream with a vinyl chloride contamination

below 8 ppm(w/w). Of these processes, based on their performance, two systems are recommended.

A five-step MIL-100(Fe) PSA cycle, operated at a temperature of 343 K and between a pressure range of 0.1 to 7 bar, achieved a vinyl chloride productivity and recovery capacity of 3.52 mol/kg_{ads}.h and 71.89 kg_{VCM}/(m³_{unit}.h) for thermal energy consumption of 2.48 MJ/kg_{VCM}.

A six-step Maxsorb MT-TPSA unit, designed for an operating range of 1 to 2.5 bar and 303 to 393 K, achieved a vinyl chloride productivity and recovery capacity of 8.41 mol/kg_{ads}.h and 69 kg_{VCM}/(m³_{unit}.h). A total thermal energy consumption of 3.05 MJ/kg_{VCM}, of which 1.82 MJ/kg_{VCM}, is necessary to supply thermal energy during the heating stages and electrical energy for the operation of the gas and liquid pumps.

For ethylene and propylene recovery, a PSA and an MT-TPSA cycle each, were successfully developed using MIL-100(Fe), capable of producing a nitrogen stream with monomer contamination below 20 ppm(v/v) and a monomer stream with at least 95 %(v/v) purity. For the recovery of ethylene, the PSA cycle is preferred, while for propylene recovery, both cycles are presented as possible solutions.

For ethylene recovery, a five step MIL-100(Fe) PSA system, operated at a temperature of 343 K and pressure range of 0.3 to 9 bar, is designed to achieve an ethylene productivity and recovery capacity of 2.23 mol/kg_{ads}.h and 21.03 kg_{C₂H₄}/(m³_{unit}.h), for an equivalent thermal energy consumption of 2.48 MJ/kg_{C₂H₄}.

For propylene recovery, a five-step MIL-100(Fe) PSA cycle, operated at a temperature of 343 K and between a pressure range of 0.3 to 8 bar, achieved propylene productivity and recovery capacity of 1.48 mol/kg_{ads}.h and 21.03 kg_{C₃H₆}/(m³_{unit}.h) for a total equivalent thermal energy consumption of 4.37 MJ/kg_{C₃H₆}.

A six-step MIL-100(Fe) MT-TPSA cycle, designed for an operating range of 1 to 5 bar and 303 to 393 K, was capable of accomplishing a propylene productivity and recovery capacity of 6.72 mol/kg_{ads}.h and 38.91 kg_{C₃H₆}/(m³_{unit}.h), for a total thermal energy consumption of 7.46

MJ/kg_{C₃H₆}. Additionally, only 4.65 MJ/kg_{C₃H₆} are necessary to supply thermal energy during the heating stages and electrical power for the operation of the gas and liquid pumps.

Resumo

O foco deste trabalho foi direcionado para o desenvolvimento de sistemas de separação por adsorção para recuperar monómeros não reagidos em correntes de purga ricas em azoto das indústrias de policloreto de vinilo, polietileno e polipropileno.

Uma microbalança de suspensão magnética foi usada para a obtenção de dados de adsorção de equilíbrio para cloreto de vinilo e azoto em amostras de Maxsorb, Carbotech DGK e MIL-100(Fe). Isotérmicas de equilíbrio de adsorção foram também obtidas para etileno e propileno em MIL-100(Fe). Todas as medições de equilíbrio foram realizadas numa gama de pressão de 0 a 5 bar e para uma temperatura de 303, 323 e 373 K, exceto para o cloreto de vinilo, medido só até 2.5 bar. Uma breve caracterização dos novos materiais adsorventes é reportada, e a variação do calor isostérico é calculado para as isotérmicas de equilíbrio medidas.

O comportamento de adsorção dinâmico de etileno, propileno e azoto é quantificado por curvas de rutura de componente puro, misturas binárias e experiências pseudo-binárias, usando uma unidade de PSA de uma coluna de escala laboratorial. Por sua vez, as experiências de rutura foram usadas para a validação dos modelos de equilíbrio puro e multicomponente e do modelo matemático representante de uma coluna de adsorção.

Com base nos dados de equilíbrio obtidos na literatura, trabalho preliminar foi desenvolvido para capturar e recuperar cloreto de vinilo no carvão ativado Pittsburgh PCB. A viabilidade e desempenho da separação proposta foram testados neste trabalho, e o processo MT-TPSA foi desenvolvido e validado usando um modelo matemático de uma coluna de adsorção a 2D e 1D equivalente. Juntamente com os dados de equilíbrio de adsorção obtidos experimentalmente, um total de 6 ciclos de separação por adsorção foram desenhados com sucesso para a separação e recuperação de uma mistura de cloreto de vinilo/azoto, produzindo uma corrente de cloreto de vinilo com 95 % (v/v) de pureza e uma corrente de azoto com uma contaminação de cloreto de vinilo abaixo de 8 ppm(w)/w). Destes processos, com base no seu desempenho, 2 sistemas são recomendados:

Um ciclo de PSA com cinco passos em MIL-100(Fe), operado a 343 K e a uma gama de temperaturas de 0.1 a 7 bar, é capaz de alcançar uma produtividade e capacidade de recuperação de 3.52 mol/kg_{ads}.h e 71.89 kg_{VCM}/(m³_{unit}.h), para um consumo energético térmico de 2.48 MJ/kg_{VCM}.

Um ciclo de MT-TPSA com seis passos em Maxsorb, desenhado para uma gama operacional de 1 a 2.5 bar e 303 a 393 K, alcançou uma produtividade e capacidade de recuperação de 8.41 mol/kg_{ads}.h e 69 kg_{VCM}/(m³_{unit}.h). Um consumo energético térmico total de 3.05 MJ/kg_{VCM}, do qual 1.82 MJ/kg_{VCM} é necessário para fornecer energia térmica durante os estágios de aquecimento e energia elétrica para a operação das bombas de gás e líquido.

Para a recuperação de etileno e propileno, um ciclo de PSA e MT-TPSA cada foram desenvolvidos com sucesso usando MIL-100(Fe), capazes de produzir uma corrente de azoto com uma contaminação de monómero abaixo de 20 ppm(v/v) e uma corrente de monómero com uma pureza mínima de 95 %(v/v). Para a recuperação de etileno, o ciclo de PSA é preferido; para a recuperação de propileno, ambos os ciclos são apresentados como possíveis soluções.

Para a recuperação de etileno, um ciclo de PSA com 5 passos em MIL-100(Fe), operado a uma temperatura de 343 K e uma gama de pressão de 0.3 a 9 bar, é desenhado para atingir uma produtividade e capacidade de recuperação de 2.23 mol/kg_{ads}.h e 21.03 kg_{C₂H₄}/(m³_{unit}.h), para um consumo energético térmico equivalente de 2.48 MJ/kg_{C₂H₄}.

Para a recuperação de propileno, um ciclo de PSA com 5 passos em MIL-100(Fe), operado a uma temperatura de 343 K e numa gama de pressão de 0.3 a 8 bar, é capaz de atingir uma produtividade e capacidade de recuperação de 1.48 mol/kg_{ads}.h e 21.03 kg_{C₃H₆}/(m³_{unit}.h), para um consumo energético térmico equivalente de 4.37 MJ/kg_{C₃H₆}.

Um ciclo de MT-TPSA com seis passos em MIL-100(Fe), desenhado para uma gama operacional de temperatura e pressão de 303 a 393 K e 1 a 5 bar, é capaz de atingir uma produtividade e capacidade de recuperação de 6.72 mol/kg_{ads}.h e 38.91 kg_{C₃H₆}/(m³_{unit}.h) e com um consumo energético térmico de 7.46 MJ/kg_{C₃H₆}. Adicionalmente, apenas 4.65

$\text{MJ/kg}_{\text{C}_3\text{H}_6}$ são necessários para fornecer energia térmica nos estágios de aquecimento e energia elétrica para a operação das bombas de gás e líquidas.

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List of Symbols

Nomenclature

a_p	particle specific area (m^2)
b	affinity parameter (bar^{-1})
b_0	pre-exponential factor (bar^{-1})
Bi_h	thermal Biot number
C_g	gas phase concentration ($mol\ m^{-3}$)
$C_{g\ t}$	total gas phase concentration ($mol\ m^{-3}$)
Clr	tube clearance (m)
C_p	specific heat at constant pressure ($J\ mol^{-1}\ K^{-1}$)
D_{ax}	axial dispersion coefficient ($m^2\ s^{-1}$)
$D_{i,j}$	binary molecular diffusivity ($m^2\ s^{-1}$)
D_K	Knudsen diffusivity ($m^2\ s^{-1}$)
D_m	molecular diffusivity ($m^2\ s^{-1}$)
d_p	particle diameter (m)
D_p	pore diffusivity ($m^2\ s^{-1}$)
D_r	radial dispersion coefficient ($m^2\ s^{-1}$)
e	wall thickness (m)
E	energy consumption ($J\ kg_{product}^{-1}$)
E_{gas}	gas pumps electrical energy consumption ($J\ kg_{product}^{-1}$)
E_{liquid}	liquid pumps electrical energy consumption ($J\ kg_{product}^{-1}$)
E_{th}	thermal energy consumption ($J\ kg_{product}^{-1}$)

f	friction factor
F	molar flowrate ($mol\ s^{-1}$)
g	gravitational acceleration constant ($m\ s^{-2}$)
G_S	shell side cross flow mass velocity ($kg\ s^{-1}$)
H	Henry constant ($mol\ kg^{-1}\ bar^{-1}$)
h	heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
h_{clear}	heat transfer coefficient without fouling ($W\ m^{-2}\ K^{-1}$)
h_{dirty}	heat transfer coefficient with fouling ($W\ m^{-2}\ K^{-1}$)
h_f	film heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
h_{shell}	shell side heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
h_w	wall heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
h_w^0	static contribution to the wall heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
ID	inner diameter of the column/tube (m)
J_C	correction factor for baffle configuration
J_L	correction factor for baffle leakage
J_B	correction factor for bundle and pass partition bypass streams
J_S	correction factor for larger baffle spacing at the inlet and outlet sections
J_R	correction factor for any adverse temperature gradient buildup in laminar flows
j	Colburn j-factor
k_{eff}^0	effective stagnant bed thermal conductivity ($W\ m^{-1}\ K^{-1}$)
k_g	thermal conductivity ($W\ m^{-1}\ K^{-1}$)
k_{SM}	geometric factor for the shape of the particle
k_{LDF}	LDF constant (s^{-1})

m	mass (kg)
$\dot{m}$	mass flowrate ($kg\ s^{-1}$)
M_w	molecular weight ($kg\ mol^{-1}$)
N_B	Number of baffles
N_t	Number of tubes
$N_{t\ cc}$	effective number of tubes crossed in one cross flow section between baffles tips
$N_{t\ cw}$	effective number of tubes rows in window
OD	outer tube diameter (m)
P	pressure (bar)
Pe_r	radial Peclet number
Pr	Prandtl number
P_T	tube pitch (m)
q	solid phase concentration ($mol\ kg^{-1}$)
Q	volumetric flowrate ($m^3\ s^{-1}$)
q^*	solid phase concentration in equilibrium with the gas phase ($mol\ kg^{-1}$)
r	radial direction (m)
R_{dirty}	fouling factor ($m^2\ K\ W^{-1}$)
Re	Reynolds number
R_B	correction factor for bundle bypass effect
R_g	ideal gas constant ($m^3\ bar\ K^{-1}\ mol^{-1}$)
R_L	correction factor for baffle leakage
r_p	average pore radius (m)
Sc	Schmidt number

St	Stanton number
t	time (s)
T	temperature (K)
T_{∞}	external temperature (K)
u	superficial gas velocity ($m\ s^{-1}$)
U_{tube}	tube side overall heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
U_w	external heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)
V	Volume (m^3)
y	molar fraction
z	axial direction (m)

Greek Letters

α	selectivity
α_w	ratio of internal surface area to the volume of the column wall (m^{-1})
α_{wl}	ratio of the log mean surface area to the volume of the column wall (m^{-1})
γ	ratio between the specific heat of the gas mixture at constant pressure and constant volume
ΔH	adsorption enthalpy ($J\ mol^{-1}$)
ΔP	pressure drop (bar)
ΔP_C	pressure drop from central baffles (bar)
ΔP_E	pressure drop from entrance and exit baffles (bar)
ΔP_{shell}	shell side pressure drop (bar)
ΔP_W	pressure drop from window section (bar)

ε	porosity
ε_i/k	minimum pair potential energy (K)
η	efficiency
λ_{ax}	heat axial dispersion coefficient ($Wm^{-1}K^{-1}$)
λ_r	heat radial dispersion coefficient ($Wm^{-1}K^{-1}$)
μ	viscosity (Pa.s)
ρ	density ($kg\ m^{-3}$)
σ	Boltzmann constant
$\sigma_{i,j}$	Characteristic length of the Lennard Jones potential (Å)
τ	tortuosity
Ω	ratio between the tube outer surface area and the clearance volume in the neighborhood of each tube
Ω_D	collision integral

Subscripts

b	bulk
c	cell
eq	equilibrium
f	fluid
g	gas
HX	heat exchanger fluid
i	component
$isos$	isosteric

<i>l</i>	liquid
<i>p</i>	particle
<i>r</i>	radial direction
<i>s</i>	solid
<i>sat</i>	saturation
<i>w</i>	wall
<i>z</i>	axial direction

Abbreviations

1D – 1-dimensional

2D – 2-dimensional

AC – Activated Carbon

BET – Brunauer-Emmett-Teller

C₂H₄ – Ethylene

C₃H₆ – Propylene

DSL – Dual Site Langmuir

HDPE – High Density Polyethylene

LDF – Linear Driving Force

LDPE – Low Density Polyethylene

LLDPE – Linear Low Density Polyethylene

LO – Light Olefins

LUB – Length of Unused Bed

MOF – Metal Organic Framework

MTA – Multitubular Adsorber

MTR – Membrane Technology and Research Inc.

N₂ – Nitrogen

OSHA – Occupational Safety and Health Administration

PE – Polyethylene

PP – Polypropylene

PSA – Pressure Swing Adsorption

PVC – Poly(vinyl Chloride)

TPSA – Temperature Pressure Swing Adsorption

TSA – Temperature Swing Adsorption

VCM – Vinyl Chloride Monomer

VOC – Volatile Organic Compounds

Chapter 1

Introduction



1.1. Relevance and Motivation

Used to describe a pliable or easily moldable material, the term “plastics” is commonly used to depict the wide selection of organic polymers of high molecular mass present in our everyday life. Although human-made polymers existed as early as 1863, the first synthetic plastic invention goes to Leo Baekeland in 1909. Advertised for its myriad applications in the emerging electrical and automotive industries, Bakelite was a cheap, moldable, and quickly set thermosetting material, characteristics that lead to its advantage in mass production processes and set the standards for the future plastic industry.¹

With the increased demand for alternative materials brought forward by world events in the early 20th century, the plastic polymer industry investment led to the discovery, specialization, and application of the many plastic materials that are still used today. With applications in packaging, building and construction, automotive, electrical, agricultural, household, leisure, sports, medical, and others, plastic polymers are as present in everyday life as wood or metal (Figure 1.1). As such, it is not surprising that they represent a growing 359 million tonnes yearly global demand industry². The most common thermoplastic materials are polyethylene, polypropylene, and poly(vinyl chloride), created by a polymerization reaction from the respective monomers: ethylene, propylene, and vinyl chloride. While ethylene and propylene are products of the petrochemical refinery process, vinyl chloride can be produced from either dichloroethane or acetylene.

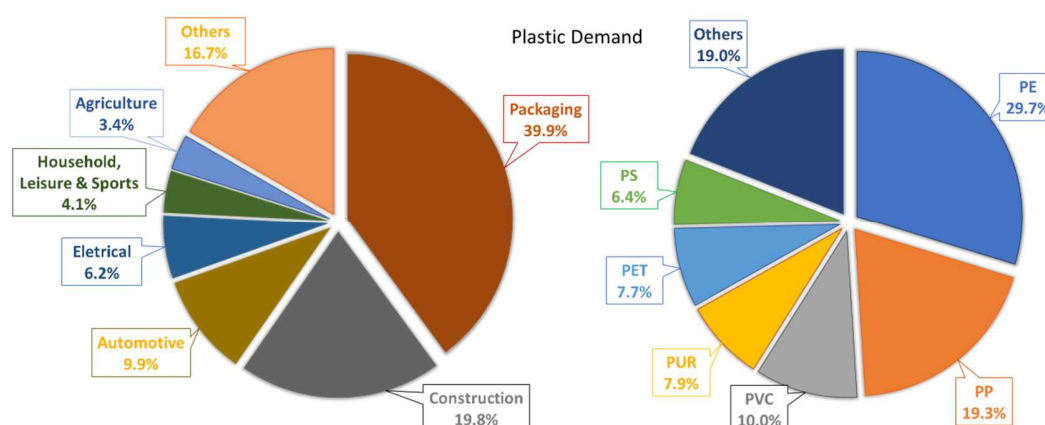


Figure 1.1: Plastic Demand for the EU28+NO/CH by Application (left) and by Polymer Type (right) ²

The polymerization reaction for each monomer can be performed through different processes to create polymers with diverse characteristics and applications. However, depending on the process and the monomer used, a percentage of unreacted monomer will remain in the final polymer. The monomer is purged from the polymer by using a degassing system. Indeed, the polymer is blown to atmospheric pressure and then stripped with a hot inert gas, commonly nitrogen. Together, the emissions from the reactor vent and other equipment purges, the polymer degassing streams have a typical composition of approximately 30:70 % (v/v) monomer/nitrogen. For polyethylene and polypropylene, unreacted monomer accounts for 1 to 2 % (v/v) of the feedstock. For poly(vinyl chloride), this percentage can increase from 10 to 15 % (v/v).^{3,4} In many plants, either due to quality or environmental and health concerns, these vent streams are sent to a flare for incineration. However, as in a typical polyolefin plant, these losses could amount from 2000 to 4000 tonnes of monomer a year; incineration is economically disadvantageous and heavily contributes to increasing the plastic industry carbon footprint. As such, the development of monomer recovery technologies has always been significantly incentivized.

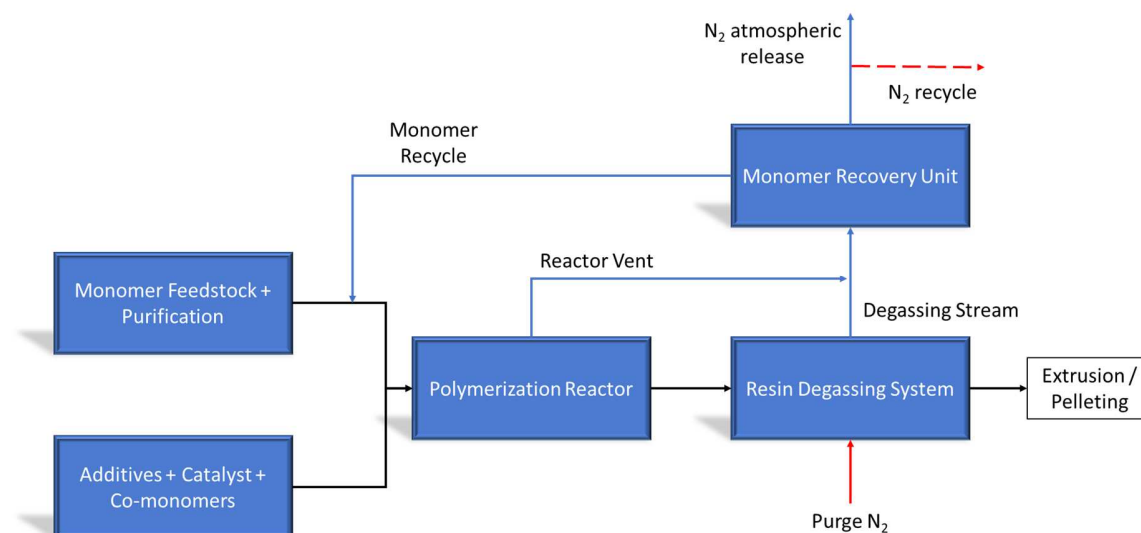


Figure 1.2: Polymer Production Process with a monomer recovery unit

Of the available technologies, the membrane system, coupled with a condenser proposed by the company Membrane Technology and Research Inc., has shown the most success over

the years.⁵ However, the use of high operating pressures and cryogenic refrigeration until the monomer condensation point, while still requiring the use of a flare to release the vented nitrogen, shows that improvement is still possible.

Based on previous work developed by the group^{6,7}, the Metal-Organic Framework (MOF) material MIL-100(Fe) has shown great aptitude for separating a propylene/nitrogen mixture. Capable of achieving a nitrogen and propylene purity of 99.9 % (v/v) and 97.9 % (v/v) by Pressure Swing Adsorption (PSA), it is expected of MIL-100(Fe) to be capable of achieving the same positive results for other monomers. Especially for the separation of a vinyl chloride/nitrogen mixture. The performance of other potential adsorbent materials such as the Maxsorb and Carbotech DGK will be investigated for the recovery of vinyl chloride.

This work will focus on developing cyclic adsorption-based separation systems to separate and recover monomers from purge streams of the plastic polymer industry, mainly polyethylene, polypropylene, and poly(vinyl chloride). This monomer recovery unit must be capable of producing a stream heavy on the monomer, with a high enough purity to be recycled back into the polymerization reactor, and a nitrogen-heavy stream with a monomer content inferior to the respective atmospheric emission limit. The performance of different regeneration and operating schemes, namely PSA and Temperature Swing Adsorption (TSA), and their applicability in the industry will be compared and discussed.

1.2. Objective and Outline

The present work's main objective is to study and develop adsorption-based separation processes for monomer recovery in nitrogen-rich streams from the top producing polymer industries. The applicability of the developed PSA, TPSA, and MT-TPSA cyclic processes in an industrial setting will be discussed and compared to the existing solutions. The adsorption performance of the MOF material MIL-100(Fe) will be tested for the separation of ethylene, propylene, and vinyl chloride in nitrogen mixtures. While the separation

performance of the Pittsburgh, Maxsorb, and Carbotech activated carbons will be investigated solely for the separation of vinyl chloride and nitrogen.

Chapter 1 shows the motivation behind and proposed objectives for developing this thesis and detailing the general outline of this work.

In **Chapter 2**, state of the art concerning the present polymer industry, the focus on monomer emissions, as well as the proposed technologies to control them will be expanded. An exposition is given on adsorption-based separation technology, together with the details and advantages of each of the selected cyclic operation processes. Examples available in the literature of similar research are presented on monomer emission control topics and appropriate adsorption separation processes, and adsorbent materials.

Chapter 3 presents an overview of the adsorbent materials used in this work, a short description of their characterization, and the experimental setup and procedure used in the measurements of adsorption equilibrium and kinetics

In **Chapter 4**, a review on the theory and models used in the characterization of the pure and multicomponent adsorption equilibrium, and kinetics of the adsorbate/adsorbent pairs will be given. A summary will be presented on the theoretical considerations, balance equations, and boundary conditions used in developing the fixed bed models and the PSA, TPSA, and Multitubular (MT-) TPSA cyclic systems.

In **Chapter 5**, the focus was given to the development of a vinyl chloride recovery unit for the separation of a 40:60 %(v/v) vinyl chloride/nitrogen feed at 313 K and 1.15 bar. Based on the existing literature, a preliminary study was elaborated that details the application and performance of a TPSA and a MT-TPSA system using the Pittsburgh PCB activated carbon as the adsorbent material. This separation is later reassessed for Maxsorb, Carbotech DGK, and MIL-100(Fe) following the PSA and MT-TPSA process designs.

Chapter 6 focuses on the separation of light olefins, such as ethylene and propylene, from a nitrogen-rich mixture. MIL-100(Fe) is used as the adsorbent material for both partitions of 30:70 %(v/v) ethylene/nitrogen and propylene/nitrogen feed at 323 K and atmospheric pressure. The pure component equilibrium adsorption behavior is determined

experimentally using a gravimetric suspension balance. Breakthrough experiments on a pilot scale PSA unit are used to determine both the adsorption kinetics and multicomponent equilibrium behavior. Industrial-scale recovery systems are developed following a PSA and MT-TPSA design, and their performance and applicability are compared and discussed.

Finally, **Chapter 7** will cover the conclusions and achievements of this work and suggestions for future work.

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Chapter 2

State of the Art



2.1. Introduction

In recent years, more than half of the global plastic industry has been dedicated to the production of just three plastic polymers: polyethylene, polypropylene, and poly(vinyl chloride).¹ Polyethylene, today the most abundant plastic material overall with a global demand of 93 million metric tons as of 2016², was manufactured for the first time in 1933 as low-density polyethylene (LDPE) at ICI, UK. Depending on the production conditions and process, a wide range of polyethylene polymers with different densities and degrees of branching can be produced, resulting in polyethylene's variety of properties and respective applications. Considered as a general-purpose plastic, polyethylene is characterized for its mechanical strength, flexibility, sealing properties, easy processing, and low cost. As such, its applications generally cover packaging containers and films, plastic bags, wire and cable insulation, agriculture, gas, and water pipes, and even as elastomers and medical prothesis. Indeed, while the softer and more flexible highly-branched low-density polyethylene (LDPE) is used for flexible packaging goods, the more rigid, linear, high-density polyethylene (HDPE), is used for rigid packaging and containers, piping, and consumer goods.³

In 1957, demands for improved product performance and breakthroughs in catalytic technology led to one of the most significant advancements in polyolefins history. The development of Ziegler-Natta catalysts, initially commercialized by the Phillips Petroleum Co., was the initial push that led to the manufacture of both HDPE and polypropylene.^{4,5} Polypropylene is currently the second most popular plastic material, with global production of 56 million metric tons⁶. As propylene is an asymmetric monomer, polypropylene can be produced with different stereochemical configurations. In isotactic polypropylene, all methyl groups are located on the same side of the backbone; in syndiotactic polypropylene, methyl groups are arranged on alternating sides; and in atactic polypropylene these are arranged randomly. While atactic propylene is amorphous and has little economic value, both isotactic and syndiotactic are semi-crystalline and have high melting temperatures.³ Overall, while sharing some similar properties with polyethylene, polypropylene distinguishes itself by being lightweight, optically clear if required, hydrophobic, having good chemical resistance, and maintaining its mechanical and electrical properties at high

temperatures. As such, these properties suit applications in food packaging, consumer goods, furniture, and especially in the automotive industry, medical utensils, and industrial applications.

Discovered in 1912 by Fritz Klatte, poly(vinyl chloride) was primarily considered useless, at the time, due to its high brittleness. PVC, as it is known today, was only invented in 1925, when Waldo Semon, from the B. F. Goodrich Company, manufactured a flexible and easy-to-use PVC by means of plasticization.⁷ An historically relevant material, the most significant push for the production of PVC occurred during WW2, when PVC was seen as an ideal replacement material for rubber in electrical wires and cables in the emerging electronics industry. PVC was industrially manufactured by emulsion polymerization by H. Fikentscher in 1928 and, later in 1930, by suspension polymerization at ICI, UK and Wacker Chemie, Germany.⁸

Poly(vinyl chloride) excels due to its excellent chemical resistance, durability, and ability to maintain good mechanical properties even when highly plasticized. Indeed, PVC's ease of plasticization allows for the broadest versatility in modifying the plastics' desired properties. As such displays the most comprehensive range of applications, from only a limited range of produced polymers. PVC is also an excellent electrical insulator, as well as a flame retardant.

Having been surpassed over the years by PE and PP, PVC is currently the plastic material with the third-highest demand, at 44 million metric tons as of 2018⁹.

Unlike polyolefins, due to its durability, nowadays PVC is mainly used for long-term applications such as in the construction and building industry, where PVC acts as an alternative to traditional materials such as wood, metal, and rubber. The focus on long term applications not only gives PVC a niche market but also lowers the impact on the plastic waste and recycling industry. Depending on the molecular mass, PVC can be processed into rigid formulations to give pipes, conduits, sheet, window profiles, or flexible, highly plasticized formulations for flexible sheet, flooring, cable covering, hoses, tubing, medical

products, electrical plugs and bottles and other containers. Other applications include automotive parts, sports utilities, clothing, and household items.¹⁰

2.2. Production and Polymerization of Light Olefins

Light olefins, such as ethylene and propylene, are among the most important building blocks in chemistry, with wide applications as precursors to plastics and other chemical products.

Despite the recent research on the pursuit of an alternative, greener light olefin source^{11,12}, most of the light olefins available are still obtained from the petrochemical industry through a series of cracking processes.

While ethylene is almost exclusively produced by the steam cracking of natural gas and naphtha, propylene is mostly produced either as a byproduct of steam cracking or as the off-gas from fluid catalytic cracking of heavier oil fractions. Steam and fluid catalytic cracking are petrochemical processes in which saturated hydrocarbons are thermally, through steam, or catalytically cracked into smaller, unsaturated hydrocarbons. Steam cracking uses a feedstock of lighter crude oil cuts, such as naphtha and gas oil, or light alkanes derived from natural gas processing plants, which have the added benefit of producing exclusively light olefins. On the other hand, fluid catalytic cracking converts heavy, high molecular hydrocarbons into an off-gas of propylene and butadiene, as well as other valuable fractions, like gasoline.

As stated previously, while some of the light olefins are used as reagents for producing other chemical products, such as vinyl chloride, approximately two-thirds of their feedstock is directed to the production of their respective polymers.

Modern polyethylene plants can reach a manufacturing capacity of 650 kt/year, or an hourly production rate of 75 t/hour and are categorized according to their polymerization process.

¹³ In the high-pressure polymerization process, LDPE can be created from the free-radical polymerization of ethylene, using free radical initiators derived from organic peroxides.¹⁴ This process occurs in either an autoclave or a tubular reactor, under temperature and pressure operating conditions of 180 to 290 °C and 1500 to 3500 bar, respectively. Due to the low, 20%, monomer conversion and short residence time, separators are used to

recuperate the unreacted monomer. The recovered monomer will be reprocessed by multiple passes through the reactor.¹³

On the other hand, HDPE and LLDPE are created by coordination polymerization in the low-pressure polymerization process, with the assistance of either Phillips, Ziegler, or metallocene catalysts. This polymerization process can be performed in either a suspension, solution, or gas phase reactors, or a combination or sequence of the aforementioned. While both suspension and solution processes require a solvent, in the suspension process, the catalyst and resulting polymer remain suspended in the liquid solvent. In contrast, in the solution process, the catalyst and polymer are dissolved in the solvent. Suspension or slurry processes operate at a temperature and pressure range of 80-110 °C and up to 50 bar, respectively, and show a high monomer conversion of 95 to 98% per pass.¹⁵ In solution processes as the polymer is highly insoluble, the process must be operated at higher temperatures compared to suspension, reaching up to 200 °C and achieving a monomer conversion of 95% per pass.¹³

Without solvent use, in the gas phase process, both ethylene and the catalyst are blown into the reactor, operating as a fluidized bed reactor. Besides the economic advantage, a lack of solvent eliminates solubility and viscosity constraints present in the liquid phase processes, broadening the range of possible manufactured products. Additionally, operating in a gas phase regime facilitates polymer separation from the unreacted monomer as the monomer is in the gas phase and eliminates the need to flash any liquid solvent after the reaction train. Gas-phase processes operate at about 20 bar and in a temperature range of 70 to 105 °C, while having a low monomer conversion of 2 to 10% per pass.¹³ Figure 2.1 shows an example of an early gas phase process for the production of HDPE and LLDPE developed by UNIPOL™. This process required the use of only one fluidized bed reactor, a series of cascading blowdown vessels to recuperate part of the monomer, and a product purge bin, where a purge gas is used to remove any residual monomer and to deactivate the catalyst.¹⁴

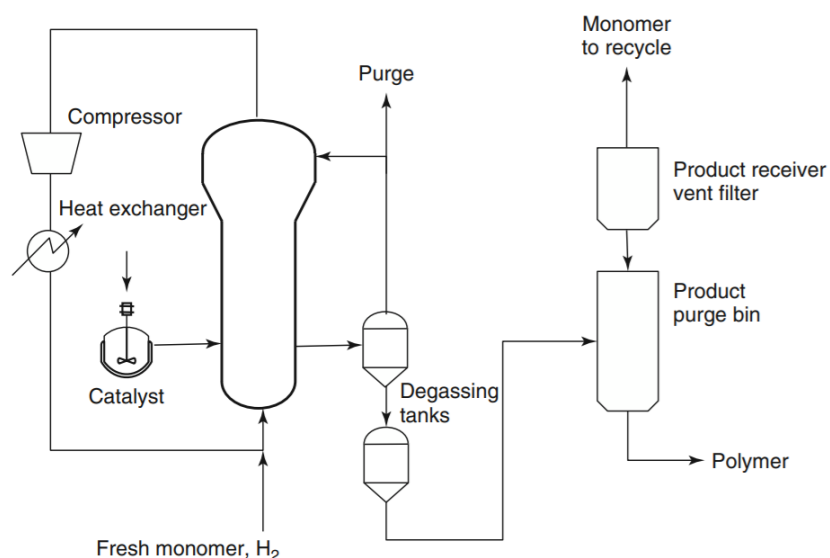


Figure 2.1: Process flow diagram for the UNIPOL™ gas phase process for the production of HDPE and LLDPE, taken from “Polyolefin Reaction Engineering”¹⁴

A state-of-the-art polypropylene plant can have a production capacity of 400 kt/year or an hourly production rate of 46 t/h. While there are many similarities in polyethylene and polypropylene production methods, polypropylene production can only be performed by coordination polymerization. The main polypropylene polymerization processes employed today follow either a gas-phase or slurry regimes, or even a combination of both, and use Ziegler-Natta and metallocene catalysts to produce isotactic propylene and some metallocene catalysts for the production of syndiotactic polypropylene.¹⁴

Polymerization in the slurry regime occurs in a liquid phase around heterogeneous catalyst particles and can be divided into diluent and bulk processes. In diluent processes, an inert diluent, such as hexane, is used to disperse the growing polymer particles. In bulk processes, the liquid monomer, propylene, is used as the polymerization medium. The use of liquid propylene as a polymerization medium maximizes the polymerization rate at the cost of lower versatility of produced polymers.

Liquid phase processes operate at a temperature of 60 to 80 °C, a pressure of 5 to 15 bar, and 40 to 50 % conversion.

Similar to and sharing the same advantages as its PE counterpart, in a PP gas phase process, mixing and polymerization are promoted by using a gaseous stream of monomer and inert gas, nitrogen or hydrogen, to fluidize the catalyst and polymer particles. Gas-phase processes have a typical conversion of 2 to 30 % per pass and operate within a temperature and pressure range of 60 to 85 °C and 25 to 30 bar.^{3,16}

Hybrid processes ensure the broadest range of manufacturable polymers with a single polymerization line. This is achieved by sequentially combining homopolymer polymerization and copolymer polymerization with ethylene.

In hybrid processes, polymerization takes place in sequential reactors that produce homopolymers and copolymers with low ethylene content in liquid propylene without inert diluent.¹⁴ These processes ensure the widest range of manufacturable polymers with a single polymerization line. The most widespread hybrid process is the Spheripol process by LyondellBasell, accounting for one-third of polypropylene production. As is shown in Figure 2.2, propylene and catalyst are feed into the loop reactors at 60-80°C and 35-50 bar to produce homopolymers. Upon exiting the loop reactors, the slurry can be depressurized and flashed or fed into a cyclone to recover the unreacted monomer. With additional monomer and comonomer, a gas-phase copolymerization is performed with the previous polymer, at 100°C and 15 bar, until a polymer with the intended molecular weight and comonomer concentration is reached. Likewise, to recover unreacted monomer, the slurry is vented to lower pressures or fed to a cyclone, and residual monomer is recuperated by stripping using steam and/or a nitrogen purge.

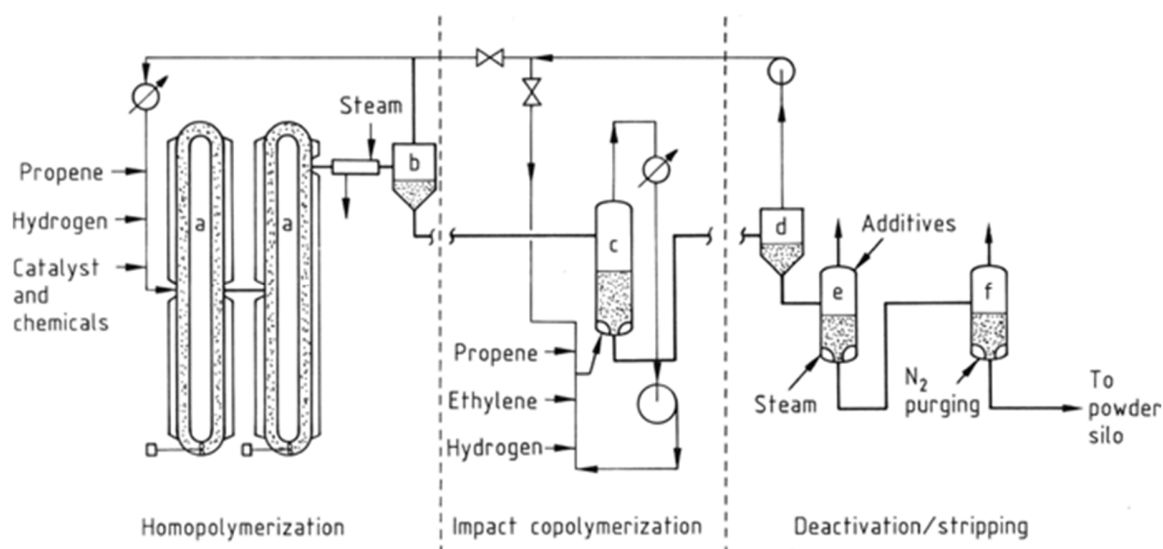
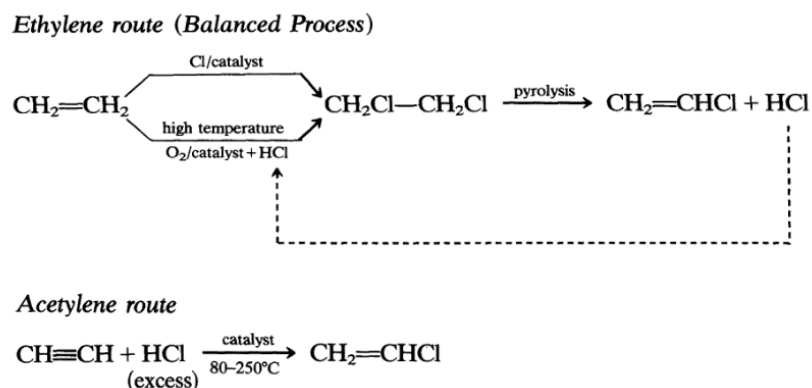


Figure 2.2: Example of the Spheripol process for the production of polypropylene from “Ullmann’s Encyclopedia of Industrial Chemistry”³ a) loop reactors; b) primary cyclone; c) copolymer fluidized bed; d) Secondary cyclone; e) deactivation; f) purging

2.3. Production and Polymerization of Vinyl Chloride

Albeit production records date as far back as 1835, only in 1912 did Fritz Klatte patent the production method for vinyl chloride via the acetylene method. Presently, vinyl chloride is manufactured by two distinct routes depending on the available feedstock, as shown in Figure 2.3. The more widespread ethylene route via dichloroethane is usually operated following the so-called balanced process. This process combines the chlorination and oxychlorination of ethylene to dichloroethane, followed by the latter’s pyrolytic dehydrochlorination to vinyl chloride. The older acetylene route tends to be preferred on smaller-scale plants due to its lower plant cost and higher energy demand. This route is especially favorable in regions with coal extraction, where acetylene can be produced from coke and quicklime via calcium carbide, thus eliminating the need for an oil-based feedstock.¹⁷

Figure 2.3: VCM production routes¹⁷

Contrary to its polymer form, VCM is a toxic, highly flammable, and, overall, hazardous material for human health. As such, it is seldom used as a final product, but as an intermediate for the production of PVC.

Poly(vinyl chloride) (PVC) is produced from the free radical polymerization of vinyl chloride monomer (VCM), a type of addition polymerization. PVC polymerization processes can be classified as precipitation suspension polymerization. Due to the insolubility of PVC in its monomer, a growing PVC chain will precipitate above a specific chain length. The polymerization reaction can be performed through three main processes: suspension, which accounts for 80% of world production, emulsion (12%), and bulk (8%) polymerization.

The suspension polymerization process is carried out by dispersing the monomer in water through vigorous agitation, creating small droplets of monomer suspended in an aqueous solution, where polymerization occurs as bulk polymerization. The reaction occurs at a temperature of 45 to 75 °C, and monomer conversions are chosen depending on the intended properties of the produced polymer. Flexible polymers are stopped at 85%, while rigid polymers at around 90 % conversion. The polymerization reaction is prematurely stopped as it is uneconomic to continue with the reaction due to the lower reaction rate and certain properties starting to deteriorate at higher conversions. Figure 2.4 shows an example of a typical example of a suspension process flow diagram for the production of PVC. After polymerization, most unreacted VCM is recovered by depressurizing and flashing

the PVC slurry in a blowdown vessel. Afterward, any residual VCM is stripped in a monomer stripping unit under a purge stream of steam or nitrogen. All vented monomer-rich streams are sent to a monomer recovery unit to be recycled to the polymerization cycle.

In a bulk process, liquid VCM is used as polymerization medium instead of water, creating a PVC powder. While the lack of a drying step increases energy efficiency, the higher reaction difficulty due to higher viscosity and lower heat transfer rates ensures that this process is less competitive than suspension.

Emulsion involves polymerization of the monomer in an aqueous solution containing surfactant and a water-soluble initiator. Polymerization takes place inside soap micelles, with the monomer being supplied by diffusion through the water phase and dissolved in the micelles. This process produces PVC latices which can be used in plastisol production.^{10,18}

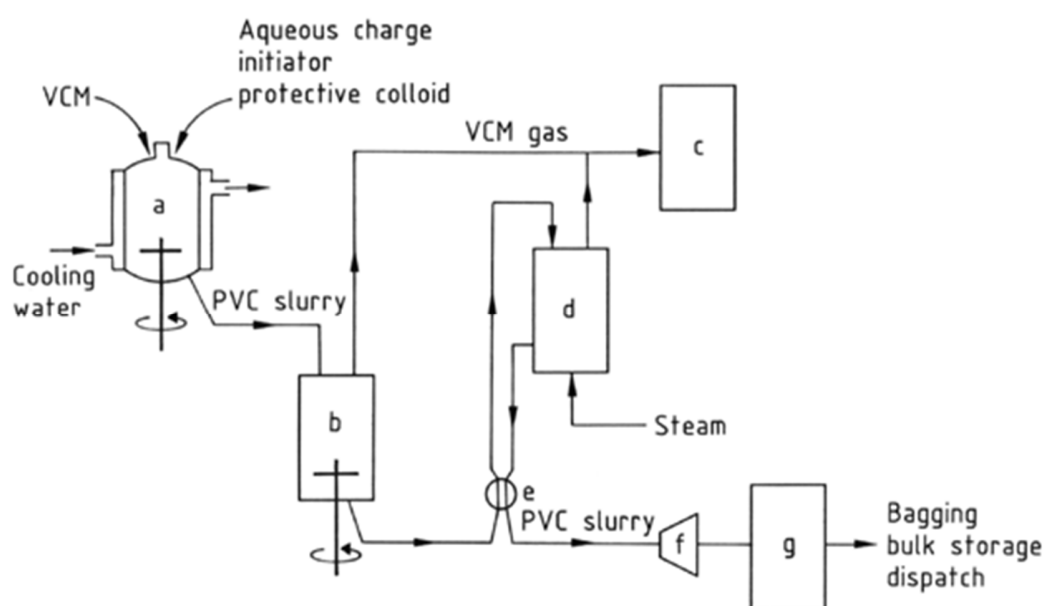


Figure 2.4: Process flow diagram example of a suspension process for the production of poly(vinyl chloride) taken from "Ullmann's Encyclopedia of Industrial Chemistry"¹⁰ a) suspension reactor; b) blowdown vessel; c) VCM recovery unit; d) monomer stripping column; e) heat exchanger; f) centrifuge; g) driers

2.4. Monomer Recovery in Polymer Plants

Although most polymer production processes employ a diverse range of polymerization methods and conditions, all polymer manufacturing processes can generally be summarized in five operational steps: raw material storage and preparation, polymerization reaction, raw material recovery, product finishing, and product storage.

One of the critical factors for obtaining quality polymers is the quality of the raw materials; as such, the first step of any polymer production process is the purification of the imported monomer feedstock. Unless there is a monomer plant on-site, the existence of a purification unit guarantees the availability of raw materials at the required purities for the chosen polymerization process and adds the capability of importing lower grade feedstocks, which provides greater operating flexibility and lower operating costs.¹⁹

To this end, in polyolefins plants, purification of the feedstocks is achieved by olefin/paraffin splitter columns, while the purification of VCM, mostly performed on the monomer plant itself, is also performed using distillation columns. When inert gases, such as nitrogen or hydrogen, are present in the feed, they build up in the overhead of the distillation columns and must be vented.

Together with the respective catalyst or initiator, the purified monomer is fed into the reactor train to be polymerized until the desired product is achieved. However, as previously seen, depending on the polymerization process, only a fraction of the feedstock reacts during a single pass through the reactor train. This requires that the unreacted monomer must be recycled back into the polymerization reactor. In this recycling process, contaminants and inert gases tend to build up over time in the reactor and must be periodically vented when unacceptable levels are reached. Particularly, for the production of linear low-density polyethylene and high-density polyethylene, control of the partial pressure of ethylene requires the addition of nitrogen.¹⁹

After polymerization, the slurry is extracted from the reactor and proceeds towards a degassing unit. Degassing systems can be one or a series of blowdown vessels and monomer stripping units used to recover and recycle unreacted monomer and solvent and regulate

the monomer concentration in the final polymer prior to extrusion. Blowdown vessels, which operate in batch, can be containers of higher volume than the polymerization reactor, where the highly pressurized polymer slurry is vented to a lower, atmospheric, or vacuum pressure, with the appropriate pump, thus flash separating the gas phase monomer from the solid polymer. In gas-phase polymerization systems, cyclone separators can be used to recover the polymer particles instead of blowdown vessels.

In monomer stripping units, residual monomer that remained dissolved and entrapped in the polymer structure is stripped in a trayed tower or packed column using steam or hot inert gas, such as nitrogen or air. This step reduces the monomer present in the slurry until acceptable levels.

Today, monomer recovery from monomer stripping is not just economically beneficial but also required by product consumer safety and environmental law, as some plastic monomers can be hazardous to human health; as such a strict monomer content control is essential.

Due to the higher difficulties of separating inert gases from monomers, steam stripping followed by a condensation unit for monomer recovery has been the standard stripping method. A further objection to air stripping of high monomer concentration streams is that an explosive mixture of monomer/oxygen can be formed. A column stripper operates continuously with the slurry entering the column from the top and with steam fed into from the bottom. Most of the steam is used to heat the slurry and the column, condensing in the upper section, while only a smaller fraction of the steam is used to transport the unreacted monomer to the condenser. This method allows for polymer production with a monomer concentration sufficient to produce food wrapping plastics.²⁰ Afterwards, if necessary, the used solvent is separated from the polymer slurry by passing it through a dryer unit, while the resulting dried polymer particles proceed towards extrusion.

Recently with improvements in stripping technology, hot nitrogen as a carrier agent in the stripping process has become more popular. Instead of steam, the use of nitrogen lowers the presence of water in the condenser, thus eliminating the formation of ice in the

machinery. It also prevents an increase of the water content in the slurry that would need to be dried afterward.²¹

On the other hand, the gas phase outputs of the degassing systems are sent to a monomer recovery unit, usually consisting of compressors and condensers, where most of the monomer is liquified and recuperated. The remaining gas phase is either sent to further recovery or the incinerator. While in the past, due to their lower relative value, these streams were usually flared or used as low-grade fuel, today the incineration of streams with such high concentration of monomer is considered both a significant economic and environmental loss. Indeed, as shown throughout the typical polymerization process, monomer losses can occur at three key stages: monomer purification, reactor purging, and product purification and finishing. These losses typically amount to 1-2% of the initial monomer feedstock in typical polyolefin plants^{3,13}, which have been estimated to account for a total of \$2 million annually in raw materials losses¹⁹. PVC plants typically report losses of up to 3% of the initial feedstock¹⁰.

2.5. Emission Control

In 1975, the U.S. Environmental Protection Agency classified VCM as a carcinogenic agent. In the previous year, several cases of angiosarcoma of the liver were reported by the workers of B.F. Goodrich Chemical Company, which was later correlated with occupational exposure to VCM.^{22,23} From this incident, new standards were created by the Occupational Safety and Health Administration to control and reduce the levels of VCM in gaseous and liquid exhaust streams.²⁴

Before this incident, there was no implemented method for the treatment or recovery of monomers, especially after the polymerization unit at the polymer plant, where the polymer slurry was commonly dried in open atmosphere.²² Later, with the implementation of the Clean Air Act Amendments of 1977, the VOC emission limits were extended to both the polyethylene and polypropylene industries.²¹ The occurrence of these events

demanded that methods were created to control monomer emissions and that studies were conducted to find the impact and efficiency of each possible method.

Control techniques can be categorized into two broad groups: combustion techniques and recovery techniques. Combustion techniques have a wider variety of applicability for VOC streams and have the advantage that certain combustion configurations may permit heat recovery. Recovery techniques have more selective applicability but are capable of conserving and reusing valuable materials. Today the selection of a control system for a particular application should be based primarily on considerations of technical feasibility, process economics, and environmental responsibility.²¹

2.5.1. Control using Incineration

Combustion is a rapid oxidation process that results in the destruction of the residual monomer by converting it to carbon dioxide, water, and, additionally, the combustion of vinyl chloride, hydrogen chloride. The efficiency of this method depends on the temperature, the type, and the residence time of the incinerator, but it is possible to achieve complete destruction of the pollutant.²¹

Four major combustion control devices can be used to control emissions from the polymer industry: flares, thermal or catalytic incinerators, and boilers. While flares can handle continuous and intermittent streams, incinerators and boilers can only handle continuous and low-volume intermittent streams. Flares are widely used control devices at PE and PP manufacturing plants. Still, for PVC with the production of hydrogen chloride, an open-air incinerator is not a viable long-term solution. Hydrogen chloride, formed from the combustion of VCM, must be neutralized with a caustic solution or scrubbed with water, which will incur into extra costs. As such, incineration should be used as secondary or final emission control, processing only residual emissions that other methods have already treated.²⁵

2.5.2. Control using Condensation

Refrigeration systems are widely used to recover organics with high boiling points, and as such, are not the most effective means of reducing monomer emissions in polyolefin and PVC industries. For these industries, refrigeration systems should be used in conjunction with other control equipment to reduce the load on the secondary control system. A condenser located upstream of an incinerator, adsorber, or other will reduce the organic load entering the downstream control device by condensing the bulk of the monomer. The downstream device will lower the organic content to the established emission limit.²⁴

The effectiveness of these systems increases with decreasing temperature and increasing pressure, and as such, is limited by the sharply increased costs associated with cooling and compressing the gas and freezing if water is present in the stream.²⁶

Additionally, the amount of inerts that have to be released by the condenser is the main controlling factor of monomer emissions because the ratio of monomer to inerts emitted is constant. Emissions are then dependent on the inert volume present in the condenser, and by reducing the volume of inerts in the feed, the volume of monomer emitted is also lowered.²⁵

2.5.3. Control using Adsorption

Adsorption utilizes the ability of certain solids to preferentially adsorb and therefore concentrate certain compounds from a fluid mixture onto their surface. Activated carbon is the most common industrial adsorbent. It is commonly used to remove organic compounds from gaseous streams due to its affinity for organic materials instead of a highly reactive functional group. Desorption is obtained by heating the carbon, usually with saturated steam or hot inert gas. However, if steam is used or if the feed contains water, the carbon needs to be dried before the start of the new cycle. The outlet mixture of steam and monomer is sent to a condenser. The steam is liquified and separated from the monomer, which is recycled.²¹

Alternatively, the use of indirect heating to promote the desorption of VCM from the activated carbon could be a more beneficial method. Without the direct contact between the steam and the carbon adsorbent, both the drying step of the adsorbent and the post treatment of the recovered monomer could be skipped.²⁷

Activated carbon adsorption is not economical to recover large volumes of gas with low concentrations of organic compounds. The larger the gas volume, the larger the carbon bed needed to treat the effluent, which increases the investment cost and increases the cost to desorb the organic compound. The applicability of activated carbon in the recovery of monomers has been questioned due to the possibility of polymerization in the carbon, which would plug the bed. However, accounts of vendors and polymer manufacturers confirmed that this does not take place. A PVC manufacturer has used an activated carbon bed to collect VCM from a monomer recovery system vent and a slurry blend tank bed for over 7000 cycles with an outlet concentration of less than 10 ppm of VCM.^{21,24}

Carbon adsorption is most effective for high concentration, low volume, and lower temperature streams. Still, it can be fouled by fine particles, and precautions must be taken to guarantee the absence of combustible mixture in the presence of oxygen.

2.5.4. Control using Absorption

Absorption is a gas-liquid mass transfer operation in which a gas mixture is contacted with a liquid solvent to preferentially dissolve one or more components of the gas. The solvents are chosen for a high VOC solubility, and VOC control by gas absorption is done by packed or plate columns. The operation involves introducing the gas mixture through the bottom, which will rise through the packing material. The solvent is introduced at the top of the tower, contact counter-currently with the gas phase, and absorb and carry the VOC out of the tower. The purified gas that exits at the top of the tower can be released or sent to incineration. The selection of absorption for VOC control depends on the availability or not of an appropriate solvent for the specific VOC. Overall, absorbers have found limited use as a VOC emission control device in the polymer industry.²⁴

2.5.5. Control using Membranes

Membranes can be defined as barriers capable of separating two phases and, simultaneously, selectively limiting chemical components transport.²⁸ The use of membranes as a control system for monomer emissions shows several advantages: high selectivity, low maintenance, simple operation and design, and low energy costs. However, membranes have difficulties with their durability; there is the possibility of fouling, as olefin-related separations membranes are prone to plasticization, compromising their performance²⁹, and membranes cannot deal with very large volume streams.

In 1992, a membrane separation unit was installed in a PVC plant to separate VCM from inert gases in a reactor vent stream by the Membrane Technology and Research Inc. (MTR). In the gas separation process, the membranes used are selectively permeable to organic compounds while impermeable to air and nitrogen. A pressure difference between the feed and permeate sides of the membrane is the driving force for the separation.

The pilot-scale experiment reported 63-96% recovery of the remaining VCM.³⁰ Since then until 2006, 40 other similar systems were installed in PVC plants to recuperate feeds with 50% VCM concentration, which reported more than 99% recovery.³¹

In terms of polyolefin applications, membrane technologies were applied to monomer/nitrogen separation in 1996, also with the MTR system.^{28,32} The proposed unit consists of a gas permeation system that combines membrane and cryogenic separation technologies. In this PP process, the off-gas of the polymer degassing bin is compressed to 14 bar and cooled to -30°C, resulting in a portion of the monomer condensing. The condenser overhead stream composed of a monomer/nitrogen mixture is sent to the membrane system, containing two membrane units in series. The first membrane produces a permeate stream enriched in monomer and a residue stream containing 97-98% nitrogen, which can be recycled into the process or feed to the second membrane to obtain better than 99% nitrogen. The proposed MTR process reported a hydrocarbon recovery of 91%(m/m) and nitrogen recovery of 50%(m/m). Until 2006, almost 50 of these systems have

been installed all over the world.³¹ Since then, a substantial amount of research has been performed on this subject, and new membrane materials have been proposed.³³⁻³⁵

2.6. Adsorption

The ability of porous solids to reversibly adsorb large volumes of vapor was first recognized in the 18th century. Yet, the application of adsorption as a means of separating mixtures into two or more streams, each enriched in a valuable component is a more recent development. Adsorption always occurs in the vicinity of an interface and, as such, this effect is dependent on the extent of the interfacial area of a given solid. For this reason, all industrial adsorbents are either highly porous materials or composed of very fine particles, which generally have a specific surface area of over $100 \text{ m}^2\text{g}^{-1}$.³⁶

Adsorption can be understood as all the physical (physisorption) or chemical (chemisorption) interactions between molecules in the fluid phase and the adsorbent material surface.

Physical adsorption or physisorption studies all the adsorbate/adsorbent interactions developed by non-bonded intermolecular forces, which are the same as those responsible for the condensation of vapors and the deviations from ideal gas behavior. Physisorption is a general phenomenon with a relatively low degree of specificity. It involves interactions with mostly low energy thresholds, which results in a rapid and easily reversible phenomenon. It has a low isosteric heat of adsorption and maintains the identity of the adsorbate. Although adsorption depends on the contact with the adsorbent surface, at higher adsorbate concentrations, physisorption occurs as a multilayer, with the formation of adsorbate/adsorbate interactions.

Non-bonded intermolecular forces comprise van der Waal forces, *i.e.*, nonspecific dispersion-repulsion forces, or electrostatic forces, which includes interactions regarding charges, permanent and induced dipoles, and other multipoles. Van der Waal dispersion-repulsion forces are always present in adsorption phenomena. At the same time,

electrostatic interactions are only considered depending on the nature of the adsorbent material, namely in zeolites with an ionic structure.³⁶

Electrostatic interactions are easier to understand, as they arise from the Coulomb force between charges. These interactions can involve charges, ions, permanent dipoles, and quadrupoles. Electrostatic forces also include polarization interactions that arise from the dipole moments induced in atoms and molecules by the electric fields of nearby charges and permanent dipoles, namely in the adsorbent surface.³⁷

On the other hand, van der Waal dispersion-repulsion forces are quantum mechanical in nature, as their behavior can be understood at an atomic or subatomic scale.

While not as strong as Coulombic or hydrogen-bond interactions, dispersion or London forces are one of the most important intermolecular forces due to their constant presence; non-specificity, as they act between all atoms and molecules, even neutral ones such as helium and hydrocarbons. Therefore, they have a central role in many phenomena such as adhesion; surface tension; physical adsorption; wetting; properties of gases, liquids and thin films; the strength of solids; the flocculation of particles in liquids; and the structure of condensed macromolecules such as proteins and polymers.

Dispersion or London forces are attractive interactions and arise from the electric moment induced in an atom by the instantaneous fluctuations in electron density of a neighboring atom.³⁶ On the other hand, repulsive forces are steric in nature and arise from the overlap of electronic clouds between atoms. These forces act at very small interatomic distances and ultimately determine how close two atoms or molecules can approach each other.³⁸

Chemisorption essentially involves forming new chemical bonds, either by donation (ionic bonds) or sharing (covalent bonds) of electrons between the molecular structure of the adsorbate and the reactive sites of the adsorbent. Due to its reactive nature, these interactions are highly specific, adsorption is restricted to a monolayer, and the chemical structure of the adsorbate can be altered, possibly even undergoing dissociation. Together with the high energy threshold of these interactions, the resulting irreversibility makes

chemisorption inadequate for the development of cyclic adsorption separation processes.

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2.7. Separation by Cyclic Adsorption Processes

Separation defines all processes capable of transforming a mixture of substances into two or more products with different compositions by exploiting the differences in the physical and chemical properties that each substance in the mixture share.

As opposed to mixing, separation is an inherently complex process to accomplish, as it goes against the second law of thermodynamics. Accordingly, since all natural processes lead to an increase of entropy in the system, separation can only be accomplished by externally supplying an equivalent amount of thermodynamic work for the separation to occur. For this reason, separation processes not only accounts for a significant part of the production costs in chemical and petrochemical industries^{39,40} but are also estimated to account for 10 to 15% of the world's energy consumption.⁴¹

Due to its simplicity and near-universal applicability, distillation has a dominant role in separation technology. It is usually the standard separation process to which other processes are benchmarked. In the last decades, the combined increase of energy prices and the inherent low energy efficiency of distillation processes have incentivized the development of alternative, more efficient separation technologies.

In recent years, the development of a new generation of more selective adsorbent materials has enabled adsorption-based separation processes to successfully compete with the other traditional separation technologies, such as cryogenic distillation and absorption.⁴² Adsorption-based separation systems, although usually having a higher acquisition cost, are economically advantageous as they are significantly more energy-efficient. Additionally, adsorption-based systems are capable of higher separation performances if an adsorbent material can be found, in which the adsorption separation factor is higher than the relative volatility of the mixture. As the relative volatility between the components in a mixture lowers, adsorption becomes a more economical approach. However, designing an industrial

size adsorption-based separation system usually requires high quantities of adsorbent material with high separation efficiency and acceptable economic cost, emphasizing the importance of developing new and improving upon existing production methods for new adsorbent materials.⁴³

Adsorption-based separation processes require an adsorbent material to have the ability to preferably adsorb one component over others, from a mixture of two or more. *i.e.*, only an adsorbent that can display selectivity between two chemical species can separate a mixture of said species.

As such, adsorption-based separation methods can rely on three distinct selective mechanisms: steric, kinetic, and equilibrium. In steric separations, the adsorbent has pores with dimensions such that only specific smaller-sized molecules can enter while excluding larger ones, a mechanism exclusive to zeolites and molecular sieves. Kinetic separation relies on the different diffusion rates that different chemical species display while traveling through the porous structure of the same material. In this case, separation occurs by controlling the exposure time between the mixture and adsorbent so that the faster diffusing species gets adsorbed while preventing or limiting the adsorption of others. Equilibrium separations depend on an adsorbent material's ability to establish different strength attractive interactions for each adsorbed species, resulting in certain species being preferentially adsorbed over others in a mixture.⁴⁴

All adsorption-based separation processes operate in a cyclic behavior and can be divided into two classes: cyclic fixed bed systems, like the PSA or TSA, and continuous flow systems, such as the True and Simulated Moving Bed. In this work, the focus will be given solely to cyclic batch systems.

In cyclic batch systems, the adsorbent material is typically shaped or extruded from the initial powder form into either spherical pellets, tablets, monoliths, or other shapes to reduce the pressure drop in the system and is then packed into a fixed bed. Separation occurs by injecting the feed stream into the fixed bed, which results in the adsorption of the more preferentially adsorbed components and the formation of two or more concentration

fronts. In the typical Skarström cycle ⁴⁵, the least adsorbed (light) component will pass through the bed mostly unhindered and eventually break through, and leave the fixed bed as raffinate. In contrast, the preferentially adsorbed (heavy) component will be delayed and concentrated on the surface of the adsorbent. Before the heavy component breakthroughs, the feed is stopped, and the system is regenerated to recover the heavy component, creating the extract. Depending on the pressure and temperature conditions under which the adsorption step took place and the feed composition, regeneration can be obtained by altering one or more of these parameters in a way that promotes desorption of the heavy component.

The primary methods of regeneration include pressure swing, temperature swing, purge gas stripping, and displacement desorption. In a pressure swing process, regeneration is achieved by lowering the adsorption column pressure at a constant temperature, thus purging the adsorption bed by reducing the partial pressure of the gas phase adsorbate. As adsorption is an exothermic phenomenon, temperature swing processes regenerate the adsorption bed by increasing the temperature inside the column, either by direct or indirect methods, while maintaining a constant pressure. In the purge gas stripping method, an inert, non-adsorbable fluid is used to purge the adsorption bed, while in the displacement desorption method, a competitive adsorbed species is used instead. ⁴³

For the separation of any mixture, the optimal separation process, and thus the most appropriate regeneration methods, is a choice that must take into account the feed composition and physical conditions, the adsorbent material, economic factors, and technical considerations. ⁴³

2.7.1. Pressure Swing Adsorption

Although industrial applications of adsorption-based separation processes have been reported as early as the 1940's ^{46,47}, these applications have been limited to the removal of small concentrations of gases, and regeneration was still mostly limited to the use of direct heating by purging with a hot inert gas.⁴⁸ It wasn't until 1958 that efficient pressure-swing

processes were concurrently patented by Skarström⁴⁵ and Montgareuil⁴⁸ for the specific example of air fractioning.

Pressure Swing Adsorption (PSA) is then an adsorption-based separation process in which the regeneration of the packed bed is primarily achieved by lowering the total pressure, and thus the partial pressure of the adsorbed species, rather than raising the temperature or purging the bed with a displacing gas.⁴⁹ As such, in any PSA process, the pressure inside the adsorption column will alternate between at least two operating pressures. Adsorption of the feed mixture and raffinate production will be promoted at higher pressures while regeneration and recovery of the extract are achieved at a lower pressure.

The main advantage of PSA processes lies in how rapidly the pressure inside the adsorption column can be changed. Since regeneration can be rapidly accomplished by lowering the pressure, PSA processes are more adequate for bulk separations. A faster saturation of the adsorption column during the feed step will enable overall faster process cycling, thereby increasing the adsorbent efficiency.⁵⁰

On the other hand, PSA systems are very dependent on the performance of the adsorbent material, being restricted to species that are somewhat weakly adsorbed. When the heavy component is too strongly adsorbed, an uneconomically strong vacuum may be required to regenerate the bed effectively.⁴⁹ As shown in Carmo et al.⁵¹, in more severe cases, PSA systems may be incapable of adequately regenerate the bed, which leads to the saturation of the bed and the eventual breakthrough of the heavy component. As such, as the strength of the adsorbed component increases, TSA becomes a more favorable alternative.

PSA is a highly versatile technology and, since it was first patented, has had phenomenal growth in research and development, with improvements in separation performance and energy requirements. Some key applications of the PSA technology include gas drying, carbon dioxide removal⁵²⁻⁵⁴, solvent vapor recovery, air fractioning⁴⁷, noble gas purification⁵⁵⁻⁵⁷, hydrogen purification⁵⁸ and petroleum refinery off-gases, methane upgrading^{59,60}, paraffin separation⁶¹, and alcohol dehydration.^{50,62}

On monomer/nitrogen separation by PSA, the few explicit examples available in the literature are all related to the separation of olefin/nitrogen. A patent was filed for the recovery of nitrogen and light hydrocarbons from polyalkene purge gas, using a system composed of a condenser followed by a PSA unit packed with silica gel or activated alumina. The proposed system was capable of producing a nitrogen purity of at least 95%(v/v) and almost complete hydrocarbon recovery.⁶³

Han et al.⁶⁴ reported the performance of a bench-scale PSA unit for the separation of a 35/15/50 %(v/v) propylene/propane/nitrogen mixture using an AgNO₃ impregnated silica substrate. A propylene purity and recovery of 91.9 and 86.5 %(v/v) were achieved, with more than 99% of the nitrogen removed from the feed.

Narin et al.⁶⁵ and Ribeiro et al.²⁹ studied the separation and recovery of a propylene/nitrogen mixture using MIL-100(Fe) tablets and reported the development of two industrial-scale PSA cycles: one for nitrogen recovery and the other for nitrogen and propylene recovery. For the propylene/nitrogen recovery, a 6-step 3 column PSA was used to produce a nitrogen and propylene rich stream with a purity of 96.2% and 97.6% and a recovery of 98.4% and 91.0%, respectively. Nitrogen and propylene productivities of 4.61 and 1.83 mol/kg.h were achieved and an energy consumption of 383 Wh/kg_{N2} was required. The reported system displayed sufficient separation and a higher energy efficiency than the corresponding combined membrane and condensation separation process. This process was patented by the authors.⁶⁶

2.7.2. Temperature Swing Adsorption

Temperature swing adsorption is the oldest and most completely developed cyclic adsorber process. Taking advantage of the fact that adsorption is an exothermic phenomenon, the regeneration of the adsorbent in the TSA process is achieved by increasing the temperature of the packed bed. As such, TSA processes operate by periodically alternating the temperature inside the bed between two setpoints.⁶⁷ At a lower temperature, adsorption and separation are promoted by increasing the adsorbent capacity and selectivity between

the feed mixture, respectively. The adsorbent can be regenerated adequately at the higher temperature without suffering dilution, resulting in an extract with higher purity. Nonetheless, when the extract's high purity is not required, TSA regeneration is still most efficiently accomplished by purging the bed with a preheated gas, such as part of the raffinate, feed mixture, or other inert gases. In this fashion, the driving force for desorption can be enhanced by the concurrent reduction of the partial pressure.

The main advantage of the TSA processes is the ability to desorb strongly adsorbed species, as a small temperature change can result in the desorption of a large quantity of adsorbate.

⁴³ This grants the process much higher flexibility regarding the choice of adsorbent material.

However, the disadvantage of TSA processes is that they have a high energy consumption, which can be highly uneconomical unless the units are properly integrated with the industrial plant energy integration system, and require large quantities of adsorbent material, because the regeneration step takes an extensive amount of time.⁶⁸

The regeneration step in a TSA cycle involves heating and regenerating the adsorbent and cooling the adsorption bed. ³⁹ Since heating is a slow and often rate-limiting step, TSA processes are usually preferred for purification rather than bulk separations. In that case, the time length of the adsorption step is comparable to the regeneration.

As described in Carmo et al. ⁵¹, not only does the standard TSA process suffer from long cycle duration and high adsorbent inventory, but in cases where the raffinate purity is premium, the adsorbent efficiency is reduced. As a consequence of the long duration of the cycle steps, at the end of the adsorption step, the heavy component concentration front tends to disperse, via a concentration driving force, and eventually contaminate the raffinate. To prevent this, a length of the unused bed (LUB) is kept as a guard at the end of the active adsorbent zone, ensuring the raffinate's purity at the cost of a lower adsorbent efficiency.

Based on the aforementioned reasons, it is understandable that one of the leading research directions on TSA processes involves the reduction of the regeneration step duration from hours/days to the more manageable time scale of a few minutes. ⁶⁷

Traditionally, most TSA cycles use steam or hot inert gas to heat up the adsorbent material on contact and promote regeneration. However, direct heating using steam requires that the adsorbent material be dried out after steam circulation. Additionally, it requires a secondary unit to separate the adsorbate from the spent steam or water, depending on the miscibility of the adsorbate in water. In the case of hot inert gas, the resulting heavy component will be diluted, which might require an additional separation process. Due to these reasons, new TSA processes tend to avoid direct heating in favor of other alternatives, such as those based on electrothermal desorption⁶⁹, microwaves⁷⁰, thermoelectric devices⁷¹, or indirect heating^{27,72-74}. Cooling is generally done by indirect heating through an external cooling jacket.⁷⁵

TSA applications include removing trace impurities in pre-purification units, volatile organic compound control in air streams, carbon capture⁷⁶, air purification⁶⁷, gas drying⁷⁷, and methane purification^{78, 67,79}

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Chapter 3

Materials and Methods



3.1. Adsorbent Materials

The choice of adequate adsorbent materials is restricted by the relative affinity and selectivity developed between the components in the adsorbate mixture and the adsorptive capacity of the material towards the more strongly adsorbed component. Even if an adsorbent exhibits an adequate selectivity, if the proposed separation requires the use of an excessively high adsorbent inventory, then the process will still be economically unfavorable. For this reason, the requirement for adequate adsorptive capacity restricts the choice of adsorbents for practical separation processes to materials with pore diameters ranging between a few and a few tens of ångströms.¹ In this work, the adsorbent material focus was given primarily to activated carbons (AC) and Metal-Organic Framework (MOF) materials.

Activated carbons are highly porous materials produced from carbon-rich precursors such as wood, peat, coals, petroleum coke, bones, coconut shell, and fruit nuts by some form of thermal or chemical activation.

In activated carbons, the activation process essentially involves the removal of carbonized products formed during pyrolysis, thereby developing the porosity of the material and increasing the surface area and pore volume, which follows a size distribution controlled by the manufacturing process.¹

Thermal activation involves the thermal decomposition or carbonization of a carbonaceous material, eliminating the bulk of the volatile material. This step is followed by gasification with steam or carbon dioxide at elevated temperatures, which develops the porosity and surface area of the carbon material. On the other hand, chemical activation depends on the use of inorganic additives that degrade and dehydrate the cellulose materials, at significantly lower temperatures, while preventing shrinkage during carbonization.²

The unique property of carbons is that their surface is essentially nonpolar. However, a slight polarity may arise due to surface oxidation, which enables carbons to preferentially adsorb more nonpolar or weakly polar organic molecules compared to other adsorbents.

Metal-organic frameworks, on the other hand, are a class of crystalline hybrid porous materials built of a network of polytopic organic ligands coordinated around inorganic subunits, such as metal ions or clusters. These types of materials are mainly characterized by their high tenability. Indeed, the ligands and the inorganic clusters can be interchanged for other species of the same class to alter the shape and size of the pore structure, as well as forming specific interactions with the adsorbates. Together with their well-defined crystal structure, it results in their potential high surface areas and pore volume, selective adsorption capabilities, permanent porosity, and lack of non-accessible bulk volume.³

The collected characterization data, as well as the experimental methodology used for the adsorption equilibrium and kinetic data measurements used in this work will be described in this chapter.

3.1.1. Pittsburgh PCB 12x8 AC

Pittsburgh-type PCB is an activated carbon produced from coconut shell and marketed by Calgon Corporation. The characterization of the material was supplied by the manufacturing company and has already been reported elsewhere. The total surface was calculated using the BET method with nitrogen gas, and the adsorbent particle density was measured by mercury displacement.^{4,5} All pertinent characterization details regarding this carbon are shown in Table 3.1.

Table 3.1: Characteristics of the Pittsburgh PCB 12x30 Activated Carbon^{4,5}

Total Surface Area	$1.15 \times 10^6 - 1.25 \times 10^6$	m^2/kg
Average Particle Diameter	1.14×10^{-3}	m
Apparent density	4.4	kg/m^3
Particle Density	850	kg/m^3
Specific Heat @ 373 K	1200	$\text{J}/\text{kg} \cdot \text{K}$
Pore Volume	7.20×10^{-2}	m^3/kg
Particle Porosity	50.0	%

3.1.2. Maxsorb Activated Carbon

Maxsorb is an activated carbon produced from petroleum coke by the Kansai Coke and Chemicals Company, Ltd., advertised for its high surface area (over 3000 m²/g) and excellent adsorption capacity. The methodology involved in the production of this adsorbent has been extensively reported elsewhere.⁶

The characterization of the Maxsorb activated carbon was performed by the “Laboratorio Sólidos Porosos” at the “Departamento de Química Inorgánica” from the University of Malaga (UMA). The solid density was obtained from helium pycnometry using a Micromeritics AccuPyc II 1340 V1.09; the particle porosity, bulk and apparent density were obtained from mercury intrusion using a Micromeritics AutoPore IV 9500 V1.10; the BET surface area and the micropore volume were determined by nitrogen adsorption at 77 K using a Micromeritics ASAP 2420 V2.09.02; and the pore volume was obtained by carbon dioxide adsorption at 273 K using a Micromeritics ASAP 2020 V4.02.

The characterization results obtained for the Maxsorb activated carbon sample are shown in Table 3.2. An illustration of the Maxsorb sample is shown in Figure 3.1.

Table 3.2: Characteristics of the Maxsorb Activated Carbon

Shape	Powder	
BET Surface Area	3.371 x 10 ⁶	m ² /kg
Bulk Density	204	kg/m ³
Apparent Density	676	kg/m ³
Solid Density	2451	kg/m ³
Micropore Volume	1.425 x 10 ⁻³	m ³ /kg
Total Pore Area	2.37 x 10 ⁵	m ² /kg
Pore Volume	1.870 x 10 ⁻³	m ³ /kg
Particle Porosity	69.76	%



Figure 3.1: Maxsorb powdered sample used in the adsorption equilibrium gravimetric experiments

3.1.3. CarboTech DGK 4X8/60 Activated Carbon

CarboTech DGK 4X8/60 is a commercial granular activated carbon produced from coconut shells manufactured by CarboTech AC GmbH. The characterization of the Carbotech activated carbon was also performed by the “Laboratorio Solidos Porosos” at the “Departamento de Química Inorgánica” from the University of Malaga (UMA). The equipment and methodologies used were the same as those described previously for the characterization of the Maxsorb AC. The main characteristics obtained from these analyses are reported in Table 3.3. An illustration of the Carbotech sample is shown in Figure 3.2.

Due to the original carbonaceous material used, the Maxsorb AC has a highly microporous structure and is excellently suitable for removing organic micropollutants like volatile hydrocarbons and odors from exhaust air.

Table 3.3: Characteristics of the CarboTech DGK Activated Carbon

Shape	Granular	
Average Particle Diameter	3.56×10^{-3}	m
Langmuir Surface Area	1.341×10^6	m ² /kg
Bulk Density	861	kg/m ³
Apparent Density	1105	kg/m ³

Solid Density	2032	kg/m ³
Micropore Volume	4.548×10^{-4}	m ³ /kg
Total Pore Area	2.40×10^4	m ² /kg
Pore Volume	5.079×10^{-4}	m ³ /kg
Particle Porosity	22.10	%



Figure 3.2: CarboTech DGK granules sample used in the adsorption equilibrium gravimetric experiments

3.1.4. MIL-100(Fe) MOF

MIL-100(Fe), where MIL stands for Material of the Institute Lavoisier, is a porous metal-organic framework built from trimers of octahedral iron sharing a common vertex and linked by trimesic acid or benzene-1,3,5-tricarboxylate (BTC) moieties, which leads to the formation of hybrid super tetrahedra. As seen from Figure 3.3, this composition leads to the formation of two types of mesoporous cages (25 and 29 Å in diameter), accessed through microporous windows (4.7 ~ 5.5 and 8.6 Å in size).^{7,8}

After synthesis, two of the three iron octahedra are terminated by water molecules, while the third one is terminated by either a fluoride or a hydroxide anion, depending on the synthesis method. As shown from IR spectroscopic studies on MIL-100(Fe), the terminal

water molecules can be removed from the framework by heating above 373 K either under vacuum or in a stream of gas, which leads to the formation of a large number of iron (III) coordinatively unsaturated sites (CUSs) that act as Lewis acids within the pores.⁹

Interestingly, if the adsorbent is activated at higher temperatures, the anionic ligands are also released, which leads to the reduction of the existing iron(III) metal sites to iron(II). Although the formation of iron (II) sites decreases the Lewis acidity of the iron sites, the presence of the additional d electron in iron (II) sites allows for the formation of a stronger interaction (π back-donation) between the metal sites and unsaturated gas molecules.

Indeed, MIL-100(Fe) stands out as an adsorbent material due to its high adsorption capacity, environmental friendliness, decent production capacity, and tunable coordinatively unsaturated metal sites that promote the adsorption of selective adsorption of unsaturated gas molecules, such as olefins.^{7,9}

Based on the data collected from the literature, the granular MIL-100(Fe) MOF characterization is summarized in Table 3.4. The apparent and the solid density were calculated from pycnometry and mercury intrusion measurements. At the same time, the surface areas and pore volumes were determined by physical sorption of N₂ at 77 K. An illustration of the MIL-100(Fe) sample is shown in Figure 3.3.

The environmentally friendly MIL-100(Fe) used in this work was hydrothermally synthesized and supplied by the Korea Research Institute of Chemical Technology (KRICT) at 433 K for 8 hours using a large scale fluorine-free method, as described in the literature.¹⁰ The shaping process into granules was performed as described by Ribeiro et al.⁸

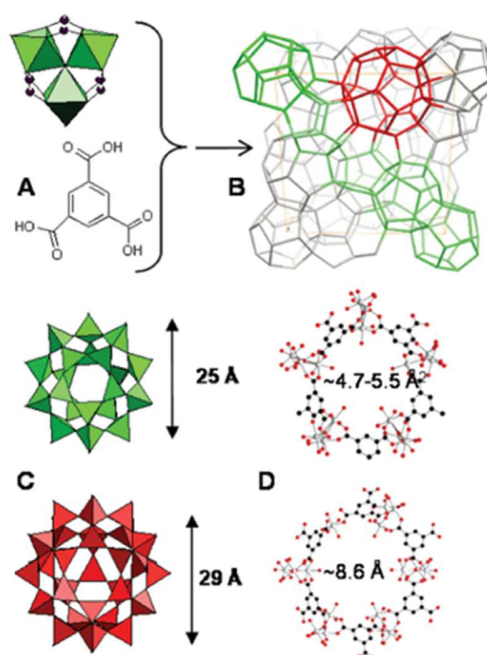


Figure 3.3: Structure of MIL-100(Fe). (A) A trimer of iron octahedra and trimesic acid. (B) Schematic view of one unit cell of MIL-100(Fe). (C) the two types of cages in polyhedral mode. (D) Pentagonal and hexagonal windows in balls and sticks (Fe: grey; O: red; C: black).

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Table 3.4: Characteristics of the MIL-100(Fe) MOF granulates¹²

Shape	Granular	-
Particle Diameter	2.5×10^{-3}	m
Apparent density	436	kg/m ³
Solid Density	2180	kg/m ³
Crystal Radius	1.7×10^{-7}	m
BET Surface Area	1.568×10^6	m ² /kg
Micropore Area	1.457×10^6	m ² /kg
External Surface Area	1.109×10^5	m ² /kg
Micropore Volume	5.8×10^{-4}	m ³ /kg



Figure 3.4: MIL-100(Fe) granular sample used in the fixed bed and gravimetric experiments

3.2. Gases

For the experiments described in this chapter, various gas phase adsorbates and auxiliary gases were used. Ethylene N35 (purity higher than 99.95 % (v/v)), propylene N25 (purity higher than 99.5 % (v/v)) and nitrogen (purity higher than 99.995 % (v/v)) were used and supplied by Air Liquide S.A. For the adsorption equilibrium gravimetric experiments, vinyl chloride with a purity higher than 99.96 % (w/w) was supplied by Shin-Etsu CIREs. For the helium pycnometry measurements and the activation and regeneration of the adsorbent bed in the fixed bed experiments, helium with a purity higher than 99.999 % (v/v) was used, also supplied by Air Liquide S.A. All gases were used without pre-treatment.

3.3. Adsorption Equilibrium Isotherms– Gravimetric Method

In this work, the adsorption equilibrium isotherm data for the proposed pure gas components were experimentally obtained using a gravimetric method, for three different temperatures. The measurements were performed in a closed batch system using the magnetic suspension balance Rubotherm[®], with a precision of 10 μg . An illustration and a schematic of the used magnetic suspension balance is shown in Figure 3.5 and 3.6, respectively.

Summarily, the gravimetric method involves attaching a basket containing a sample of the adsorbent material to a setup with a permanent magnet. In turn, the permanent magnet is kept in a free suspension mode by an electromagnet fixed to the under floor weighing hook of a microbalance. The microbalance will then weigh the known mass of the magnets together with the sample, thus accurately measuring the mass of the sample. Together with the addition of an electronic controlling unit (see Figure 3.5b), this method allows for high-pressure measurements and the ability to perform zero-point correction and balance calibrations during any time of the recording measurements. As a result of these improvements, mass changes in a sample can be recorded with utmost accuracy.

Prior to the experiment, the basket, the glass wool, responsible for preventing any adsorbent spillage, and a sample of the adsorbent material are separately weighted in an analytical balance. The basket, filled with the measured adsorbent sample and the glass wool, is introduced to the balance measuring cell, where an inert metal hook suspends it. After the basket is correctly attached to the system, the measuring cell is closed, bolted, and sealed using a heavy metal jacket, preventing leakage and lower shaking. A coil resistance envelops the metal jacket, which, together with the external ceramic casing and the electronic controlling unit, are responsible for controlling the temperature inside the measuring cell. The gas reservoirs and the inlet of the vacuum pump are connected to the measuring cell by a system of lines and valves. At the same time, the pressure and temperature are registered using three pressure transducers located at the inlet of the balance, each operating between 0 – 200 bar, 0 – 10 bar, and 0 – 100 mbar and a type K thermocouple, respectively. A dedicated software provided by Rubotherm controls and records the mass, temperature, and pressure data acquisition, while a LabVIEW program records the output of the more sensible pressure transducer. (Figure 3.5c)



Figure 3.5: Magnetic Suspension balance Rubotherm (a), Electronic Control Unit (b) and Data acquisition system (c)

Having finished the assembly, each adsorbent sample must first be activated in situ to dry the sample and remove any adsorbed contaminants. The adsorbent sample is continuously submitted to vacuum (0.01 bar), via the adjacently connected vacuum pump and is gradually heated up according to specifications. All activated carbons were activated at 393 K, while the MIL-100(Fe) was activated at 433 K. All samples were activated for at least eight hours until no more mass loss was registered for at least one hour. After the activation process, the adsorbent is cooled to 303 K under vacuum.

The equilibrium measurements are obtained by gradually introducing the adsorbate gas into the measuring cell until the desired pressure of pure gas is reached. Equilibrium with the adsorbent material is attained for the target temperature. Indeed, the sample is considered to be in equilibrium when the mass history remain constant (± 0.00001 g) for more than 30 minutes. The adsorption component of the equilibrium isotherm is then constructed by repeatedly increasing the pressure of the gas species and registering the sample mass when each equilibrium is achieved. To check the reversibility of the isotherm and the possible existence of hysteresis, the desorption component of the isotherm is also

plotted by lowering the pressure inside the measuring cell using the vacuum pump and waiting until equilibrium is achieved.

At the end of each isotherm measurement, the adsorbent sample is again subjected to continuous vacuum to regenerate the sample so that any of the remaining adsorbed species does not influence the next isotherm. If the sample mass does not return to the initial post-activation dry mass, the sample should be heated to its activation temperature again, until the original mass is obtained.

Due to the high precision required in these measurements, the buoyancy effect can be a significant inaccuracy in the gravimetric method, especially at higher pressures. In this regard, the calculated adsorbed amount must be corrected, using Equation 3.1, to account for this effect

$$q = \frac{\Delta m + \rho_G(V_s + V_C)}{m_s M_w} \frac{\rho_{Ads}}{\rho_{Ads} - \rho_G} \quad (\text{Equation 3.1})$$

where Δm is the weight difference between the mass measured by the balance and the initial mass of the system loaded with the activated sample, V_s is the adsorbent volume, V_C is the inert components volume (glass wool, permanent magnet, suspension shaft, and sample support), ρ_G is the adsorbed gas density at the measuring conditions, ρ_{Ads} is the adsorbate liquid density, m_s is the adsorbent mass and M_w is the adsorbate molecular weight.¹³ To calculate the adsorbate mass and volume, and the inert components volume, two helium pycnometry measurements must be performed. One of the helium pycnometry was performed with only the permanent magnet, metal hook, basket, and the glass wool. In contrast, the second was performed with the addition of the activated adsorbent sample. Both measurements were carried out at 303 K.

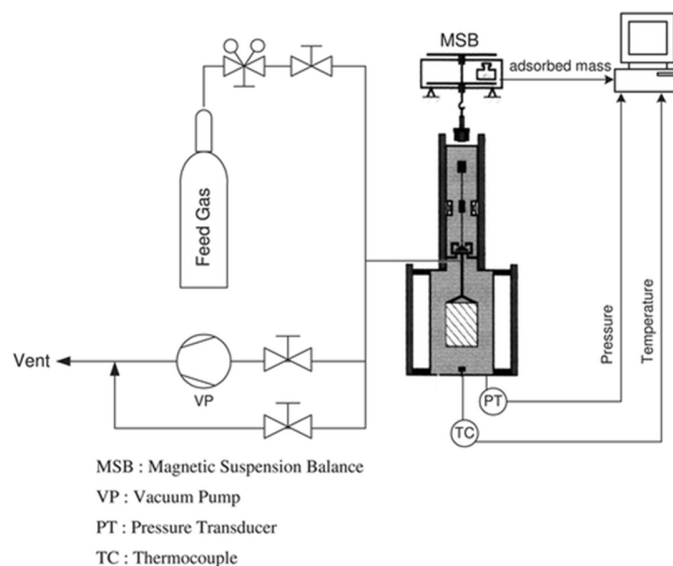


Figure 3.6: Schematic Diagram of the experimental installation used for the adsorption isotherms measurements ¹⁴

3.4. Fixed Bed Breakthrough Experiments

For both ethylene/nitrogen and propylene/nitrogen mixtures, the adsorption breakthrough experiments were performed on a bench-scale single column fixed bed PSA unit, packed with MIL-100(Fe). While the present installation, shown in Figure 3.7, has already been described in great detail elsewhere ¹⁵, a concise version will be presented below.

The fixed bed feed flowrate and composition are obtained by mixing three adsorbate streams, each controlled by a mass flow controller (MFC1, MFC2, and MFC3, Alicat Scientific, Inc.). The MFC1 was dedicated for ethylene and propylene, MFC2 was employed for helium, while MFC3 was dedicated for nitrogen. While MFC1 and MFC2 have a maximum flowrate of 2 SLPM, MFC3 has a maximum flowrate of 1 SLPM. At the outlet of the fixed bed, the flow rate was assessed using a mass flow meter (MFM, Alicat Scientific, Inc.), and the pressure was controlled using a back pressure regulator (BPR, Bronkhorst High-Tech).

The MIL-100(Fe) adsorbent was packed inside a stainless steel column with an internal diameter of 2.1 cm and a length of 0.747 m (Figure 3.8). The fixed bed was capped using glass wool and a metal mesh to hold the adsorbent in place and prevent the loss of any powdered material into the system.

The temperature inside the fixed bed was controlled by a convection air furnace (Thermolab), equipped with three PID controllers, two motors and 12 solenoid resistances, which allowed controlled temperatures between 303 and 673 K. The temperature of the furnace is measured by one, and the temperature inside of the fixed bed is measured by three K-type thermocouples. Divided by the top, middle, and bottom positions, the three thermocouples are inserted into the fixed bed column by specifically located airtight entrances. The top thermocouple measures the wall temperature at 7 cm from the outlet of the column, while the middle and the bottom thermocouples measure the fixed bed internal temperature at 32 and 57 cm from the outlet of the column, respectively.

At any time during the breakthrough experiment, a 16 loop valve system can be used to collect up to 15 samples of the fixed bed outlet, which, in turn, can be feed to a gas chromatograph (Master GC, Dani) to determine the composition of the bed outlet at each given moment. The gas chromatograph was equipped with a capillary column (GS-GasPro 60 m x 0.32 mm x 0.01 μm , Agilent J&W) (Figure 3.9), a flame ionization detector (FID), and a thermal conductivity detector (TCD). The gas chromatograph operated isothermally at 343 K for the ethylene/nitrogen mixture and 363 K for the propylene/nitrogen mixture, with a helium carrier gas flow rate of 7.4 $\text{ml}_{\text{STP}}\text{min}^{-1}$. The FID operated at 473 K with an air, hydrogen, and helium mixture of 400, 60, and 25 $\text{ml}\cdot\text{min}^{-1}$, while the TCD operated at 363 K with a voltage of 13.50 V and negative polarity.

The electronic output of each component and the operation of the fixed bed unit are automatically controlled by a LabVIEW interface, while the gas chromatograph is controlled using the DataApex Clarity software.

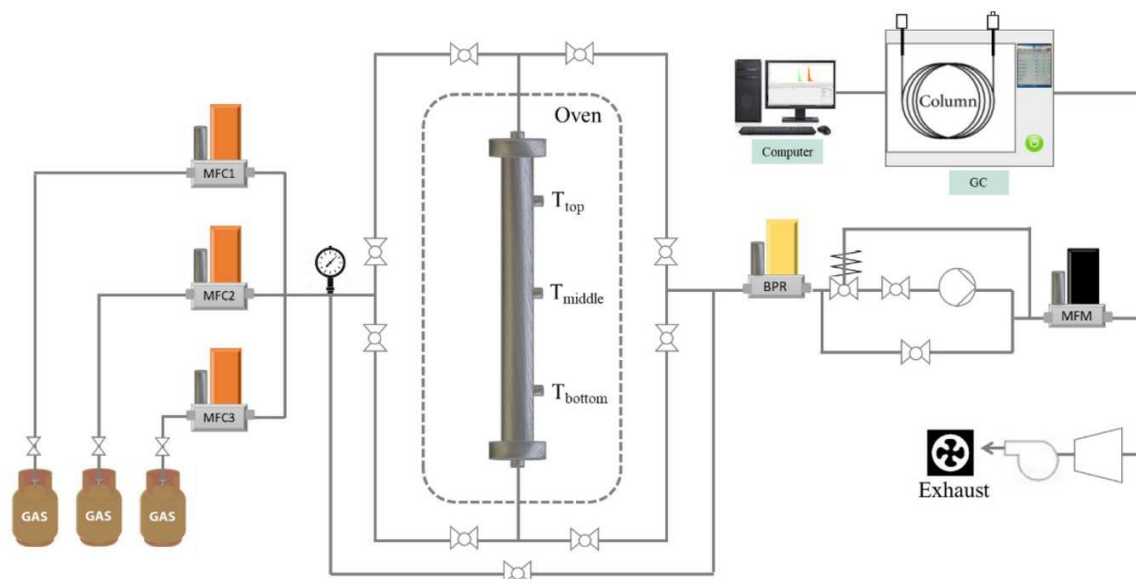


Figure 3.7: Schematic of the bench-scale fixed bed unit used for the breakthrough experiments¹²

Prior to the adsorption breakthrough experiments, the packed bed was activated overnight by gradually heating up the furnace. The average internal temperature of the fixed bed reached 433 K, and continuously purged the bed with a constant 0.5 SLPM helium flow for 18 hours. After activation, the column cooling was also performed under a helium purge.

Using some preliminary simulations, the author estimated the best temperature, pressure, and flow rate conditions for each breakthrough experiment, based on the previously obtained adsorption equilibrium data. As such, all breakthrough experiments began from an initial state of a regenerated adsorption bed with a helium saturated gas phase and were performed at 323 K, 2 bar, and under a flow rate of 1 SLPM (Standard Liter per Minute). During a breakthrough experiment, before any change to feed composition can be made, the fixed bed outlet composition and the pressure and temperature histories must be stable and equal to the respective set-point.

Three types of breakthrough experiments were planned for both olefin/nitrogen pairs: single component, binary and pseudo-binary breakthroughs.

Single component breakthroughs experiments start by feeding a pure adsorbate stream into the previously regenerated adsorption bed, initially saturated with an inert component (helium). Only after the bed is completely saturated with the adsorbate and the pressure and temperature histories inside the column have stabilized, the feed composition is changed to helium. This step allows the desorption of the adsorbate can also be recorded, and the bed is regenerated. Samples of the bed output composition should be taken during the adsorption phase, the saturation phase, and the desorption phase.

Binary breakthroughs experiments are similar to single component experiments, but the pure adsorbate feed is changed for a binary 30/70 % (v/v) olefin/nitrogen mixture feed. The proposed feed mixture can be achieved by changing the mass flow controllers set-points to match the binary fraction of the mixture. After the adsorption bed is saturated with the binary mixture, the feed composition can be changed back to helium to regenerate the bed.

In pseudo-binary breakthroughs experiments, a pure component stream (light olefin or nitrogen) is fed to a column previously filled and saturated with the other component of the proposed mixture (nitrogen or light olefin).



Figure 3.8: Fixed Bed Column packed with MIL-100(Fe) inside the oven with three internal and one external thermocouples.

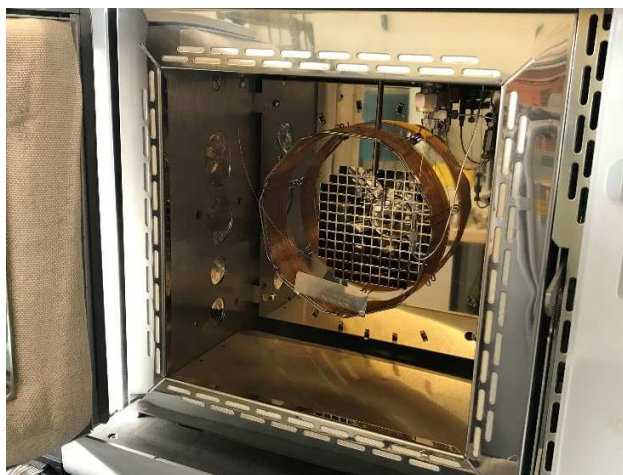


Figure 3.9: GC-GasPro 60 m x 0.32 mm x 0.01 μm gas chromatography capillary column

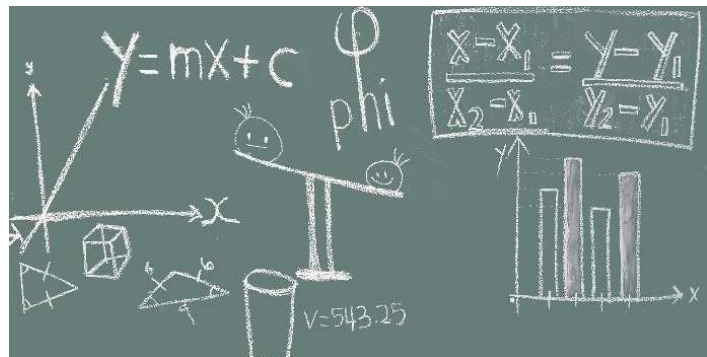
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Chapter 4

Theory and Modelling



4.1. Introduction

To analyze the results obtained from experimental measurements and develop separation units based on the data obtained from said results, the application of models is a must. In this chapter, the author will first delve into some of the theory and models used to analyze the results obtained from the adsorption equilibrium gravimetric measurements, as well as the base fixed bed mathematical model, used to analyze the results of the breakthrough experiments, and other fixed bed models used in this work. While the results of the gravimetric measurements are fitted to determine the adsorption equilibrium, the breakthrough experiments will be used to determine both the multicomponent equilibrium and the kinetic characteristics of each system.

Afterward, the author will describe the theory behind, and the mathematical models used to simulate the behavior of some classical adsorption-based separation units, such as the PSA and TPSA, as well as some other more innovative systems such as the Multi-Tubular Temperature Pressure Swing Adsorption (MT-TPSA).

The models discussed in this chapter were implemented and simulated using the gPROMS® – *general PROcess Modelling System* ModelBuilder software.

4.2. Pure Component Adsorption Equilibrium

The selection of a proper sorbent for a given separation is a complex problem. However, the predominant scientific basis for sorbent selection is the equilibrium isotherm ¹. The equilibrium isotherm of a given adsorbate/adsorbent pair relates the equilibrium relationship between the adsorbate concentration on the fluid phase and the adsorbate concentration adsorbed in the adsorbent material. As such, for an adsorption process with gaseous species, the adsorption isotherm is the relationship between the adsorption equilibrium solid phase concentration q_{eq} and the pressure of pure component P_a , at a given temperature T . ²

$$q_{eq} = f(P_a, T) \quad (\text{Equation 4.1})$$

Experimental adsorption isotherms have various characteristic shapes. These shapes are important since they provide useful preliminary information about the pore structure of the adsorbent, even before any calculations.

In 1985, an IUPAC report detailed that physisorption isotherms could be grouped into six types.³ However, in the last years, new characteristic types of isotherms have been identified and shown to be closely related to a particular pore structure. Based on the updated IUPAC report, the current eight IUPAC physisorption isotherms classifications can be seen in Figure 4.1, while the defining characteristics of each group are described in Table 4.1.

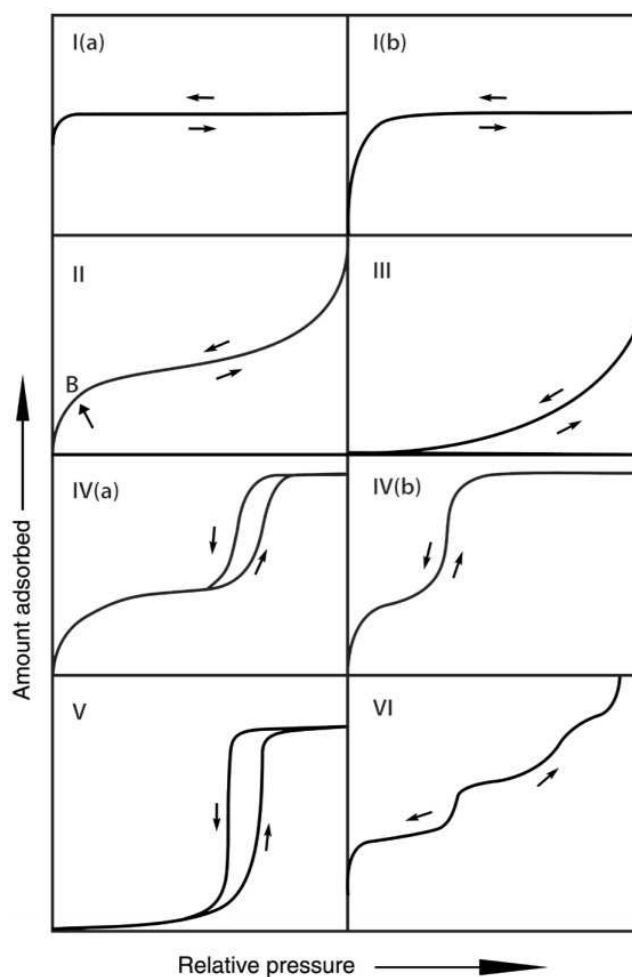


Figure 4.1: Classification of physisorption isotherms

Table 4.1: Types and characteristics of physisorption isotherms

Type	Characterization
I(a)	Microporous materials with narrow (width < 1 nm) micropores
I(b)	Materials with a pore size distribution
II	Non-porous or macroporous materials; a result of unrestricted monolayer-multilayer adsorption
III	No identifiable monolayer formation; relatively weak adsorbate-adsorbent interactions with adsorbed molecules clustered around the most favorable sites
IV(a)	Mesoporous adsorbents; presence of capillary condensation combined with hysteresis
IV(b)	Conical and cylindrical mesopores that are closed at the tapered end
V	Weak adsorbate-adsorbent interactions; at higher pressures, molecular clustering is followed by pore filling
VI	Layer-by-layer adsorption on a highly uniform non-porous surface

4.2.1. Langmuir Isotherm Model

In 1918, Irving Langmuir proposed the first coherent theory of adsorption onto a flat surface based on a kinetic viewpoint. This theory stated that an adsorption equilibrium is reached when there is a zero rate of accumulation between the continuous bombardment and adsorption of molecules onto the surface, and the corresponding evaporation (desorption) of molecules from the surface. While the Langmuir type isotherms are the most widely used for practical applications, theoretically, this model is still limited by several assumptions. The Langmuir model assumes that the adsorbent surface is homogeneous and that molecules are adsorbed at definite and localized adsorption active sites. Each active site can only accommodate one adsorbate, adsorption can only occur in a monolayer, and the presence of an adsorbed molecule does not affect the behavior of adjacent active sites. The probability of adsorption for one active site is the same as all others, as all sites are energetically equivalent, and the adsorption enthalpy is constant along the adsorbent surface.⁴ For the adsorption of a pure component, the Langmuir isotherm has the following format¹:

$$q_{eq} = \frac{q_{sat} b P_a}{1 + b P_a} \quad (\text{Equation 4.2})$$

where q_{sat} is the total amount that can be adsorbed by a unit of mass of adsorbent in a monolayer or the saturation solid phase concentration, and b is called the affinity coefficient. The affinity coefficient is a temperature-dependent parameter that follows the van't Hoff equation:

$$b = b_o e^{-\Delta H/R_g T} \quad (\text{Equation 4.3})$$

where b_o is the pre-exponential parameter, ΔH is the enthalpic parameter of the model, that in this case corresponds to the adsorption enthalpy, and R_g is the universal gas constant.

For systems with low pressure or very diluted in the adsorbate species, the isotherm is reduced to a linear form, with Henry's constant H :

$$q_{eq} = H P_a \quad (\text{Equation 4.4})$$

$$H = q_{sat} b \quad (\text{Equation 4.5})$$

4.2.2. Dual-Site Langmuir Isotherm Model

A modification of the Langmuir model, the Dual-Site Langmuir (DSL) Model tries to consider any possible heterogeneity on the surface or structure of the adsorbent, and as such, considers the possibility of the existence of two preferential adsorption sites. Each site has a different affinity for one adsorbed species, as well as a different adsorption enthalpy. Similarly, each site follows the same considerations previously described for the Langmuir model, while additionally, the behavior of one site is independent of the state of the other. The DSL model can be written as shown by Equation 4.6:

$$q_{eq} = \frac{q_{sat,1} b_1 P_a}{1 + b_1 P_a} + \frac{q_{sat,2} b_2 P_a}{1 + b_2 P_a} \quad (\text{Equation 4.6})$$

$$b_i = b_{0,i} e^{-\Delta H_i / R_g T} \quad (\text{Equation 4.7})$$

where $q_{sat,i}$ is the saturation solid-phase concentration for each site, b_i is the affinity parameter for each site, $b_{0,i}$ is the pre-exponential parameter and ΔH_i is the adsorption enthalpy for each site.

4.3. Multicomponent Adsorption Equilibrium

For a multicomponent mixture, the extended Langmuir isotherm can be used, as seen in equation 4.8. For this isotherm, it is assumed that the monolayer capacity for one component in the mixed adsorbed phase is the same as the pure component adsorption. That is, the area covered by one molecule is not influenced by the presence of other species on the surface. Additionally, following the assumption of ideal gas behavior, the partial pressure of each component can be replaced, as shown in Equation 4.8:

$$q_{eq\ i} = \frac{q_{sat,i} b_i C_{g,i} R_g T}{1 + \sum_{i=1}^n b_i C_{g,i} R_g T} \quad (\text{Equation 4.8})$$

where C_g is the molar concentration on the gas phase. Similar to the previous competitive, extended Langmuir model, a competitive Dual Site Langmuir model can also be extended to an n-component mixture, as seen in Equation 4.9:

$$q_{eq\ i} = \frac{q_{sat,1,i} b_{1,i} C_{g,i} R_g T}{1 + \sum_{i=1}^n b_{1,i} C_{g,i} R_g T} + \frac{q_{sat,2,i} b_{2,i} C_{g,i} R_g T}{1 + \sum_{i=1}^n b_{2,i} C_{g,i} R_g T} \quad (\text{Equation 4.9})$$

4.4. Isosteric Heat of Adsorption

The isosteric heat of adsorption is the ratio of the infinitesimal change in the adsorbate enthalpy to the infinitesimal change in the adsorbed amount (n – number of adsorbed moles). The property is essential in dynamic studies. Indeed, when heat is released from the exothermal adsorption process, part of this heat is absorbed by the adsorbent and the other part dissipates to the surroundings. The heat absorbed by the adsorbent increases the particle temperature, and consequently, increasing the adsorption

kinetics but decreasing the equilibrium adsorption amount, affecting the general dynamic behavior of the adsorption bed ⁴.

The isosteric heat adsorption can be calculated by the van't Hoff equation, displayed in equation 4.10:

$$(-\Delta H_{isost}) = R_g T^2 \left(\frac{\partial \ln P_i}{\partial T} \right)_q \quad (\text{Equation 4.10})$$

Where ΔH_{isost} is the isosteric heat of adsorption of the component i and P_i is the partial pressure of the component i . Suppose the heat capacity of the adsorbate in the solid and fluid phase are neglected. In that case, the isosteric heat of adsorption becomes independent of the temperature and can be calculated by direct integration, resulting in equation 4.11:

$$\ln P_i = \text{constant} - \frac{\Delta H_{isost}}{R_g T} \quad (\text{Equation 4.11})$$

The isosteric heat of adsorption can be obtained by fitting a linear regression to the plot of the $\ln P_i$ vs T , at a given q , obtaining the value for $\frac{\Delta H_{isost}}{R_g}$ as the slope of the linear regression.

As described in literature ⁴, the variation of the isosteric heat with loading can be estimated for the Dual Site Langmuir model, as shown in Equation 4.12:

$$-\Delta H_{isost} = \frac{\sum_{j=1}^N q_{sat,j} \frac{b_j (-\Delta H_j)}{(1 + b_j P)^2}}{\sum_{j=1}^N q_{sat,j} \frac{b_j}{(1 + b_j P)^2}} \quad (\text{Equation 4.12})$$

4.5. Selectivity

For adsorption equilibrium-based separations, choosing an adsorbent with high selectivity is required for an economical process. Using the pure component adsorption equilibrium isotherms, the ideal selectivity of a given component A over component B ($\alpha_{A/B}$) can be calculated as follows:

$$\alpha_{A/B} = \frac{q_{eq(A)} / q_{eq(B)}}{y_{(A)} / y_{(B)}} \quad (\text{Equation 4.13})$$

where y_i is the gas phase molar fraction.

4.6. Fixed Bed Mathematical Model

Used as the basis for a significant number of reaction, separation and heat storage units, fixed beds are typically cylindrical and rigid vessels, with at least one inlet and one outlet, packed with some form of packing, catalyst, or adsorbent. They are operated in such a way that the packing remains fixed or not fluidized under the effect of the flow rates that pass parallelly through it.

In the present work, two fixed bed mathematical models will be developed and used to simulate the dynamic behavior of an adsorption column following a cylindrical geometry. A one-dimensional (axial direction, 1D) model will be used to simulate and predict the adsorption and desorption behavior of the single and multicomponent breakthrough experiments, as well as simulate the behavior of most of the proposed adsorber designs. The two-dimensional (axial and radial directions, 2D) will be used to simulate any adsorber designs in which the mathematical balances must be considered in the radial direction. Both fixed bed models will consider plug flow behavior with mass and energy axial dispersion, while the 2D model will additionally consider mass and energy radial dispersion.

All the mathematical models are composed of a set of mass, energy, and momentum balances. The mass transfer will be considered solely between the gas and the solid phase, while energy transfer will be considered between the gas phase, solid phase, column wall, and the external environment. Onwards, depending on the chosen system design, the previous energy transfer to an external environment can refer either to open ambient temperature or to a heat exchange fluid in a jacketed or a shell and tube/multitubular heat exchanger. If a heat exchange fluid is used, then the necessary mass, energy, and momentum balances will also be considered.

4.6.1. 1D Fixed Bed Model

For the 1D model, the partial differential and algebraic equations (PDAE) are discretized along the axial (z) direction, using the second-order orthogonal collocation on finite elements method. The resulting ordinary differential equations (ODE) with respect to time are solved using the DASOLV solver from gPROMS® Model Builder. The mathematical model used to describe the dynamic behavior of a fixed bed multicomponent adsorption column is based on the following assumptions and models ⁵:

- The gas-phase follows ideal gas behavior;
- The mass, temperature, and momentum balances have no gradients in the radial direction;
- The internal mass transfer resistance was expressed by the Linear Driving Force (LDF) model;
- The external mass and energy transfer resistances are expressed by the film model;
- The column porosity, cross section area, and particle density are constant along the column;
- The temperature profile is homogeneous inside the particle;
- The Ergun equation is valid locally, and only the pressure drop, and the velocity change are considered in the momentum balance;

Gas Phase Mass Balance:

$$\varepsilon \frac{\partial C_{g,i}}{\partial t} = - \frac{\partial (u_0 C_{g,i})}{\partial z} + \varepsilon \frac{\partial}{\partial z} \left(D_{ax} C_{gt} \frac{\partial (y_i)}{\partial z} \right) - \rho_b \frac{\partial q_i}{\partial t} \quad (\text{Equation 4.14})$$

where ε is the bed porosity (column void fraction), u_0 is the gas phase superficial velocity, D_{ax} is the mass axial dispersion coefficient, C_{gt} is the total molar concentration on the gas phase, ρ_b is the bulk density, and q is the solid phase concentration.

Solid Phase Mass Balance, with the internal mass transfer resistance expressed by the LDF model:

$$\frac{\partial q_i}{\partial t} = 15 \frac{D_{p,i}}{r_p^2} (q_{eq,i} - q_i) = k_{LDF,i} (q_{eq,i} - q_i) \quad (\text{Equation 4.15})$$

where D_p is the pore diffusivity, r_p is the averaged particle radius and $k_{LDF,i}$ is the LDF parameter for each component.

Momentum Balance represented by the Ergun equation:

$$\frac{\partial P}{\partial z} = \frac{150\mu}{(2r_p)^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} u_0 + \frac{1.75\rho_f}{(2r_p)} \frac{(1-\varepsilon)}{\varepsilon^3} u_0^2 \quad (\text{Equation 4.16})$$

where P is the absolute pressure, μ is the gas phase viscosity and ρ_f is the gas phase density.

Ideal gas equation:

$$P = C_{gt} R_g T \quad (\text{Equation 4.17})$$

Energy balance in the gas phase:

$$\begin{aligned} \lambda_{ax} \frac{\partial^2 T}{\partial z^2} - u_0 C_{gt} \sum_{i=1}^n (y_i C_{p,i}) \frac{\partial T}{\partial z} + \varepsilon R_g T \sum_{i=1}^n \frac{\partial C_{g,i}}{\partial t} - (1-\varepsilon) a_p h_f (T - T_p) \\ - 4 \frac{h_w}{d_w} (T - T_w) - \varepsilon C_{gt} \sum_{i=1}^n (y_i C_{p,i}) \frac{\partial T}{\partial t} = 0 \end{aligned} \quad (\text{Equation 4.18})$$

where λ_{ax} is heat axial dispersion coefficient, C_p is the gas molar specific heat at constant pressure, a_p is the particle specific area, h_f is the film heat transfer coefficient, T_p is the particle temperature, h_w is the wall heat transfer coefficient, d_w is the diameter of the column and T_w is the wall temperature.

Energy balance in the solid phase:

$$\begin{aligned} (1-\varepsilon) \left(\rho_p \sum_{i=1}^n (q_i C_{p,i}) + \rho_p C_{p,s} \right) \frac{\partial T_p}{\partial t} \\ = \rho_b \sum_{i=1}^n (-\Delta H_i q_i) + (1-\varepsilon) a_p h_f (T - T_p) \end{aligned} \quad (\text{Equation 4.19})$$

where ρ_p is the adsorbent particle density and $C_{p,s}$ is the particle specific heat.

Energy balance in the column wall:

$$\rho_w C p_w \frac{\partial T_w}{\partial t} = \alpha_w h_w (T - T_w) + \alpha_{wl} U_w (T_w - T_\infty) \quad (\text{Equation 4.20})$$

where ρ_w is the wall density, $C p_w$ is the wall specific heat, α_w is the ratio of the internal surface area to the volume of the column wall, α_{wl} is the log mean surface area to the volume of the column wall, U_w is the external heat transfer coefficient and T_∞ is the temperature outside of the adsorption column.

Due to the mass flux equality at the particle surface, the solid mass balance can be written by the Linear Driving Force Model. The momentum balance on a fixed-bed column will be calculated locally from the Ergun equation with varying velocity and fluid density. For the energy balance, due to the small size of the particles and the thinness of the column wall, radial temperature gradients inside the particle and wall are not considered.

To resolve the present system of algebraic and partial differential equations, a set of initial and boundary conditions are necessary to describe the fixed bed behavior. As shown in Table 4.2, the column was initially filled with inert gas, helium, and was set to a predefined operating temperature and pressure for the breakthrough experiments. The Danckwerts boundary conditions were used for the simulation of the breakthrough experiments. For the simulation of the pseudo-binary breakthroughs, the initial conditions presented in Table 4.2 must change to reflect the correct initial gas composition.

Table 4.2: Initial and Boundary conditions used in the 1D Fixed bed Mathematical Model

Initial Conditions
$y_{inert} = 1$
$C_{g,i} = 0, i \neq \text{inert}$
$C_{gt} = C_{g,inert}$
$T_g = T_p = T_w = T_\infty$
Boundary Conditions

Inlet of the column (z=0)	$u_{z \text{ inlet}} C_{g,i \text{ inlet}} = u_z C_{g,i} - \varepsilon \frac{D_{ax,i} \partial(C_{g,i})}{\partial z}$ $u_{z, \text{inlet}} C_{gt \text{ inlet}} = \sum_{i=1}^n u_z C_{g,i}$ $u_{z \text{ inlet}} C_{gt \text{ inlet}} \sum_{i=1}^n y_{i \text{ inlet}} C_{p,i} T_{\text{inlet}} = u_z C_{g,i} \sum_{i=1}^n y_i C_{p,i} T - \frac{\lambda_{ax} \partial(T)}{\partial z}$
Outlet of the column (z=L)	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $P = P_{\text{high}}$ $\frac{\partial(T)}{\partial z} = 0$

4.6.2. 2D Fixed Bed Model

To simulate a cylindrical 2D fixed bed model, the PDAE must be discretized along both the axial (z) and radial (r) directions, using a second order orthogonal collocation on finite elements method for both directions. Similar to the previous 1D model, the resulting ODEs are solved using the DASOLV solver from the gPROMS® Model Builder. The considerations are similar to those taken for the 1D model except for the presence of radial gradients and radial mass and thermal dispersion and convection phenomena.

The Gas Phase Mass Balance accounts for convective and dispersion contributions on both axial and radial direction and the mass transfer between the gas and solid phase, as seen in Equation (4.21).

$$\begin{aligned} \varepsilon \frac{\partial C_{g,i}}{\partial t} = & -\frac{\partial(u_z C_{g,i})}{\partial z} - \frac{1}{r} \frac{\partial(u_r r C_{g,i})}{\partial r} + \varepsilon \frac{\partial}{\partial z} \left(D_{ax} C_{gt} \frac{\partial(y_i)}{\partial z} \right) \\ & + \frac{\varepsilon}{r} \frac{\partial}{\partial r} \left(D_r C_{gt} r \frac{\partial(y_i)}{\partial r} \right) - \rho_b \frac{\partial q_i}{\partial t} \end{aligned} \quad (\text{Equation 4.21})$$

where u_z is the superficial gas phase velocity in the axial direction, u_r is the superficial gas phase velocity in the radial direction, and D_r is the mass radial dispersion coefficient.

As the internal mass transfer resistance is expressed with the LDF model, the Mass Balance in the Solid Phase is identical to the one from the 1D model, shown by Equation 4.15.

The Ergun equation represents the Momentum Balance locally through the column, with varying velocity and fluid density, in both the axial (Equation 4.22) and radial (Equation 4.23) directions:

$$\frac{\partial P}{\partial z} = \frac{150\mu}{(2r_p)^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} u_z + \frac{1.75\rho_f}{(2r_p)} \frac{(1-\varepsilon)}{\varepsilon^3} u_z^2 \quad (\text{Equation 4.22})$$

$$\frac{\partial P}{\partial r} = \frac{150\mu}{(2r_p)^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} u_r + \frac{1.75\rho_f}{(2r_p)} \frac{(1-\varepsilon)}{\varepsilon^3} u_r^2 \quad (\text{Equation 4.23})$$

The gas phase follows the ideal gas equation, Equation 4.17.

The Energy Balance to the Gas Phase accounts for convective and dispersive contributions on both axial and radial direction, as well as energy transfer between gas and solid phases (equation 4.24). The energy transfer to the tube wall is considered in the gas phase energy boundary conditions.

$$\begin{aligned} \varepsilon C_{gt} \sum_{i=1}^n (y_i C_{p,i}) \frac{\partial T}{\partial t} = & \lambda_{ax} \frac{\partial^2 T}{\partial z^2} + \frac{\lambda_r}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) - u_z C_{gt} \sum_{i=1}^n (y_i C_{p,i}) \frac{\partial T}{\partial z} \\ & - u_r C_{gt} \sum_{i=1}^n (y_i C_{p,i}) \frac{\partial T}{\partial r} + \varepsilon R_g T \sum_{i=1}^n \frac{\partial C_{g,i}}{\partial t} - (1 - \varepsilon) a_p h_f (T - T_p) \end{aligned} \quad (\text{Equation 4.24})$$

where λ_{ax} is axial heat dispersion coefficient, and λ_r is radial heat dispersion coefficient.

The Energy Balance in the Solid Phase is the same as Equation 4.19.

The Energy Balance for the Column Wall is shown in Equation 4.25.

$$\rho_w C_{pw} \frac{\partial T_w}{\partial t} = \alpha_w h_w (T|_{r=ID/2} - T_w) + \alpha_{wl} h_{shell} (T_w - T_{HX}) \quad (\text{Equation 4.25})$$

where ID is the internal diameter of the adsorption column, h_{shell} is the shell side heat transfer coefficient and T_{HX} is the temperature of the heat transfer fluid.

The energy balance for the Heat Exchanger fluid is shown in Equation 4.26.

$$\rho_{HX} C_{p,HX} \frac{\partial T_{HX}}{\partial t} = -\rho_{HX} C_{p,HX} u_{HX} \frac{\partial T_{HX}}{\partial z} + \Omega h_{shell} (T_w - T_{HX}) \quad (\text{Equation 4.26})$$

where ρ_{HX} is the shell side fluid density, $C_{p,HX}$ is the shell side fluid specific heat, u_{HX} is the shell side fluid velocity and Ω is the ratio between the tube outer surface area and the clearance volume in the closest neighborhood of each tube, according to tube layout.

To resolve the present system of algebraic and partial differential equations, a set of initial and boundary conditions are necessary to describe the fixed bed behavior. As shown in Table 4.3, the column was initially filled with inert gas, helium, and was set to a predefined operating temperature and pressure.

Table 4.3: Initial and Boundary conditions used in the 2D Fixed bed Mathematical Model

Initial Conditions	
$y_{inert} = 1$ $C_{g,i} = 0, i \neq \text{inert}$ $C_{gt} = C_{g,inert}$ $T_g = T_p = T_w = T_{HX}$	
Boundary Conditions	
Inlet of the column (z=0)	$u_{z \text{ inlet}} C_{g,i \text{ inlet}} = u_z C_{g,i} - \varepsilon \frac{D_{ax,i} \partial(C_{g,i})}{\partial z}$ $u_{z \text{ inlet}} C_{gt \text{ inlet}} = \sum_{i=1}^n u_z C_{g,i}$ $u_{z \text{ inlet}} C_{gt \text{ inlet}} \sum_{i=1}^n y_{i \text{ inlet}} C_{p,i} T_{inlet} = u_z C_{g,i} \sum_{i=1}^n y_i C_{p,i} T - \frac{\lambda_{ax} \partial(T)}{\partial z}$
Outlet of the column (z=L)	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $P = P_{high}$ $\frac{\partial(T)}{\partial z} = 0$
Center of the column (r=0)	$\frac{\partial(C_{g,i})}{\partial r} = 0$ $\frac{\partial(T)}{\partial r} = 0$ $\frac{\partial(P)}{\partial r} = 0$

The periphery of the column ($r=ID/2$)	$\frac{\partial(C_{g,i})}{\partial r} = 0$ $\frac{\partial(T)}{\partial r} = \frac{h_w}{\lambda_r} (T_w - T)$ $\frac{\partial(P)}{\partial r} = 0$

4.6.2.1. Equivalent 1D Model

Although a 2D model allows for a more thorough analysis of the phenomena in play, it does come at an increased computational power and simulation time cost. However, for process designing and optimization, the increased resource costs of 2D simulations are amplified when it is necessary to perform a significant number of cyclic simulations, all under different operating conditions until cyclic steady state is achieved. As such, to cut down on the computational and time costs, while continuing to accurately predict the performance of the proposed cyclic adsorption separation system, an equivalent 1D model, which approximates the radial thermal behavior by a lumped contribution of the radial heat dispersion and the wall heat transfer coefficient, was developed.

For the equivalent 1D model, the contributions for the thermal transport in the radial direction are accounted using the derivation proposed by Froment ⁶, which estimates a tube side heat transfer coefficient U_{tube} from the theoretical sum of the wall and bulk radial diffusion resistances, as shown in Equation 4.27.

Tube Side Overall Heat Transfer Coefficient (U_{tube}):

$$\frac{1}{U_{tube}} = \frac{1}{h_w} + \frac{ID}{8\lambda_r} \quad (\text{Equation 4.27})$$

Except for the use of the overall heat transfer coefficient referred to in Equation 4.27 in the Energy balance to the column wall, the mathematical balance system for the equivalent 1D model is identical to the system described for the 1D model. Mass transfer occurs between the gas and solid phase, and energy transfer occurs between the gas and solid phases,

column wall, and heat exchanger fluid. The equivalent 1D model follows the same assumptions as of the 2D model.

4.7. Cyclic Adsorption System Model

As exemplified in the works of Skarström and Guerin-Domine, any cyclic adsorption system is composed of a series of sequential operational steps. As such, to model the operation of a cyclic adsorption system, one has to recreate the dynamic operating conditions of every step integral to the operation of the cycle. Since all adsorption systems developed in this work are based in the fixed bed mathematical model, each operational step is recreated by changing the boundary conditions of the fixed bed model to best reproduce the flow, pressure and temperature characteristics and changes particular to each step. To complete a cycle, the fixed bed mathematical model must be solved for the boundary conditions of each of the chosen operational steps for a given length of time, using the final state of the previous step as the initial conditions of the present one. All the steps in a cycle must be solved sequentially until the cycle is complete and restarted. The first step in the simulation of a cyclic adsorption system model (Feed) is initialized with a fixed bed at constant pressure and temperature conditions and saturated with an inert gas, such as helium.

In an industrial setting, to meet the ever-increasing demands for performance, most units are optimized to operate in a continuous state. As such, despite the systems described in this work operating batchwise, the continuity of the process is assured by extending from a single to a multibed design. A multibed design guarantees that the system as a whole operates as a continuous one, with constant consumption of feed and, possibly, a constant production of enriched streams if the bed schedule allows it.⁷ Likewise, as the behavior of a continuous unit under constant feed conditions will tend towards a steady state, a cyclic adsorption system under the same conditions will tend to a cyclic steady state (CSS), which can be characterized by identical transient concentration profiles during each step, between two cycles.⁸

4.7.1. Pressure Swing Adsorption Model

In a PSA cycle, separation and production are promoted by a swing in the internal pressure conditions of the bed. For this purpose, the elementary steps in a PSA cycle are “Pressurization”, “Feed”, “Blowdown”, “Purge”, “Pressure Equalization”, and “Rinse”.⁷ Below, a short description of each of these steps will be given, followed by the respective boundary conditions used to represent their behavior in a mathematical model.

The Feed step consists of the inlet of the untreated binary gas mixture stream into the adsorption column, with the production of a purified stream rich in the light component.

In the Rinse step, part of the recovered heavy component is concurrently refeed into the adsorption column. The injection of a high heavy component concentration stream causes the displacement of most of the remaining gas-phase and solid-phase light component, leading to an increase in the recovery of the light component, and the purity of the heavy component product. The Rinse step is especially advantageous for systems with a low heavy component concentration feed or a high heavy component purity requirement. When applied to a solid phase system close to saturation, a rinse step can increase the purity of the heavy product at a very low productivity cost.

In the Blowdown step, the adsorption bed internal pressure is lowered from the adsorption pressure (P_{high}) to the regeneration pressure (P_{low}). Depending on the specifications of the system, the column blowdown can be accomplished by opening one end of the adsorption column to the atmospheric pressure ($P_{low} = 1 \text{ bar}$) or by employing a vacuum pump ($P_{low} < 1 \text{ bar}$). A co-current blowdown, rich in raffinate, can be used to increase the recovery of raffinate at the cost of its purity. While the counter-current blowdown accounts for most of the production of the heavy component extract. The depressurization rate is controlled by an electronic valve, which can follow an exponential or linear function.

In the Purge step, part of the light component product is used to counter-currently purge the adsorption bed and promote further desorption of the heavy component. Additionally, a reverse-flow purge ensures that the more strongly adsorbed components are pushed back towards the bed inlet and do not contaminate the raffinate product in the next cycle.

Raffinate purity tends to increase with the increase in purge until a specific limit while lowering the purity of the extract. The increase in volume due to the depressurization means that the fraction of the product stream required to purge is relatively small, and a purge step is generally beneficial for high-performance separations.⁹

In the Pressurization step, either part of the light product or the system feed is typically used to increase the pressure inside the column from the regeneration pressure (P_{low}) to the adsorption pressure (P_{high}). Pressurization using part of the light product occurs counter-currently and improves separation, as it displays similar behavior to the counter-current purge. Pressurization using the feed mixture occurs co-currently and is less efficient than with only light product, as a part of the feed is adsorbed during pressurization; however, using the feed to pressurize the column can significantly increase the productivity of the system and facilitate the scheduling of the cycle in general.

The Pressure Equalization step takes advantage of the multibed design of most PSA systems to reduce the pressurization costs of a PSA system. This step occurs by connecting the ends of two adsorption columns at different operating pressures and venting the contents of the higher pressure column into the lower pressure one, resulting in two columns with an intermediate pressure. Besides the obvious economic advantage of saving energy costs on pump operations, a well-performed pressure equalization can also increase the purity of the heavy product and recovery of light product, but to a lesser degree than with the rinse step.

All the PSA designs in this work were developed at a constant environmental temperature (T_{∞}). If necessary, the pressure swings were accomplished using vacuum and pressurization pumps. The boundary conditions for each of the PSA cycle steps used in this work are reported in Table 4.4. The performance parameters used to evaluate a PSA separation system and their mathematical implementation into the model, are represented in Equations 4.28-4.33 and 4.40.

Table 4.4: Boundary Conditions for each step in the PSA cycle

Counter Current Pressurization	
$z = 0$	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $u_z = 0$ $\frac{\partial(T)}{\partial z} = 0$
$z = L$	$u_{z,press} C_{g,i,press} = u_z C_{g,i} - \varepsilon \frac{D_{ax,i} \partial(C_{g,i})}{\partial z}$ $u_{z,press} C_{gt,press} = \sum_{i=1}^n u_z C_{g,i}$ $u_{z,press} C_{gt,press} \sum_{i=1}^n y_{i,press} C_{p,i} T_{press} = u_z C_{g,i} \sum_{i=1}^n y_i C_{p,i} T - \frac{\lambda_{ax} \partial(T)}{\partial z}$
Feed	
$z = 0$	$u_{z,inlet} C_{g,i,inlet} = u_z C_{g,i} - \varepsilon \frac{D_{ax,i} \partial(C_{g,i})}{\partial z}$ $u_{z,inlet} C_{gt,inlet} = \sum_{i=1}^n u_z C_{g,i}$ $u_{z,inlet} C_{gt,inlet} \sum_{i=1}^n y_{i,inlet} C_{p,i} T_{inlet} = u_z C_{g,i} \sum_{i=1}^n y_i C_{p,i} T - \frac{\lambda_{ax} \partial(T)}{\partial z}$
$z = L$	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $P = P_{high}$ $\frac{\partial(T)}{\partial z} = 0$
Rinse	
$z = 0$	$u_{z,rinse} C_{g,i,rinse} = u_z C_{g,i} - \varepsilon \frac{D_{ax,i} \partial(C_{g,i})}{\partial z}$

	$u_{z,rinse} C_{gt,rinse} = \sum_{i=1}^n u_z C_{g,i}$ $u_{z,rinse} C_{gt,rinse} \sum_{i=1}^n y_{i,rinse} C_{p,i} T_{low} = u_z C_{g,i} \sum_{i=1}^n y_i C_{p,i} T - \frac{\lambda_{ax}}{\partial z} \frac{\partial(T)}{\partial z}$
$z = L$	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $P = P_{high}$ $\frac{\partial(T)}{\partial z} = 0$
Blowdown	
$z = 0$	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $P = P_{high} + (P_{low} - P_{high}) * t/t_{blow}$ $\frac{\partial(T)}{\partial z} = 0$
$z = L$	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $u_z = 0$ $\frac{\partial(T)}{\partial z} = 0$
Purge	
$z = 0$	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $P = P_{low}$ $\frac{\partial(T)}{\partial z} = 0$
$z = L$	$u_{z,purge} C_{g,i,purge} = u_z C_{g,i} - \varepsilon \frac{D_{ax,i}}{\partial z} \frac{\partial(C_{g,i})}{\partial z}$

$$u_{z,purge} C_{gt,purge} = \sum_{i=1}^n u_z C_{g,i}$$

$$u_{z,purge} C_{gt,purge} \sum_{i=1}^n y_{i,purge} C_{p,i} T_{purge} - u_z C_{g,i} \sum_{i=1}^n y_i C_{p,i} T - \frac{\lambda_{ax} \partial(T)}{\partial z}$$

4.7.2. Temperature Pressure Swing Adsorption Model

As indicated by its name, separation in a Temperature Pressure Swing Adsorption (TPSA) cycle is accomplished by both pressure- and a temperature-swing in the system's operating conditions. Adsorption is promoted at higher pressures and lower temperatures, while regeneration is performed at lower pressures and higher temperatures. Similar to the methodology used in typical TSA cycles, the regeneration of the adsorption bed can be enhanced by using a heated purge gas stream. In this work, pressure-swing is accomplished by the use of pressurization and vacuum pumps, while a jacketed heat exchanger performs the external temperature control of the TPSA cycles. A thermal jacket consists of an outer cylinder surrounding the adsorption column, creating an annular space between the column and the jacket walls, in which the heat transfer fluid circulates ¹⁰. The TPSA model developed also assumes that the jacketed heat exchanger is oversized to maintain a constant temperature profile on the heat exchanger side during the duration of each step.

In addition to all the cycle steps previously discussed for the PSA system, the TPSA mathematical model also includes a “Closed Heating” step and a “Closed Cooldown” step, which respectively accounts for a controlled pre-heating, and cooling of the adsorption bed. An “Idle” step was also included to account for any idle cycle time that could originate from any mismatch in the cycle schedule. The boundary conditions used for each of the TPSA cycle steps are reported in Tables 4.5 and 4.6, depending on the used fixed bed model. The performance parameters used in the TPSA process are also dependent on the used fixed bed model and are described by Equations 4.28-4.39, 4.41. The operating costs of the heating jacket are not accounted for in this work.

Table 4.5: Boundary Conditions in the Axial direction for the 1D and 2D model

Counter Current Pressurization	
$z = 0$	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $u_z = 0$ $\frac{\partial(T)}{\partial z} = 0$
$z = L$	$u_{z,press} C_{g,i,press} = u_z C_{g,i} - \varepsilon \frac{D_{ax,i} \partial(C_{g,i})}{\partial z}$ $u_{z,press} C_{gt,press} = \sum_{i=1}^n u_z C_{g,i}$ $u_{z,press} C_{gt,press} \sum_{i=1}^n y_{i,press} C_{p,i} T_{press} = u_z C_{g,i} \sum_{i=1}^n y_i C_{p,i} T - \frac{\lambda_{ax} \partial(T)}{\partial z}$
Feed	
$z = 0$	$u_{z,inlet} C_{g,i,inlet} = u_z C_{g,i} - \varepsilon \frac{D_{ax,i} \partial(C_{g,i})}{\partial z}$ $u_{z,inlet} C_{gt,inlet} = \sum_{i=1}^n u_z C_{g,i}$ $u_{z,inlet} C_{gt,inlet} \sum_{i=1}^n y_{i,inlet} C_{p,i} T_{inlet} = u_z C_{g,i} \sum_{i=1}^n y_i C_{p,i} T - \frac{\lambda_{ax} \partial(T)}{\partial z}$
$z = L$	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $P = P_{high}$ $\frac{\partial(T)}{\partial z} = 0$
Rinse	
$z = 0$	$u_{z,rinse} C_{g,i,rinse} = u_z C_{g,i} - \varepsilon \frac{D_{ax,i} \partial(C_{g,i})}{\partial z}$

	$u_{z,rinse} C_{gt,rinse} = \sum_{i=1}^n u_z C_{g,i}$ $u_{z,rinse} C_{gt,rinse} \sum_{i=1}^n y_{i,rinse} C_{p,i} T_{low} = u_z C_{g,i} \sum_{i=1}^n y_i C_{p,i} T - \frac{\lambda_{ax}}{\partial z} \frac{\partial(T)}{\partial z}$
$z = L$	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $P = P_{high}$ $\frac{\partial(T)}{\partial z} = 0$
Heating/Cooldown/Idle	
$z = 0$	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $u_z = 0$ $\frac{\partial(T)}{\partial z} = 0$
$z = L$	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $u_z = 0$ $\frac{\partial(T)}{\partial z} = 0$
Blowdown	
$z = 0$	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $P = P_{high} + (P_{low} - P_{high}) * t/t_{blow}$ $\frac{\partial(T)}{\partial z} = 0$
$z = L$	$\frac{\partial(C_{g,i})}{\partial z} = 0$

	$u_z = 0$ $\frac{\partial(T)}{\partial z} = 0$
Purge	
$z = 0$	$\frac{\partial(C_{g,i})}{\partial z} = 0$ $P = P_{low}$ $\frac{\partial(T)}{\partial z} = 0$
$z = L$	$u_{z,purge} C_{g,i,purge} = u_z C_{g,i} - \varepsilon \frac{D_{ax,i} \partial(C_{g,i})}{\partial z}$ $u_{z,purge} C_{gt,purge} = \sum_{i=1}^n u_z C_{g,i}$ $u_{z,purge} C_{gt,purge} \sum_{i=1}^n y_{i,purge} C_{p,i} T_{purge} = u_z C_{g,i} \sum_{i=1}^n y_i C_{p,i} T - \frac{\lambda_{ax} \partial(T)}{\partial z}$

Table 4.6: Boundary Condition in the Radial direction for the 2D model

All Steps	
$r = 0$	$\frac{\partial(C_{g,i})}{\partial r} = 0$ $\frac{\partial(T)}{\partial r} = 0$ $\frac{\partial(P)}{\partial r} = 0$
$r = ID$	$\frac{\partial(C_{g,i})}{\partial r} = 0$ $\frac{\partial(T)}{\partial r} = \frac{h_w}{\lambda_r} (T_w - T)$ $\frac{\partial(P)}{\partial r} = 0$

4.7.3. Multitubular Temperature Pressure Swing Adsorption Model

In a typical TSA unit, as the heat transfer occurs mostly in the radial direction, the scale-up of this type of unit usually leads to a decrease in its performance. Unless the column diameter is kept constant, scale-up leads to a reduction in the heat transfer surface area to column volume ratio, resulting in longer temperature swing step durations, and consequently, higher adsorbent loads and column heights to maintain the cyclic behavior of the unit. A solution would then consist in increasing the surface transfer area to column volume ratio while keeping to a manageable column height. A design that achieves these requirements is one that follows the geometry of a multi-tubular heat exchanger, in which the adsorbent material is split up and packed into several tubes while the heat transfer fluid flows on the shell side. A multitubular design is beneficial for gas-phase applications, in which the overall heat transfer coefficient between the adsorption media and the heat exchanging fluid is predicted to be quite small. By using a higher number of tubes with smaller diameters, the increased heat transfer area can compensate for the lower heat transfer coefficient, resulting in faster heat transfer and, thus, lower adsorbent loads ¹¹. While this technology has seen extensive use in other similar areas in the chemical industry, namely as multitubular reactors for the Fischer-Tropsch synthesis ^{12,13}, only few patents and studies ¹⁴⁻¹⁶ have been published that reported the successful use of these designs for similar adsorption-based separations. Its upscaling can be easily achieved by increasing the number of tubes.

Besides the considerations previously discussed for the 1D and 2D fixed bed model, the development of the MT-TPSA process model additionally follows the following assumptions pertaining to the shell-side and design of the unit:

- The header tube arrangement achieves uniform flow distribution;
- The shell heat transfer performance is similar over all the tubes in the shell cross-section;
- The shell side energy transfer resistance in the neighborhood of each tube is negligible.

Based on these considerations, the MTA geometry can be represented by the translation symmetry of each packed tube, as shown in Figure 4.2. As such, to model the behavior of the proposed equipment, only the tube side of the equipment needs to be simulated. Considering that the packed tube side of the multitubular unit follows the same behavior as a typical fixed bed, the MT-TPSA design can be solved using the same cycle steps and corresponding initial and boundary conditions (Tables 4.5 and 4.6), as the ones detailed for the previous TPSA design. Yet, an additional consideration must be taken, the additional shell side energy balance to the heat transfer fluid. Pressure variations are controlled by the use of pressurization and vacuum pumps, while the TSA cycle can be divided into three main stages, as shown in Figure 4.3: “Adsorption,” when the heat transfer fluid is used to maintain a low temperature along the fixed bed and remove the energy from the adsorption phenomenon; “Heating,” when a heat transfer fluid is used to increase the temperature of the fixed bed and promote desorption; and “Cooldown” when the temperature inside the column is lowered again to prepare the fixed bed for the next “Adsorption” stage.

The heat transfer coefficients from the tube and shell side of the equipment must consider the occurrence of fouling. The multitubular adsorber was designed by adapting the typical values found in the literature for shell and tube heat exchangers¹⁷. The shell-side heat transfer coefficient and the heating fluid pressure drop were calculated following the Bell-Delaware method^{18,19}. The proposed mathematical model was solved using the gPROMS ModelBuilder environment. The discretization on both the axial and radial directions was performed using a second-order orthogonal collocation on finite elements method.

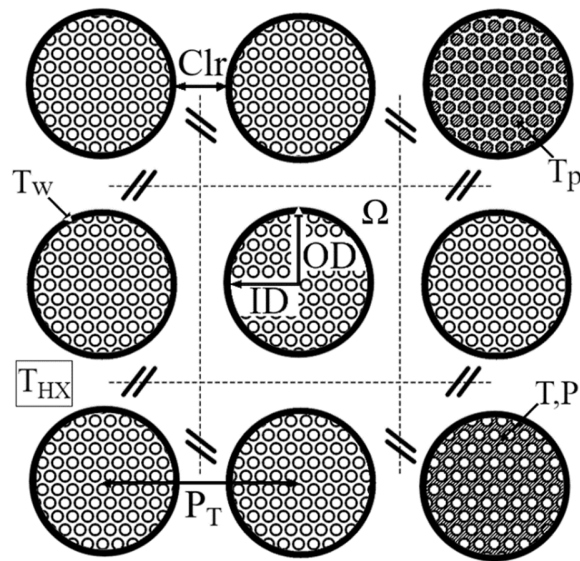


Figure 4.2: Sketch of the tube layout with adsorbent material within the tubes, together with illustrations for the inner tube diameter (ID), outer tube diameter (OD), tube clearance (Clr), tube pitch (P_T), gas phase temperature (T) and pressure (P), particle temperature (T_p), wall temperature (T_w), heat transfer fluid temperature (T_{HX}) and the ratio between the tube outer surface area and the clearance volume in the closest neighborhood of each tube (Ω).

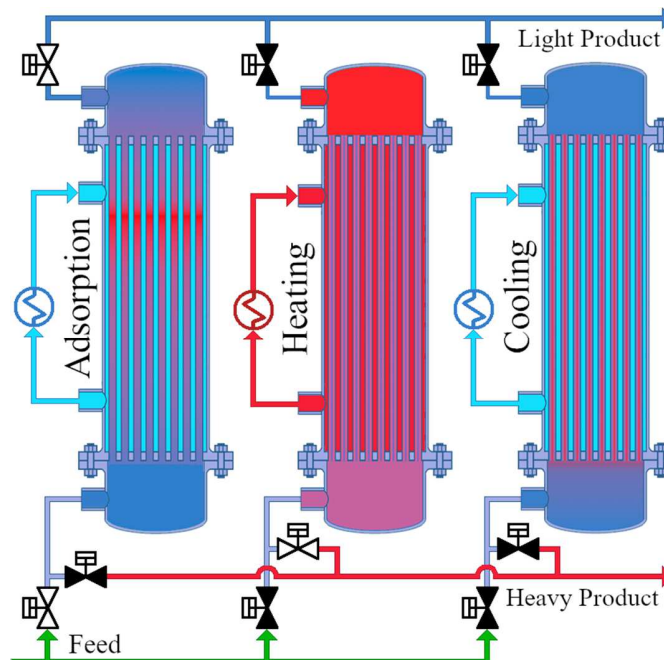


Figure 4.3: Illustration of a 3 column MT-TPSA system, depicting the three primary temperature-swing cycle stages.

4.7.4. Performance Parameters

To verify the product stream's purity requirements and to evaluate and compare the performance of the developed adsorption-based separation units, precise performance parameters must be specified and preferentially implemented into the cyclic system model. For this purpose, the performance parameters of purity, recovery, productivity, and energy consumption can be calculated for a binary mixture as shown in Equations 4.28 to 4.45. Purity (Equations 4.28, 4.29, 4.34, 4.35) can be calculated based on the composition of the outlet molar flow rates during each of the production sequences. Recovery (Equations 4.30, 4.31, 4.36, 4.37) measures the quantity of successfully separated species compared to the initially fed amount of that same species. Additionally, Productivity (Equations 4.32, 4.33, 4.38, 4.39) again measures the quantity of successfully separated species but as a function of production time and adsorbent mass or unit of volume. The energy consumption is determined depending on the studied process. In a PSA process (Equation 4.40), the main operating cost comes from the electrical energy consumption derived from the use of the gas phase pumps. The electrical energy consumption (E_{el}) is the energy necessary to operate the vacuum pumps during the regeneration steps and the pressurization pumps when inlet pressures higher than the atmospheric pressure are used and is calculated as described in Ribeiro et al.²⁰. In a TPSA process (Equation 4.41), the operating costs come from both the electrical energy consumption of the pumps and the thermal energy consumption. The thermal energy consumption (E_{th}) is determined by calculating the heat transferred to and from the heat exchanger to the outer layer of the column wall during any step of the cycle. As no heat integration was employed in any of the designs, the energy duties of the cooling and heating phases are additive. In an MT-TPSA process (Equation 4.42), additionally to the electrical and thermal energy consumption, one also has to consider the electrical energy consumption that comes from operating the shell side liquid pump. The shell side pump energy consumption (E_{liquid}) accounts for the electrical energy consumed by the liquid pump in the pressurization of the heat exchange fluid and make-up for the shell side pressure losses. To calculate the total energy consumption of a

temperature swing process, the electrical energy consumption is converted into thermal energy consumption by considering the average 35% energy efficiency of a power plant.

Light Component Purity in the 1D Model:

$$\frac{\int_0^{t_{feed}} C_{g \text{ light}} u_0|_{z=L} dt + \int_0^{t_{rinse}} C_{g \text{ light}} u_0|_{z=L} dt}{\sum_{i=1}^n \int_0^{t_{feed}} C_{g,i} u_0|_{z=L} dt + \sum_{i=1}^n \int_0^{t_{rinse}} C_{g,i} u_0|_{z=L} dt} \quad (\text{Equation 4.28})$$

Heavy Component Purity in the 1D Model:

$$\frac{\int_0^{t_{blow}} C_{g \text{ heavy}} u_0|_{z=0} dt + \int_0^{t_{purge}} C_{g \text{ heavy}} u_0|_{z=0} dt}{\sum_{i=1}^n \left(\int_0^{t_{blow}} C_{g,i} u_0|_{z=0} dt + \int_0^{t_{purge}} C_{g,i} u_0|_{z=0} dt \right)} \quad (\text{Equation 4.29})$$

Light Component Recovery in the 1D Model:

$$\frac{\int_0^{t_{feed}} C_{g \text{ light}} u_0|_{z=L} dt + \int_0^{t_{rinse}} C_{g \text{ light}} u_0|_{z=L} dt - \int_0^{t_{purge}} C_{g \text{ light}} u_0|_{z=L} dt - \int_0^{t_{press}} C_{g \text{ light}} u_0|_{z=L} dt}{\int_0^{t_{feed}} C_{g \text{ light}} u_0|_{z=0} dt} \quad (\text{Equation 4.30})$$

Heavy Component Recovery in the 1D Model:

$$\frac{\int_0^{t_{blow}} C_{g \text{ heavy}} u_0|_{z=0} dt + \int_0^{t_{purge}} C_{g \text{ heavy}} u_0|_{z=0} dt - \int_0^{t_{rinse}} C_{g \text{ heavy}} u_0|_{z=0} dt}{\int_0^{t_{feed}} C_{g \text{ heavy}} u_0|_{z=0} dt} \quad (\text{Equation 4.31})$$

Light Component Productivity in the 1D Model:

$$\frac{\int_0^{t_{feed}} C_{g \text{ light}} u_0|_{z=L} dt + \int_0^{t_{rinse}} C_{g \text{ light}} u_0|_{z=L} dt - \int_0^{t_{purge}} C_{g \text{ light}} u_0|_{z=L} dt - \int_0^{t_{press}} C_{g \text{ light}} u_0|_{z=L} dt}{t_{cycle} \times \text{Mass of Dry Adsorbent}} \quad (\text{Equation 4.32})$$

Heavy Component Productivity in the 1D Model:

$$\frac{\int_0^{t_{blow}} C_{g \text{ heavy}} u_0|_{z=0} dt + \int_0^{t_{purge}} C_{g \text{ heavy}} u_0|_{z=0} dt - \int_0^{t_{rinse}} C_{g \text{ heavy}} u_0|_{z=0} dt}{t_{cycle} \times \text{Mass of Dry Adsorbent}} \quad (\text{Equation 4.33})$$

Light Component Purity in the 2D Model:

$$\frac{\int_0^{t_{feed}} \int_0^{ID/2} 2\pi r C_{g \text{ light}} u_z|_{z=L} dr dt + \int_0^{t_{rinse}} \int_0^{ID/2} 2\pi r C_{g \text{ light}} u_z|_{z=L} dr dt}{\sum_{i=1}^n \left(\int_0^{t_{feed}} \int_0^{ID/2} 2\pi r C_{g i} u_z|_{z=L} dr dt + \int_0^{t_{rinse}} \int_0^{ID/2} 2\pi r C_{g i} u_z|_{z=L} dr dt \right)} \quad (\text{Equation 4.34})$$

Heavy Component Purity in the 2D Model:

$$\frac{\int_0^{t_{blow}} \int_0^{ID/2} 2\pi r C_{g \text{ heavy}} u_z|_{z=0} dr dt + \int_0^{t_{purge}} \int_0^{ID/2} 2\pi r C_{g \text{ heavy}} u_z|_{z=0} dr dt}{\sum_{i=1}^n \left(\int_0^{t_{blow}} \int_0^{ID/2} 2\pi r C_{g i} u_z|_{z=0} dr dt + \int_0^{t_{purge}} \int_0^{ID/2} 2\pi r C_{g i} u_z|_{z=0} dr dt \right)} \quad (\text{Equation 4.35})$$

Light Component Recovery in the 2D Model:

$$\frac{\int_0^{t_{feed}} \int_0^{ID/2} 2\pi r C_{g \text{ light}} u_z|_{z=L} dr dt + \int_0^{t_{rinse}} \int_0^{ID/2} 2\pi r C_{g \text{ light}} u_z|_{z=L} dr dt - \int_0^{t_{purge}} \int_0^{ID/2} 2\pi r C_{g \text{ light}} u_z|_{z=L} dr dt - \int_0^{t_{press}} \int_0^{ID/2} 2\pi r C_{g \text{ light}} u_z|_{z=L} dr dt}{\int_0^{t_{feed}} \int_0^{ID/2} 2\pi r C_{g \text{ light}} u_z|_{z=0} dr dt} \quad (\text{Equation 4.36})$$

Heavy Component Recovery in the 2D Model:

$$\frac{\int_0^{t_{feed}} \int_0^{ID/2} 2\pi r C_{g \text{ heavy}} u_z|_{z=0} dr dt - \int_0^{t_{feed}} \int_0^{ID/2} 2\pi r C_{g \text{ heavy}} u_z|_{z=L} dr dt}{\int_0^{t_{feed}} \int_0^{ID/2} 2\pi r C_{g \text{ heavy}} u_z|_{z=0} dr dt} \quad (\text{Equation 4.37})$$

Light Component Productivity in the 2D Model:

$$\frac{\int_0^{t_{feed}} \int_0^{ID/2} 2\pi r C_{g \text{ light}} u_z|_{z=L} dr dt + \int_0^{t_{rinse}} \int_0^{ID/2} 2\pi r C_{g \text{ light}} u_z|_{z=L} dr dt - \int_0^{t_{purge}} \int_0^{ID/2} 2\pi r C_{g \text{ light}} u_z|_{z=L} dr dt - \int_0^{t_{press}} \int_0^{ID/2} 2\pi r C_{g \text{ light}} u_z|_{z=L} dr dt}{t_{cycle} \times \text{Mass of Dry Adsorbent}} \quad (\text{Equation 4.38})$$

Heavy Component Productivity in the 2D Model:

$$\frac{\int_0^{t_{feed}} \int_0^{ID/2} 2\pi r C_{g \text{ heavy}} u_z|_{z=0} dr dt - \int_0^{t_{feed}} \int_0^{ID/2} 2\pi r C_{g \text{ heavy}} u_z|_{z=L} dr dt}{t_{cycle} \times \text{Mass of Dry Adsorbent}} \quad (\text{Equation 4.39})$$

where t_{feed} is the duration in seconds of the Feed step, t_{rinse} is the duration of the Rinse step, t_{blow} is the duration of the Blowdown step, t_{purge} is the duration of the Purge step, t_{press} is the duration of the Counter Current Pressurization Step and t_{cycle} is the total duration of the cycle.

Energy Consumption:

$$E_{PSA} = E_{el} \quad (\text{Equation 4.40})$$

$$E_{TPSA} = E_{th} + 3 E_{el} \quad (\text{Equation 4.41})$$

$$E_{MT-TPSA} = E_{th} + 3 E_{gas} + 3 E_{liquid} \quad (\text{Equation 4.42})$$

Electrical Energy Consumption:

$$E_{el} = \frac{1}{\eta} \frac{1}{\text{Mass of Recovered Product}} \int_0^{t_{step}} F R_g T \frac{\gamma}{\gamma - 1} \left[\left(\frac{P_{High}}{P_{Low}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (\text{Equation 4.43})$$

where F is the output molar flow of the step, γ is the mixture heat capacity ratio, and η is the pump's efficiency. For pressurization pumps $\eta = 85\%$, while $\eta = 60\%$ for vacuum pumps.

Thermal Energy Consumption:

$$E_{th} = \frac{1}{\text{Mass of Recovered Product}} \int_0^{t_{step}} \int_0^L \pi (ID + 2e) U_w (T_w - T_{HX}) \quad (\text{Equation 4.44})$$

Shell Side Electrical Energy Consumption:

$$E_{liquid} = \frac{10.197 \dot{m}_{HX} g \Delta P_{HX} t_{step}}{N_t \eta \times \text{Mass of Recovered Product}} \quad (\text{Equation 4.45})$$

where $\dot{m}_{HX}$ is the shell side mass flow rate, g is the gravitational acceleration constant, ΔP_{HX} is the differential height in meters of water, and N_t is the number of tubes used in the MTA design.

4.8. Parameter Estimation

Some of the necessary parameters for the previous balances must be calculated separately from the main mathematical system. All the parameters obtained in this fashion were calculated for the feed conditions of the studied processes. These parameters can either be found in literature or can be estimated by the following equations and correlations:

Pore diffusivity:

$$\frac{1}{D_{p,i}} = \tau_p \left(\frac{1}{D_{m,i}} + \frac{1}{D_{k,i}} \right) \quad (\text{Equation 4.46})$$

where τ_p is the particle tortuosity, D_m is the molecular diffusivity and D_k is the Knudsen diffusivity.

Knudsen diffusivity:

$$D_{k,i} = 0.97 r_p \sqrt{T/M_i} \quad (\text{Equation 4.47})$$

where r_p is the pore radius, and M_i is the molar mass.

$$D_{m,i} = \frac{1 - y_i}{\sum_{j=1, j \neq i}^n \frac{y_j}{D_{i,j}}} \quad (\text{Equation 4.48})$$

where $D_{i,j}$ is the binary molecular diffusivity between two different components.

Binary Molecular diffusivity:

$$D_{i,j} = \frac{2.66 \times 10^{-2} T^{1.5}}{P M_{ij}^{0.5} \sigma_{ij}^2 \Omega_D} \quad (\text{Equation 4.49})$$

where M_{ij} represents the molar mass of the gas mixture between two species, σ_{ij} is the characteristic length of the intermolecular force law and Ω_D is the collision integral.

The collision integral Ω_D is a function of temperature and varies depending on the choice of the intermolecular force law between colliding molecules that is being used. In this model, Ω_D is tabulated for the Lennard-Jones potentials.²¹

$$\Omega_D = \frac{A_1}{\omega^{A_2}} + \frac{A_3}{e^{A_4} \omega} + \frac{A_5}{e^{A_6} \omega} + \frac{A_7}{e^{A_8} \omega} \quad (\text{Equation 4.50})$$

with $A_1 = 1.06036$, $A_2 = 0.1561$, $A_3 = 0.19300$, $A_4 = 0.47635$, $A_5 = 1.03587$, $A_6 = 1.52996$, $A_7 = 1.76474$, $A_8 = 3.89411$ and ω_i is defined in equation.

$$\omega_i = \frac{T}{\varepsilon_i/k} \quad (\text{Equation 4.51})$$

where ε_i is the minimum pair-potential energy, and k is the Boltzmann constant.

The values for the characteristic length of the intermolecular force law and the minimum pair-potential energy can be calculated with equations (4.52) and (4.53), based on the Lennard-Jones parameters for each species.

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (\text{Equation 4.52})$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (\text{Equation 4.53})$$

Mass Axial Dispersion Coefficient:

$$\frac{\varepsilon D_{ax}}{D_m} = 20 + 0.5 Sc Re \quad (\text{Equation 4.54})$$

where Sc is the Schmidt number, the ratio between viscosity and mass diffusivity, and Re is the Reynolds number, the ratio between the inertial and the viscous forces.

$$Sc = \frac{\mu}{D_m \rho} \quad (\text{Equation 4.55})$$

$$Re = \frac{\rho u_0 d_w}{\mu} \quad (\text{Equation 4.56})$$

Mass Radial Dispersion Coefficient:

$$\frac{D_r}{u_i d_p} = \frac{1}{\tau} \frac{\varepsilon}{Re Sc} + \frac{1}{12} \quad (\text{Equation 4.57})$$

where u_i is the interstitial fluid velocity, d_p is the average particle diameter, and τ is the tortuosity.

Thermal Axial Dispersion Coefficient:

$$\frac{\lambda_{ax}}{k_g} = 7 + 0.5 Pr Re \quad (\text{Equation 4.58})$$

where k_g is the gas mixture thermal conductivity, and Pr is the Prandtl number, the ratio between the momentum and the thermal diffusivity.

$$Pr = \frac{\hat{C}_p \mu}{k_g} \quad (\text{Equation 4.59})$$

where $\hat{C}_p$ is the specific heat at constant pressure.

Thermal conductivity:

$$k_g = \sum_{i=1}^n \frac{y_i k_{g,i}}{\sum_{j=1}^n y_j \Phi_{ij}} \quad (\text{Equation 4.60})$$

where $k_{g,i}$ is the thermal conductivity for the pure component and Φ_{ij} is calculated by:

$$\Phi_{ij} = \frac{\left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{0.5} + \left(\frac{M_j}{M_i} \right)^{0.25} \right]^2}{\left[8 \left(1 + \frac{M_i}{M_j} \right) \right]^{0.5}} \quad (\text{Equation 4.61})$$

$$\mu = \sum_{i=1}^n \frac{y_i \mu_i}{\sum_{j=1}^n y_j \Phi_{ij}} \quad (\text{Equation 4.62})$$

where μ_i is the pure gas component viscosity and is determined by:

$$\mu_i = 2.669 \times 10^{-6} \frac{(M_i T)^{0.5}}{\sigma_i^2 \Omega_{\mu,i}} \quad (\text{Equation 4.63})$$

$$M_{ij} = 2 \left(\frac{1}{M_i} + \frac{1}{M_j} \right)^{-1} \quad (\text{Equation 4.64})$$

The pure gas thermal conductivity is determined by the following:

$$k_{g,i} = \left(\hat{C}_{p,i} + \frac{5}{4} \frac{R_g}{M_i} \right) \mu_i \quad (\text{Equation 4.65})$$

$$\hat{C}_p = \frac{C_p}{\sum_{i=1}^n y_i M_i} \quad (\text{Equation 4.66})$$

The gas mixture specific heat (C_p), which is calculated by the pondered average of the specific heat of the pure components:

$$C_p = \sum_{i=1}^n y_i C_{p,i} \quad (\text{Equation 4.67})$$

Thermal Radial Dispersion Coefficient:

$$\frac{\lambda_r}{u_i d_p} = \frac{1}{Pe_r} + \frac{0.3 St}{1 + 0.35 Bi_{h,s}} + \frac{2e\sigma T^3}{u_i \rho_f C_{p,f}} \quad (\text{Equation 4.68})$$

where Pe_r is the radial mass Péclet number, St is the Stanton number, $Bi_{h,s}$ is the thermal Biot number, e is the emissivity of the particle, and σ is the Boltzmann constant.

Wall Heat Transfer Coefficient:

$$h_w = h_w^0 + 1.340 \times 10^{-5} \frac{ID}{d_p} Re \quad (\text{Equation 4.69})$$

$$h_w^0 = 20 \frac{k_{eff}^0}{ID} \quad (\text{Equation 4.70})$$

where ID is the internal diameter of the tube, and h_w^0 is the static contribution to the wall heat transfer coefficient.

Effective Stagnant Bed Heat Conductivity:

$$k_{eff}^0 = k_g(1 - \sqrt{1 - \varepsilon} + \sqrt{1 - \varepsilon} k_c) \quad (\text{Equation 4.71})$$

$$k_c = \frac{2}{N} \left(\frac{B}{N^2} \frac{\left(\frac{k_p}{k_g} - 1 \right)}{\frac{k_p}{k_g}} \ln \left(\frac{k_p}{k_g B} \right) - \frac{B+1}{2} - \frac{B-1}{N} \right) \quad (\text{Equation 4.72})$$

$$N = 1 - \frac{B k_g}{k_p} \quad (\text{Equation 4.73})$$

$$B = 1.25 \left(\frac{1 - \varepsilon}{\varepsilon} \right)^{10/9} \quad (\text{Equation 4.74})$$

Particle Heat Transfer Coefficient:

$$\frac{h_f d_p}{k_g} = 2.0 + 1.1 Pr^{1/3} Re^{0.6} \quad (\text{Equation 4.75})$$

Shell Side Heat Transfer Coefficient:

$$h_{shell} = h_{ideal} (J_C J_L J_B J_S J_R) \quad (\text{Equation 4.76})$$

$$h_{ideal} = j C p_s G_S (Pr)^{-2/3} \left(\frac{\mu_S}{\mu_{S,w}} \right)^{0.14} \quad (\text{Equation 4.77})$$

where J_C is the correction factor for baffle configuration, J_L is the correction factor for baffle leakage effects, J_B is the correction factor for bundle and pass partition bypass streams, J_S is the correction factor for larger baffle spacing at the inlet and outlet sections compared to the central baffle spacing, J_R is the correction factor for any adverse temperature gradient

buildup in laminar flows j is the Colburn j -factor, C_{pS} is the heat transfer fluid heat capacity at constant pressure, and G_S is the shell side cross flow mass velocity.

Shell Side Pressure Drop:

$$\Delta P_{shell} = \Delta P_W + \Delta P_C + \Delta P_E \quad (\text{Equation 4.78})$$

$$\Delta P_W = \Delta P_{W,turb} = N_B R_L (2 + 0.6 N_{tcw}) G_W^2 / (2 \rho_S) \quad (\text{Equation 4.79})$$

$$\Delta P_C = (N_B - 1) \Delta P_{Ideal} R_L R_B \quad (\text{Equation 4.80})$$

$$\Delta P_E = \Delta P_{Ideal} (1 + N_{tcw}/N_{tcc}) R_B \quad (\text{Equation 4.81})$$

$$\Delta P_{Ideal} = 2f (G_S^2 / \rho_S) \left(\frac{\mu_S}{\mu_{S,w}} \right)^{0.14} N_{tcc} \quad (\text{Equation 4.82})$$

where ΔP_W is the pressure drop from the window section, ΔP_C is the pressure drop from the central baffles, ΔP_E is the pressure drop in the entrance and exit baffle spaces, N_B is the number of baffles, R_L is the correction factor for baffle leakage, N_{tcw} is the effective number of tube rows in the window, N_{tcc} is the effective number of tubes crossed in one cross-flow section between baffle tips, R_B is the correction factor for bundle bypass effect, and f is the friction factor.

Fouling Consideration:

$$\frac{1}{h_{dirty}} = \frac{1}{h_{clean}} + R_{dirty} \quad (\text{Equation 4.83})$$

where h_{dirty} is the heat transfer coefficient after fouling, h_{clean} is the heat transfer coefficient without fouling and R_{dirty} is the fouling factor.

The ratio of the internal surface area to the volume of the column wall (α_w) and the ratio of the log mean surface area to the volume of the column wall (α_{wl}) are calculated based on the column diameter (d_w) and the wall thickness (e).

$$\alpha_w = \frac{d_w}{e(d_w + e)} \quad (\text{Equation 4.84})$$

$$\alpha_{wl} = \frac{2}{(d_w + e) \ln \left(\frac{d_w + 2e}{d_w} \right)} \quad (\text{Equation 4.85})$$

The particle specific area is calculated by:

$$a_p = \frac{k_{sM} + 1}{r_p} \quad (\text{Equation 4.86})$$

where k_{sM} is the geometrical factor for the shape of the particle (0 for slab geometry, 1 for cylindrical geometry and 2 for spherical geometry).

The mass axial dispersion coefficient (D_{ax}), axial heat dispersion coefficient (λ_{ax}) and the particle film heat transfer coefficient (h_f) are estimated by the Wakao and Funazkri correlations ^{22,23}. The mass radial dispersion coefficient (D_r) was estimated based on the correlation proposed by Coelho and Guedes de Carvalho ²⁴. The binary molecular diffusivity ($D_{i,j}$) is estimated by the Chapman-Enskog equation and resulted from solving the Boltzmann equation ²¹, the pure component thermal conductivity ($k_{g,i}$) is estimated by the Eucken correlation and the thermal conductivity (k_g) is calculated by the Mason and Saxena modification of the Wassiljewa equation. The radial heat dispersion coefficient (λ_r) is estimated by the rearrangement of the theoretical sum of contributions from the molecular conduction, eddy conduction, radiation through void space and conduction through the solid particles ²⁵. The effective stagnant bed heat conductivity (k_{eff}^0) was calculated following the Zehner/Bauer/Schlünder model ¹⁶, and the wall heat transfer coefficient was calculated from the correlations of Wasch and Froment ²⁶. The pure gas viscosity (μ_i) is estimated by the Chapman-Enskog treatment, and the gas mixture viscosity (μ) is calculated by the Wilke method. The collision integral (Ω_D) is calculated based on the Lennard-Jones potential parameters (Table 4.7), however as the parameters for VCM are not available, the values of ethyl chloride (*), the corresponding halogenated paraffin of VCM, were used.

For the design of the multitubular adsorber, the calculation of the heat transfer coefficients and pressure drop across the equipment is termed as a rating problem. For this purpose, based on the chosen design estimations, the shell side heat transfer coefficient (h_{shell}) and the shell side pressure drop (ΔP_{shell}) will be calculated by the Bell Delaware Method ^{18,19}. During continuous operation, heat exchanger surfaces build up a deposit film, referred to

as fouling, which adds increased thermal resistance depending on the contacting fluid. Table 4.8 shows the fouling factors used for the shell side heat fluid (water) and for the tube side, standards for light hydrocarbon vapors and chlorinated hydrocarbon vapors were used.

Table 4.7: Molar Mass and Lennard-Jones parameters for each of the studied species.

Chemical Species	Molar Mass (g/mol)	σ_i ($\text{\AA}$)	ε_i/k (K)
Ethylene	28.05	4.163	225
Propylene	42.08	4.678	299
Vinyl Chloride	62.27	4.898*	300*
Nitrogen	28.014	3.667	99.8
Helium	4.003	2.576	10.2

Table 4.8: Fouling Factors

Fluids	R_{dirty} (m^2K/W)
Water	0.0003
Light Hydrocarbon vapors (clean)	0.00018
Chlorinated Hydrocarbon Vapors	0.0002

4.9. References

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Chapter 5

Vinyl Chloride / Nitrogen Separation and Recovery



5.1. Introduction

This chapter will focus on developing adsorption-based separation systems capable of purifying and recovering a vinyl chloride/nitrogen gas phase stream derived from the polymer degassing vents of poly(vinyl chloride) polymerization industries.

Shin-Etsu CIREs supplied the process specifications and product requirements, as shown in Figure 5.1. The developed vinyl chloride recovery systems must be capable of treating a 180 Nm³/h feed flow rate of a 40/60 % (v/v) VCM/N₂ mixture at 1.15 bar and 313 K and producing two product streams. The unit must produce a nitrogen stream with a vinyl chloride contamination lower than the 8 ppm (w/w), which is the emission limit for the free release of VCM contaminated air vents into the atmosphere. Additionally, a vinyl chloride-rich stream with a high enough concentration that can be blended with the raw vinyl chloride and fed into the polymerization reactor should be produced.

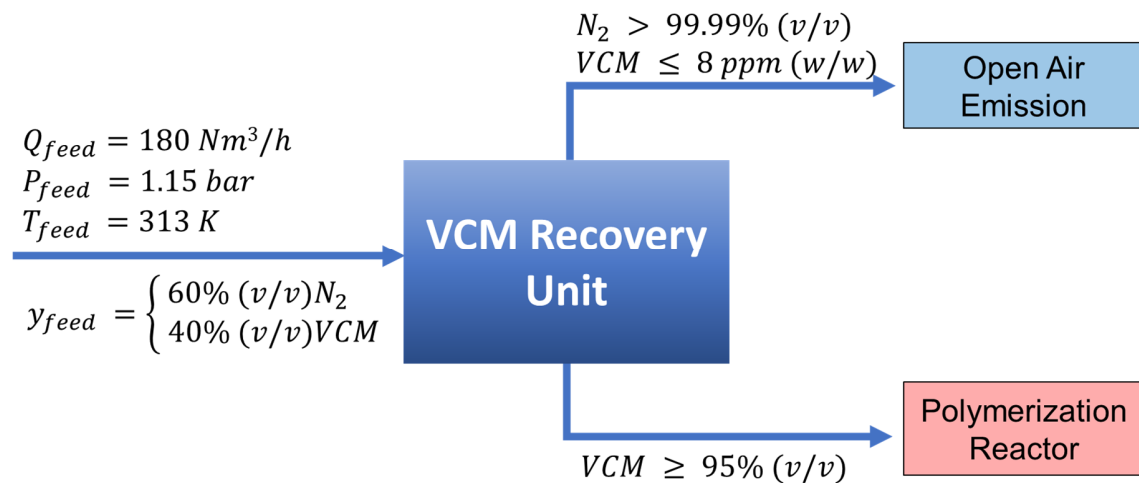


Figure 5.1: Schematic of the VCM/N₂ feed stream conditions and the separation requirements for the developed separation and recovery unit.

To ascertain the current state of the art, a literature review was performed on the adsorbent materials with available, documented adsorption equilibrium data. Based on the collected data, the most prominent adsorbent material was selected. A preliminary study was conducted on the viability of developing an adsorption-based separation unit using the

Pittsburgh PCB carbon. From this study, a 2-column TPSA system and a 3-column MT-TPSA system were successfully designed.

Additionally, using a magnetic suspension balance system, adsorption equilibrium data for vinyl chloride and nitrogen was experimentally measured for the first time on three promising adsorbent materials: Maxsorb; Carbotech DGK, and MIL-100(Fe). Due to safety concerns, breakthrough experiments were not performed using VCM on any of the adsorbent samples. As such, for the validation of the fixed bed model used in this Chapter, one should refer to the results of the breakthrough experiments reported in Section 6.4.

Based on the measured equilibrium data and the results obtained from the preliminary studies, the Maxsorb and Carbotech DGK carbons were each used to design and simulate MT-TPSA cycle, while the MIL-100(Fe) MOF was used to develop both a PSA and an MT-TPSA system. As all the proposed adsorption units could perform the required separation, a posterior performance evaluation and comparison were performed.

5.2. Literature Review – Adsorption Equilibrium Data

As the initial focus of this thesis, a literature review was elaborated on the available adsorbent materials with equilibrium data pertaining to the adsorption of vinyl chloride, and possibly nitrogen. From this research, although information regarding the use of adsorption for the treatment, capture or recovery of vinyl chloride were not uncommon, the authors found that adsorption equilibrium isotherms published for vinyl chloride on any adsorption material were challenging to come by. Even though vinyl chloride capture was mainly a practical concern for the industrial sector and laboratory data was difficult to obtain due to the gas hazardous nature, a lack of published data is difficult to reconcile with the heavy focus that was attributed to the control of vinyl chloride emissions in the late 1980s.

Chauveau et al.¹ derived the vinyl chloride adsorption equilibrium isotherms from breakthrough analysis on the G212 and G215 activated carbons from North American Carbon Inc. at 293 K. Scamehorn² also obtained vinyl chloride adsorption equilibrium

isotherms, by breakthrough experiments, on dried Pittsburgh PCB activated carbon at the temperatures of 294, 317, 339, and 368 K. Adsorption equilibrium isotherms were obtained using activated carbon impregnated with hydroquinone at 263, 278, 293, and 308 K from a patent by Raduly³, while Herdes et al. presented adsorption equilibrium isotherms for VCM in micropore aluminum methyl phosphonate- α at 293, 327, and 363 K⁴. Figure 5.2 shows the comparison between the adsorption equilibrium isotherms available in the literature at around 293 K.

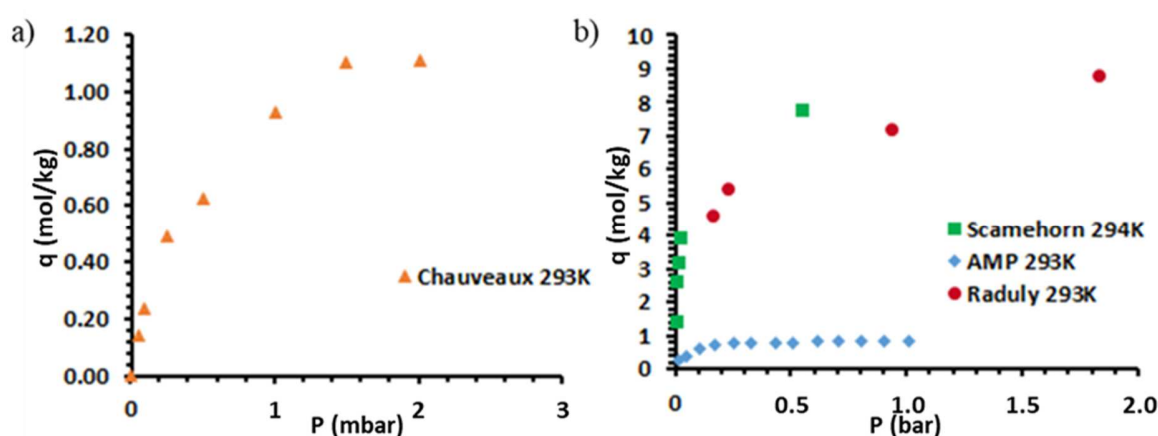


Figure 5.2: Adsorption Equilibrium Isotherms for VCM in activated carbon at 293 K until 0.250 kPa (a) and in different materials at 293 K to 294 K until 200 kPa (b).

From the collected literature, it is clear that the recurring adsorbent material is activated carbon. The predominant role of activated carbon as the adsorbent for VCM is understandable. It is the adsorbent usually used in VCM and PVC industrial plants to control VCM trace emissions, and one of the most used adsorbents in the industry, in general.

5.3. Pure Component Adsorption Equilibrium

From the data collected in the literature review, one of the reported adsorbent materials was chosen for a preliminary study on the viability of the proposed process using pre-existing data. Considering the available adsorption equilibrium isotherms, the activated carbon Pittsburgh PCB 12x30, manufactured by the Calgon Corporation, displayed the most favorable isotherm and capacity, as well as the most complete data for VCM adsorption. Figure 5.3 shows the equilibrium adsorption data reported by Scaemhorn² for pressure and temperature range of 0.5 to 550 mbar and 294 to 368 K, as well as the DSL fitting used to model the equilibrium. Equilibrium data on N₂ adsorption on the same material was obtained from a separate publication by Choi et al.⁵, but for a wider mesh size (PCB 6x16). Figure 5.4 displays the collected equilibrium data for pressure and temperature range of 0 to 16 bar and 293 to 313 K, as well as the regressed Langmuir fitting. The fitting parameters used in the DSL and Langmuir models for the VCM and N₂ adsorption on Pittsburgh PCB are listed in Tables 5.1 and 5.2, respectively.

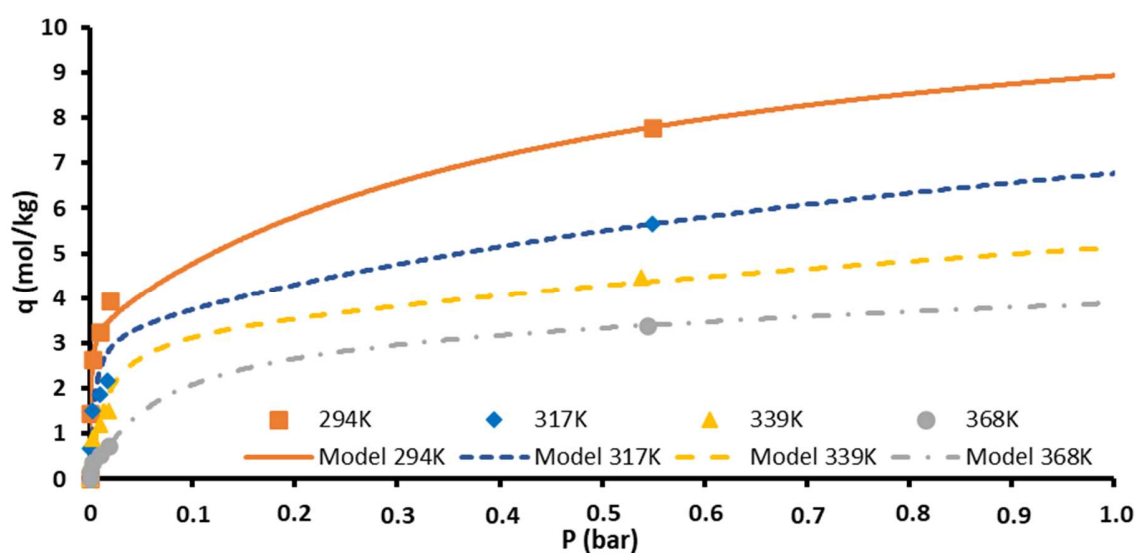


Figure 5.3: VCM adsorption equilibrium data for dry gas on dry Pittsburgh PCB carbon ² and the curves show the Dual Site Langmuir fitting

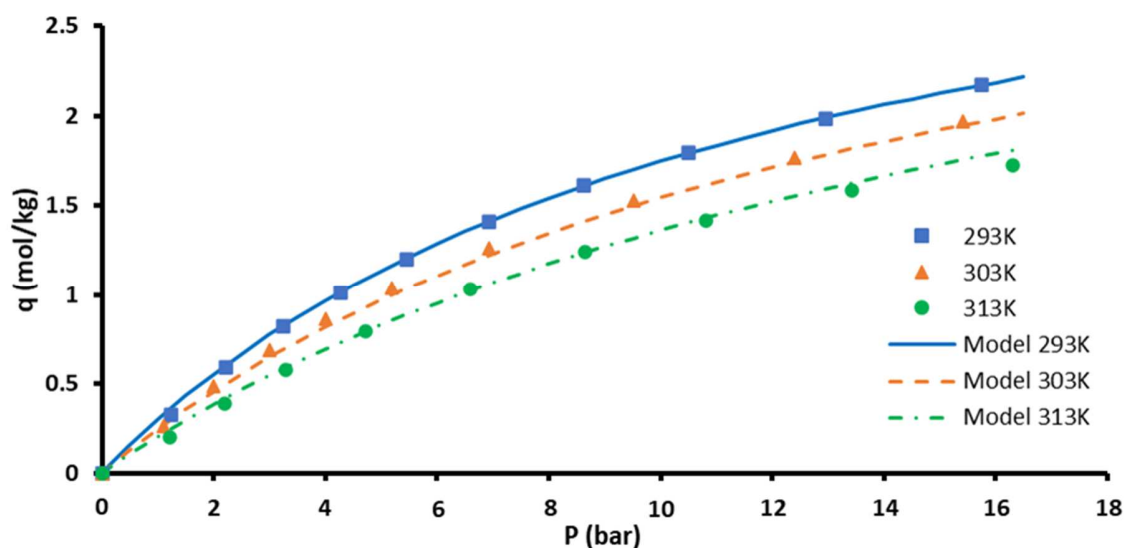


Figure 5.4: N_2 adsorption equilibrium data on Pittsburgh PCB carbon ⁵ and the curves show the Langmuir fitting used

Due to the positive results obtained from the preliminary studies, additional adsorbent materials with the potential for an improved separation performance were proposed for study. Using the magnetic suspension balance Rubotherm, detailed in Chapter 3, single-component adsorption equilibrium data for VCM were obtained for the Maxsorb, and Carbotech DGK activated carbons, and the MIL-100(Fe) metal-organic framework, up to a maximum pressure of 2.5 bar. Equilibrium adsorption data was also obtained for N_2 under the same conditions up to a maximum pressure of 5 bar, for the Carbotech and the MIL-100(Fe) samples. All the adsorption equilibrium isotherm measurements were performed for the temperatures of 303, 323, and 373 K, which would be the expected temperature range in which an adsorptive separation process will be developed. Adsorption equilibrium data for N_2 on the powdered Maxsorb sample was not measured as the group had already performed those measurements for a pelletized sample of the same material. Since the data for a pelletized sample would be more beneficial for the development of an industrial adsorption based separation unit, the equilibrium data obtained for VCM in the powdered sample of Maxsorb was adjusted to account for any loss in the capacity, due to the pelletization process, according to data in the literature. This capacity loss was calculated by modeling a capacity ratio into the DSL model and comparing the N_2 adsorption isotherms

reported by Regufe et al.⁶ for the pelletized adsorbent and the sample reported by Gomez et al.⁷, from which a capacity ratio of 83 % was shown to produce a good fit.

Due to the hazardous nature of VCM, special safety conditions were taken for the experiments regarding this gas. For the single component adsorption equilibrium isotherm measurements, the VCM tank was isolated inside a closed-off vacuum fume hood under 24 h operation. At the same time, the injection line for the Rubotherm system was kept under vacuum when not in use. For this same reason, the breakthrough experiments, and the respective multicomponent equilibrium and kinetic studies were unable to be performed as the fixed bed installation, described in Chapter 3, could not meet the necessary safety requirements.

Prior to the measurements, the activated carbon samples were activated under vacuum at 393 K, and MIL-100(Fe) at 433 K overnight or until no significant mass loss was observed for 1 hour.

The pure component adsorption equilibrium isotherms of VCM and N₂ on the Maxsorb, Carbotech DGK, and MIL-100(Fe) samples are reported in Figures 5.5 to 5.10, where the solid and hollow points represent the adsorption equilibrium data obtained during the adsorption and desorption stages of the adsorption equilibrium measurements.

The DSL and the Langmuir model fitting parameters used in this work are shown in Tables 5.1 for VCM and 5.2 for N₂. Figure 5.6 shows the N₂ adsorption equilibrium isotherm data for the pelletized Maxsorb sample, and fitting model as reported in the literature by Regufe et al.⁶

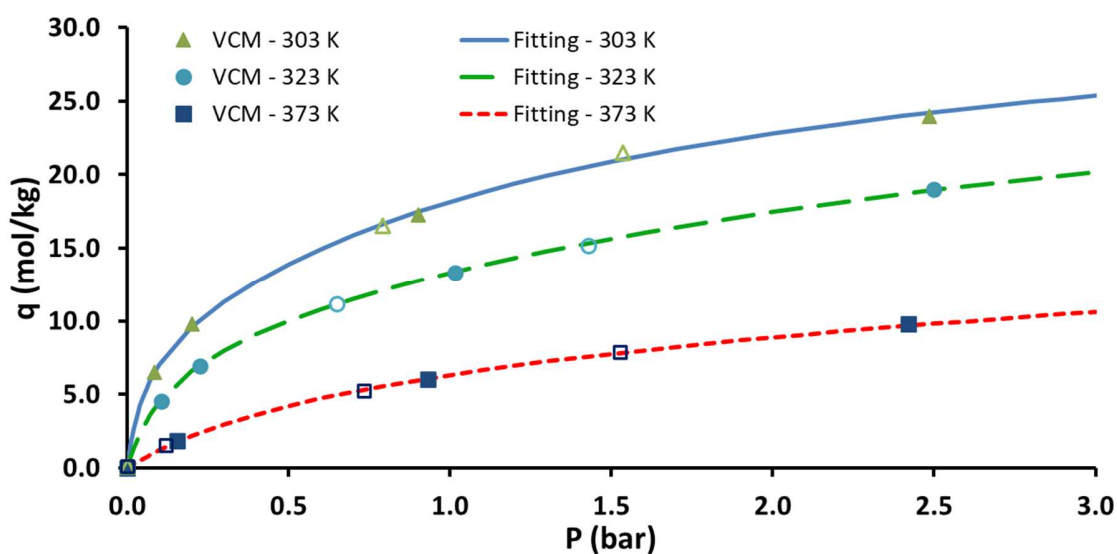


Figure 5.5: Adsorption Equilibrium experimental data and model for VCM in the Maxsorb powdered sample at 303, 323, and 373 K

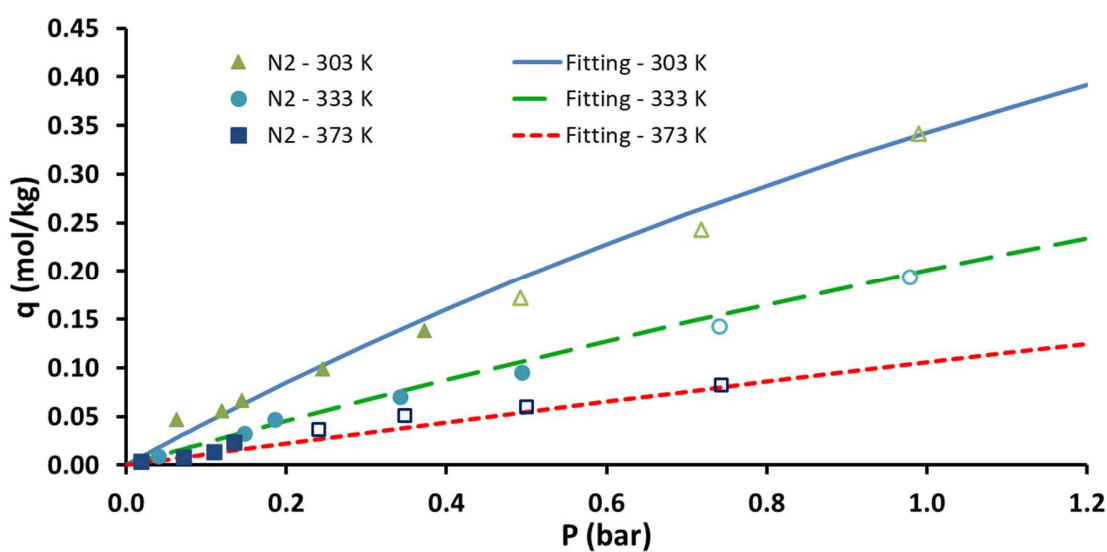


Figure 5.6: Adsorption Equilibrium experimental data and model for N₂ in the Maxsorb pellets at 303, 333, and 373 K, as reported by Regufe et al.⁶

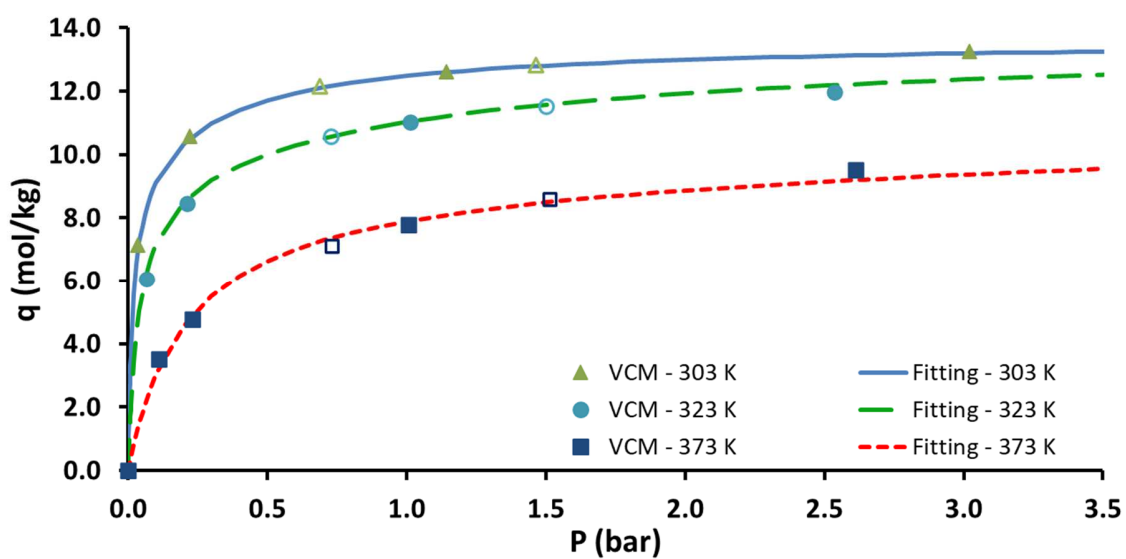


Figure 5.7: Adsorption Equilibrium experimental data and model for VCM in Carbotech DGK at 303, 323, and 373 K

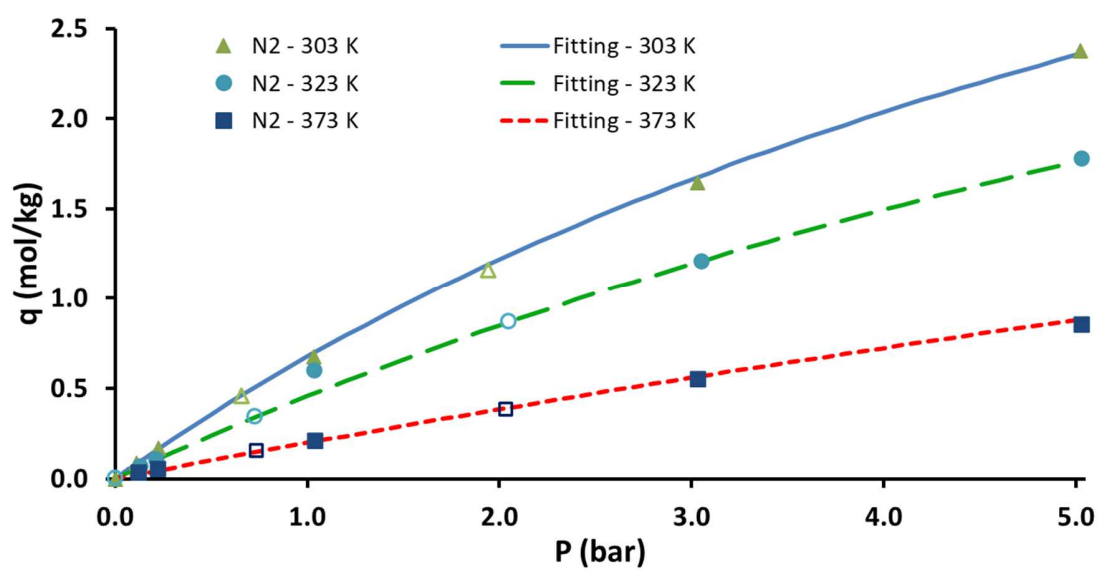


Figure 5.8: Adsorption Equilibrium experimental data and model for N_2 in Carbotech DGK at 303, 323, and 373 K

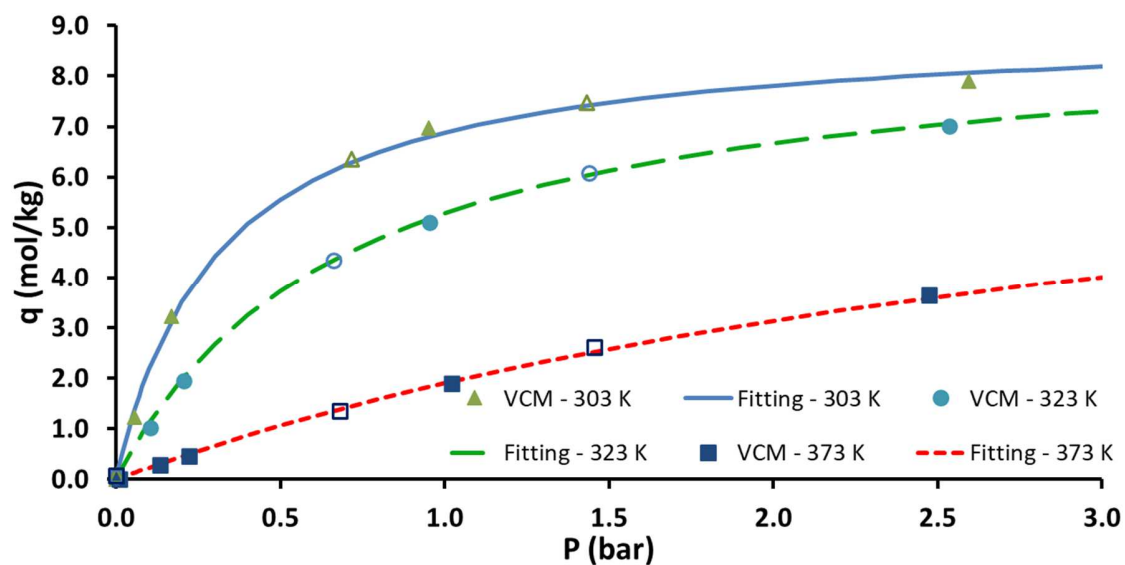


Figure 5.9: Adsorption Equilibrium experimental data and model for VCM in MIL-100(Fe) at 303, 323, and 373 K

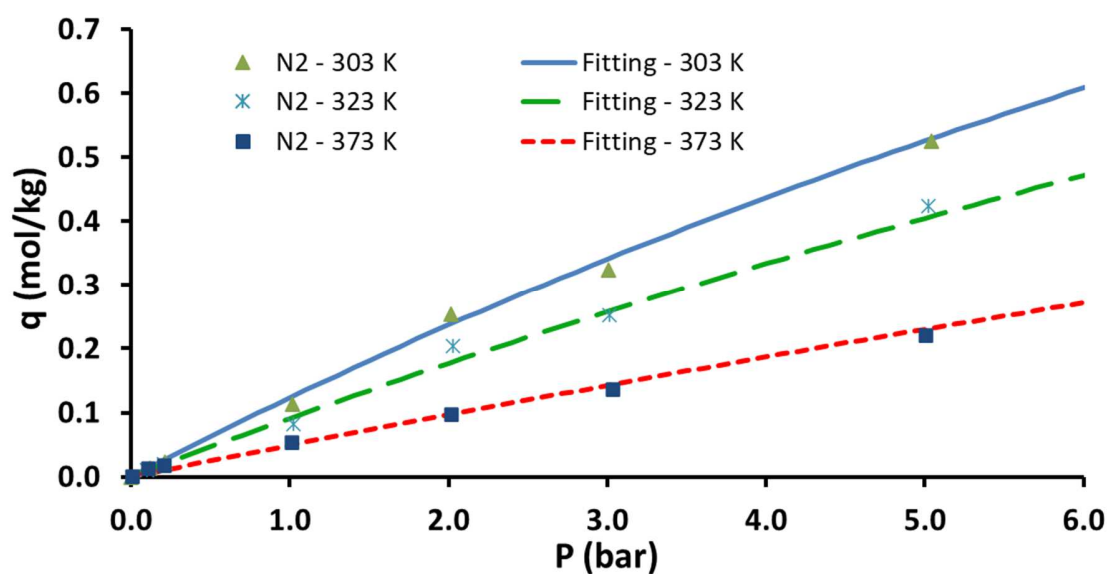


Figure 5.10: Adsorption Equilibrium experimental data and model for N₂ in MIL-100(Fe) at 303, 323, and 373 K

Table 5.1: Dual Site Langmuir and Langmuir isotherm fitting model parameters for VCM

VCM Isotherm Parameters	Pittsburgh PCB	Maxsorb	Carbotech DGK	MIL-100(Fe)	Units
$q_{sat,1}$	3.30	26.05	9.16	9.04	<i>mol/kg</i>
$q_{sat,2}$	8.15	8.21	4.47	-	<i>mol/kg</i>
$b0_1$	3.49×10^{-7}	1.79×10^{-6}	5.14×10^{-5}	5.65×10^{-6}	<i>bar⁻¹</i>
$b0_2$	5.90×10^{-7}	1.84×10^{-5}	4.15×10^{-9}	-	<i>bar⁻¹</i>
$-\Delta H_{ads,1}$	53900	32299	35528	33380	<i>J/mol</i>
$-\Delta H_{ads,2}$	37090	34980	51704	-	<i>J/mol</i>

Table 5.2: Dual Site Langmuir and Langmuir isotherm fitting model parameters for N₂

N ₂ Isotherm Parameters	Pittsburgh PCB	Maxsorb	Carbotech DGK	MIL-100(Fe)	Units
$q_{sat,1}$	3.77	1.41	18.81	2.82	<i>mol/kg</i>
$q_{sat,2}$	-	0.58	5.94	-	<i>mol/kg</i>
$b0_1$	1.15×10^{-4}	2.09×10^{-4}	2.38×10^{-6}	2.92×10^{-4}	<i>bar⁻¹</i>
$b0_2$	-	1.74×10^{-5}	1.13×10^{-4}	-	<i>bar⁻¹</i>
$-\Delta H_{ads,1}$	16130	18500	13974	12740	<i>J/mol</i>
$-\Delta H_{ads,2}$	-	7900	17672	-	<i>J/mol</i>

The pure component isotherm parameters for each of the adsorbent/adsorbate pairs were calculated by minimizing the sum of absolute errors between the experimentally determined data and the values calculated by the isotherm model. As seen from Figures 5.3 to 5.10, the proposed parameter correlations present a reasonably good fit for the experimental data. Additionally, the adsorption of VCM and N₂ on all samples has proven to be reversible since no hysteresis can be observed between the adsorption and desorption branches.

Although the adsorption equilibrium data of VCM in Pittsburgh PCB is limited, it can be inferred from the sharp adsorption intake at lower pressures followed by the slower uptake towards saturation that the Pittsburgh PCB carbon should be a highly microporous material, which would be expected of activated carbons made from coconut shells. As expected from a mostly type I(a) adsorption isotherm, the adsorption of VCM following a DSL model reveals a very high adsorption enthalpy of 53.9 and 37.1 kJ/mol, which will increase the difficulty of regenerating this material without temperature control or very high vacuum. On the other

hand, the VCM adsorption on the Maxsorb sample, seen in Figure 5.5, follows a typical type I(b) isotherm. The lower curvature isotherm shape also falls in line with the material characterization reported in Chapter 3, where Maxsorb has shown to have a pore size distribution with predominantly 76 % micropores. With a relatively lower adsorption enthalpy of 34.9 and 32.2 kJ/mol and an exceptionally high adsorption capacity, the Maxsorb material could be an excellent potential adsorbent material for any of the proposed separation systems. Similar to the Pittsburgh PCB, the Carbotech DGK carbon is also made from coconut shells. As expected, material characterization also reports it as a highly microporous material with as much as 90 % volume in micropores. The VCM adsorption equilibrium also reflects this fact; with a high adsorption enthalpy of 51.7 and 35.5 kJ/mol and an almost immediate saturation at low temperature, the Carbotech DGK displays an ideal type I(a) isotherm shape. Although the adsorption capacity decreases at higher temperatures, the equilibrium isotherms do not suffer major changes to their shape, which indicates that the material would behave similarly both at low and high temperatures. Since the MIL-100(Fe) is a metal-organic framework material, its pore structure should be relatively uniform and comprised of crystalline cages of 25 and 29 Å in diameter, except for any defects derived from the production or pelletization process. The MIL-100(Fe) is advertised as being capable of achieving mostly linear isotherms, advantageous for low-cost pressure swing systems. For the adsorption of VCM, although at lower temperatures, a curved type I(b) isotherm shape is reported, the shape of the isotherm appear to be quite sensitive to temperature, as at 373 K, the VCM adsorption isotherm is indeed mostly linear. As for the adsorption of N₂, perhaps due to its naturally weak quadrupolar moment interactions, the adsorption behavior of N₂ in all four samples is very similar and follows mostly linear isotherms, with slightly varying degrees of affinity depending on the material.

Figures 5.11 and 5.12 show a comparison of the equilibrium isotherms at 323 K between the four studied materials for VCM and N₂ in a pressure range up to 3 and 5 bar, respectively. In Figure 5.11 the VCM adsorption equilibrium isotherm on the Maxsorb

sample has already been adjusted using the 83 % adsorption capacity loss ratio from the pelletization process.

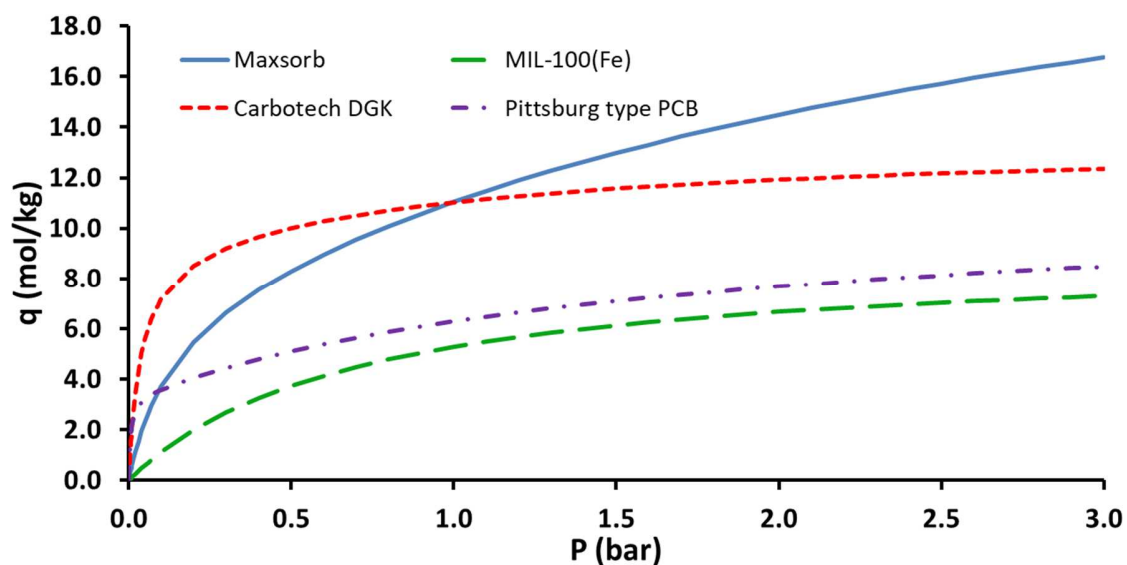


Figure 5.11: Comparison of the VCM adsorption equilibrium isotherms models at 323 K

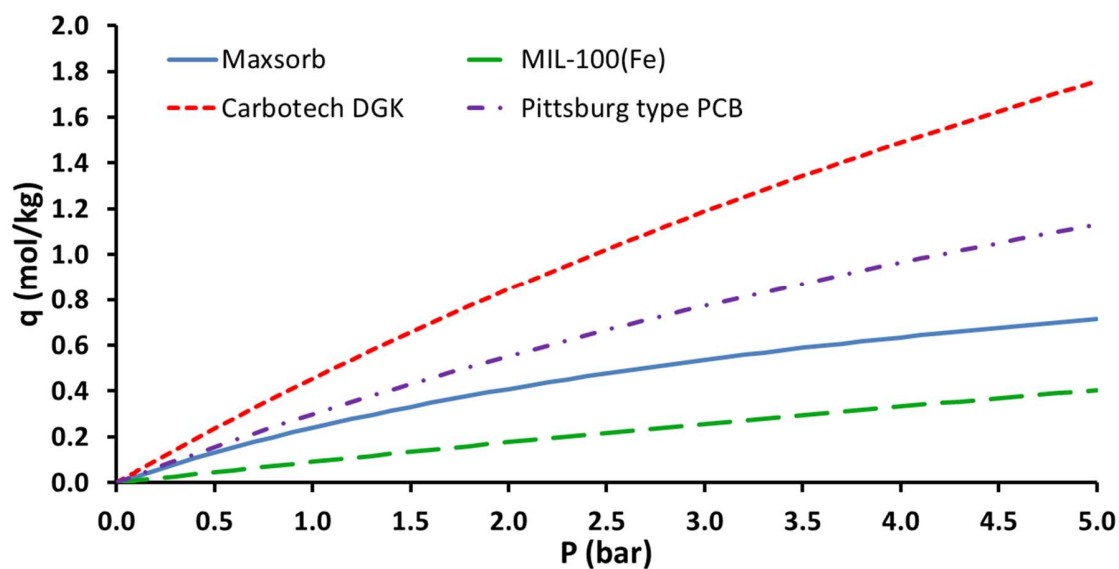


Figure 5.12: Comparison of the N_2 adsorption equilibrium isotherms models at 323 K

Taking the adsorption behavior in the Pittsburgh PCB carbon as standard, the adsorption behavior of the other three samples can be compared. The adsorption capacity of VCM in MIL-100(Fe) is lower but somewhat comparable to the Pittsburgh PCB carbon. However, the major difference between these two materials is the significantly more linear adsorption isotherms for VCM with MIL-100(Fe). The lower curvature of the VCM isotherms, together with the lower adsorption enthalpy, should facilitate the adsorption and regeneration of MIL-100(Fe) by pressure-swing, making processes such as the PSA more appealing.

Since both the Pittsburgh PCB and Carbotech DGK carbons are made from coconut shells, it is not surprising that both materials share the same isotherm shape. As seen from Figures 5.11 and 5.12, the only difference between both materials is that the adsorption capacity for both VCM and N₂ is undoubtedly higher for the Carbotech DGK sample, which in turn should be related to the preparation and activation process of the carbon samples. Considering the similar highly microporous structure of both the Pittsburgh PCB and Carbotech DGK carbons together with their high adsorption enthalpy, would suggest that these carbons are more appropriately suited for “capture”, “polishing” or low adsorbate concentration separations, as detailed in Scamehorn work, rather than the bulk separation proposed in this work. Nonetheless, due to their high VCM adsorption capacity, temperature-swing processes using these materials could still possess a competitive performance.

At low pressures ($P < 1$ bar), the Carbotech DGK displays the highest VCM adsorption. Overall, the Maxsorb sample reports the highest adsorption capacity for VCM of all four samples at 34.3 moles for kilogram of adsorbent. With a significantly less sharp isotherm than the Pittsburgh PCB, the Maxsorb adsorption isotherm shape for VCM resembles more closely the MIL-100(Fe) MOF behavior. The favorable type I(b) isotherm, together with the reported lower heat of adsorption and lower acquisition cost, shows that the Maxsorb material could also be a potential candidate material for the development of a VCM/N₂ PSA separation system.

As stated previously in chapter 4, in this work, the multicomponent adsorption equilibrium for binary mixtures will be predicted using the corresponding extended versions of the reported Langmuir and Dual Site Langmuir isotherm models.

5.4. Isostatic Heat of Adsorption

As seen from Figures 5.13 to 5.17, the isosteric heat of adsorption for vinyl chloride and nitrogen was calculated as a function of the loading for the Maxsorb, Carbotech DGK, and MIL-100(Fe) samples. The points represent the values calculated using the experimental data. The straight dashed-lines are the enthalpic parameters obtained in the Langmuir and DSL fitting. The thinner full and dashed-lines represent the variation of the isosteric heat predicted by the DSL model for each measured temperature (Equation 4.12). The values based on the experimental data were calculated for the loadings of the highest measured temperature, which could be compared to the measured loadings for the other two temperatures. The results from Figure 5.13 shows that the adsorption of VCM on Maxsorb displays a certain degree of heterogeneity, which is confirmed by the characterization of the material, since Maxsorb possesses a distribution of both micro and mesopores. Additionally, the variation of the isosteric heat appears to be very well predicted by the DSL model.

The results from Figures 5.14 and 5.15 show that the variation of isosteric heat with the loading of VCM and N₂ on Carbotech DGK is being well predicted and that surface of this material is indeed heterogeneous with a distribution of small diameter micropores.

As discussed in Chapter 3.1, as a MOF material, the heterogeneous structure of MIL-100(Fe) is clearly known. From Figures 5.16 and 5.17, results show that while for the adsorption of VCM, the isosteric heat remains mostly constant, the adsorption of N₂ reveals heterogeneity. This is likely caused by the preferential adsorption sites for both species, while VCM should mostly be adsorbed at the iron trimers, due to the formation of electrostatic interactions between the dipole moment of VCM and the iron (III) charge,

nitrogen due to its weaker quadrupolar moment should be adsorbing more uniformly on both the metal sites and ligands.

By comparing the calculated isosteric heats, it is confirmed that the isosteric heat for the adsorption of VCM and N_2 is significantly higher for the Carbotech DGK carbon than the other materials. The isosteric heat for the adsorption of VCM appears to be very similar for both the Maxsorb and MIL-100(Fe) samples.

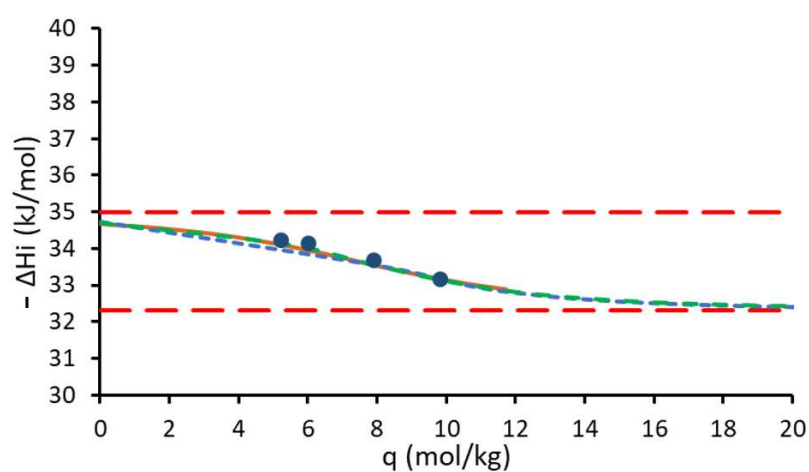


Figure 5.13: Isosteric heat of adsorption versus loading on Maxsorb powder for VCM

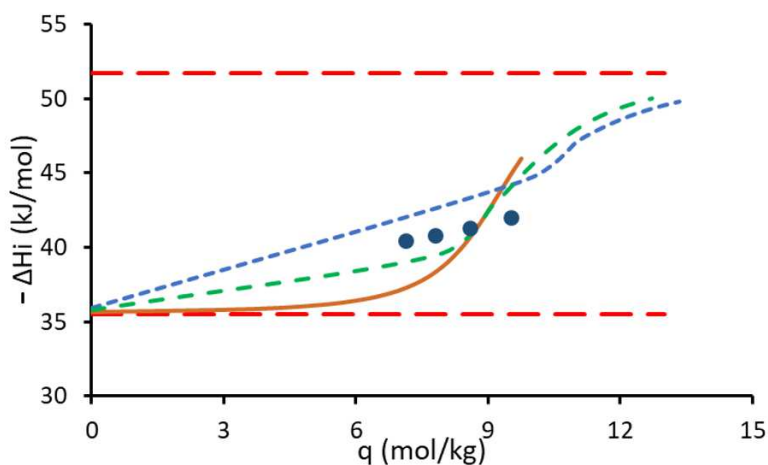


Figure 5.14: Isosteric heat of adsorption versus loading on Carbotech granulates for VCM

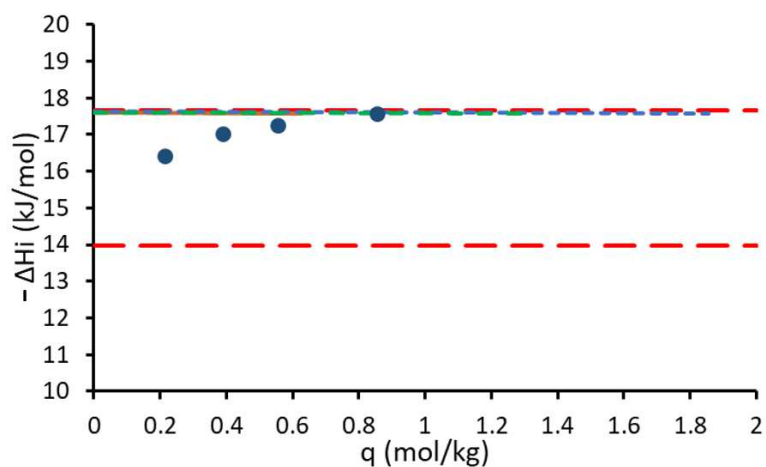
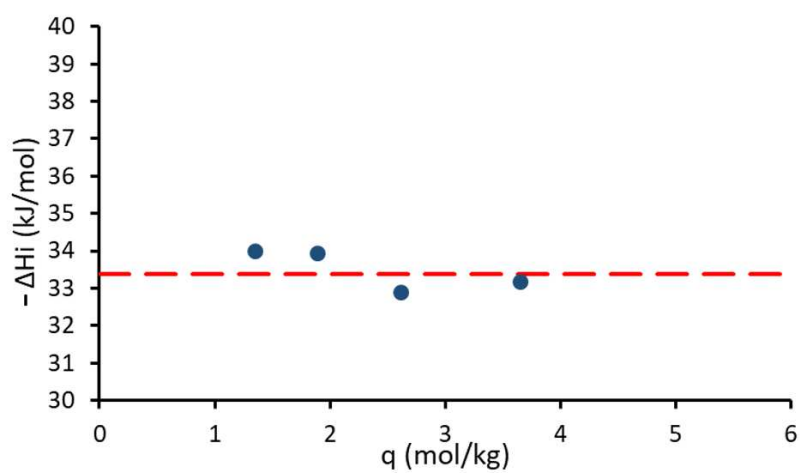
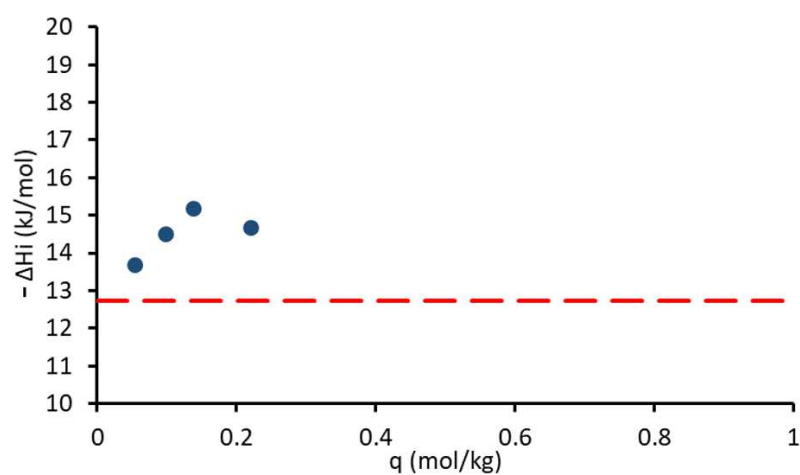
Figure 5.15: Isosteric heat of adsorption versus loading on Carbotech granulates for N_2 

Figure 5.16: Isosteric heat of adsorption versus loading on MIL-100(Fe) granulates for VCM

Figure 5.17: Isosteric heat of adsorption versus loading on MIL-100(Fe) granulates for N_2

5.5. Vinyl Chloride Recovery using Pittsburgh PCB Activated Carbon

In his work, Scamehorn² detailed an early adsorption-based process to reduce the concentration of VCM in gaseous streams to EPA allowed levels via steam regeneration on activated carbon. The process itself involved three steps: adsorption, steam regeneration and drying of the adsorbent. Like other temperature-swing processes at the time, it was heavily reliant on steam purging. As discussed in the previous chapter, the reliance on steam regeneration is a consequence of the sharp isotherm shape and the respective high adsorption enthalpy associated with the adsorption and desorption of vinyl chloride in the microporous structure of the Pittsburgh PCB carbon.

Although the Calgon Corporation specifies the Pittsburgh PCB carbon for liquid application, several works have used it for gaseous adsorbates and even compared its performance to the more indicated Calgon BPL bituminous coal granulated activated carbon⁸⁻¹⁰. Tsai and Chang⁸ reported this same performance comparison for methylene chloride and 1,1,1-trichloroethane, for various relative humidity levels. It was determined that the adsorption capacity of the PCB carbon was generally higher and less influenced by the relative humidity. An adsorbent less affected by relative humidity would be preferable, in a system that used steam purge for the adsorbent regeneration method. Otherwise, it could require a more stringent drying procedure.

However, today with the increasing restrictions on the gaseous emission levels of most chemical compounds and the tighter regulation put into effect for the control of liquid effluents, makes this steam regeneration approach impractical. Not only does steam regeneration create a liquid and a vapor effluent that must be thoroughly treated before release, but the recovered VCM itself must be dried before condensation to avoid the formation of ice in the machinery.

The physical properties of the Pittsburgh PCB activated carbon have already been reported elsewhere, but a brief summary of the most relevant ones is presented in Chapter 3.

5.5.1. TPSA Cycle Design

In designing an adsorption equilibrium-based TPSA separation unit, the specification of the optimum pressure and temperature operating conditions to achieve an optimum selectivity and the sizing of the separation unit is essential work. In this work, although the feed conditions specified a stream at 313 K, to make the most of the adsorption capacity of the Pittsburgh PCB carbon, the temperature and pressure operating range were set from 293 to 463 K and 0.5 to 1 bar. The pressure variations are controlled by pressurization and vacuum pumps, while the external temperature control is provided by a water cooler and a steam boiler. Figure 5.18 shows a comparison between the extrapolated VCM and N₂ adsorption isotherm models from 0 to 1 bar at 293 and 463 K. In Figure 5.18a, the isotherms of VCM and N₂ at 293 K are compared, where it is seen that this adsorbent has a high VCM/N₂ selectivity, with an estimated value of 59, for the feed conditions. While in Figure 5.18b, where both isotherms at 463K are compared, the selectivity can be seen to be lower, at the value of 44 for the feed conditions, which would facilitate the regeneration step.

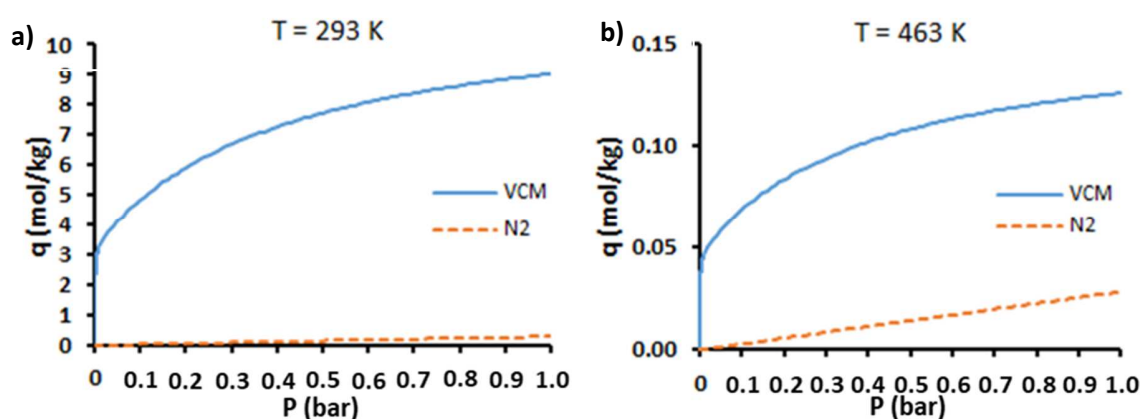


Figure 5.18: Estimated VCM and N₂ adsorption equilibrium isotherms at 293 K (5.18a) and at 463 K (5.18b) for the Pittsburgh PCB carbon

Based on the supplied feed conditions and adsorbent characteristics, the inlet velocity was set as a fraction of the minimum fluidization velocity. Which for a constant feed flow rate

allows the calculation of the cross-section area of the column and its respective diameter. Finally, by stipulating the minimum cycle duration and based on the adsorption capacity of the adsorbent, the minimum volume for the adsorption column can be calculated.

As such, for a minimum fluidization velocity of 0.092 m/s, the simulated stainless steel column would have a fixed bed length of 14.8 m and a diameter of 1.0 m, for a total mass of 6225 kg of carbon. The high length to diameter ratio of the column was chosen due to the VCM high heat of adsorption and the strict N₂ purity requirement. A low diameter is needed to promote heat transfer between the adsorption bed and the external heat exchanger. At the same time, a high column length is advised to reduce the effects of axial dispersion and ensure a sufficient Length of Unused Bed (LUB) for the production of a pure N₂ stream. Although not the most efficient method, high length to diameter ratio designs have been used to solve similar issues in the industry, such as the early designs for the Fischer-Tropsch process ²⁷ and nitrogen production processes by adsorption ²⁸. The characteristics of the adsorption column are displayed in Table 5.3, and the used simulation parameters, calculated at feed conditions, are shown in Table 5.4. The value of the external heat transfer coefficient was estimated according to the average values present for the design of shell ad tube heat exchangers.¹¹

Table 5.3: Proposed adsorption column physical properties and sizing

Bed Length	14.8	<i>m</i>
Bed Diameter	1	<i>m</i>
Bed Porosity	0.37	-
Wall density	7800	<i>kg/m³</i>
Wall Specific heat	490	<i>J/(kg.K)</i>
Wall Thickness	0.01	<i>m</i>
Adsorbent Mass	6225	<i>kg</i>

Table 5.4: Parameter values used in the TPSA simulations calculated at feed conditions

Parameter	Estimation Used		Units
	VCM	N ₂	
Pore diffusivity	1.35×10^{-8}	2.02×10^{-8}	m^2/s
Mass Axial Dispersion	5.14×10^{-3}		m^2/s
Heat Conductivity	7.71×10^{-2}		$W/(m.K)$
Heat Axial Dispersion	7.06×10^{-1}		$W/(m.K)$
Viscosity	5.05×10^{-5}	6.88×10^{-5}	$Pa.s$
Mixture Viscosity	5.92×10^{-5}		$Pa.s$
External Heat Transfer Coefficient	300		$W/(m^2.K)$
Wall Heat Transfer Coefficient	100		$W/(m^2.K)$
Particle Heat Transfer Coefficient	200		$W/(m^2.K)$

5.5.2. TPSA Simulation Results

The simulation of the present separation system was performed using the 1D fixed bed model following a TPSA cycle configuration with seven possible steps: “Feed,” “Closed Heating,” “Blowdown,” “Purge,” “Closed Cooldown,” “Counter-Current Pressurization,” and “Idle”. The typical process operation of the described system has already been detailed in Chapter 4 and will follow the step sequence illustrated in Figure 5.19.

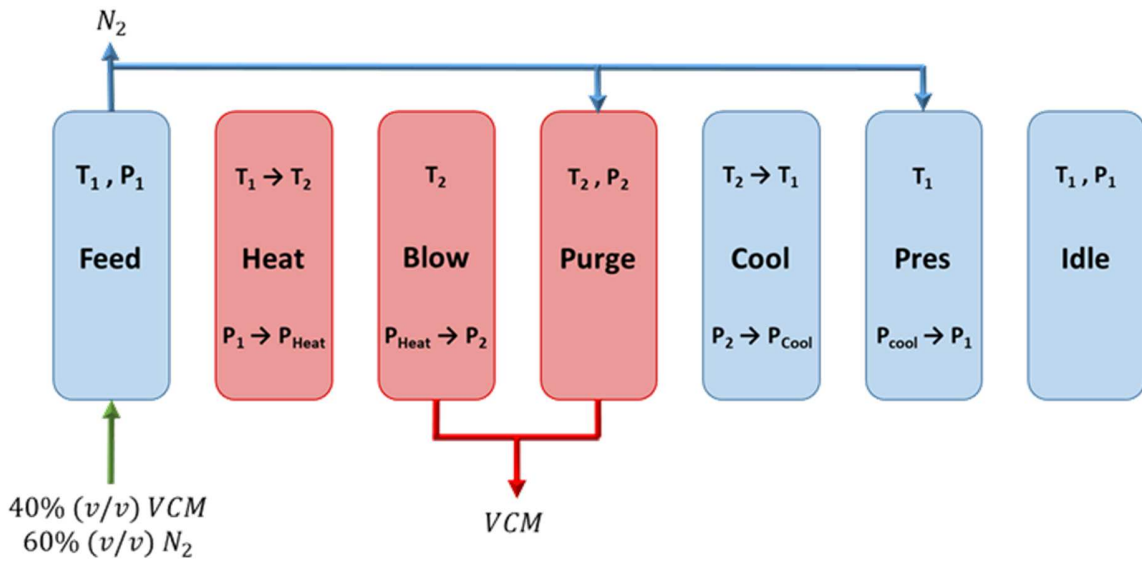


Figure 5.19: Schematic of the proposed TPSA cycle configuration



Figure 5.20: Extension of the TPSA cycle to a two-column system

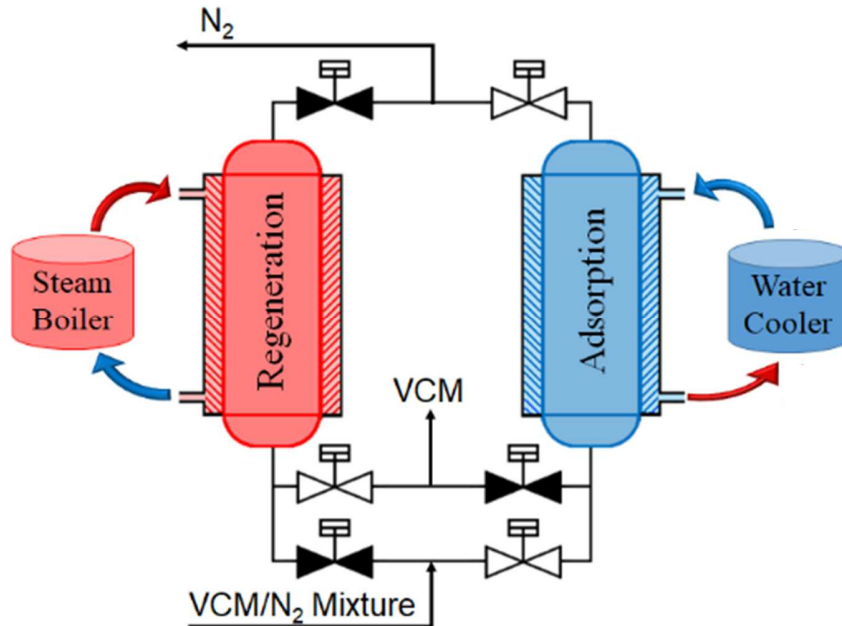


Figure 5.21: Diagram of the proposed 2-column TPSA VCM recovery unit using a steam boiler and a colling water tower to provide the heating and cooling duties of the process

For the described cycle, the expected process requirements were achieved by following TPSA step conditions stated in Table 5.5. The proposed scheduling allows its extension to a 2-column TPSA unit that guarantees a continuous feed treatment and production of a nitrogen rich stream, but not a continuous production of VCM. The proposed multicolumn schedule is shown in Figure 5.20, while Figure 5.21 illustrates the complete 2-column system proposed for the current separation, supported by a water cooling tower and a steam boiler. Based on a feed flow rate of 228 Nm³/h and inlet velocity of 0.054 m/s, to accomplish the VCM purity requirements of 95%, a purge flow rate of 19 Nm³/h with an outlet velocity of 0.25 m/s, and a pressurization flow rate of 54 Nm³/h, were used. Using these operating parameters, a product stream of nitrogen with a VCM contamination of 7.8 ppm (w/w) was produced, and nitrogen recovery of 96.50 % was achieved. The productivity of VCM was 0.46 mol/(kg.h) and 0.66 mol/(kg.h) for N₂. The proposed conditions and time steps for the TPSA cycle and performance results are shown in Table 5.5 and Table 5.6, respectively.

Table 5.5: Proposed TPSA Cycle Step Conditions

<i>Steps</i>	<i>Step time (s)</i>	<i>Pressure (bar)</i>	<i>External Temperature (K)</i>	<i>Flow Rate (Nm³/h)</i>
<i>Feed</i>	24000	1	293	228
<i>Heating</i>	2000	1 (→ 7.25)	293 → 463	-
<i>Blowdown</i>	7000	7.25 → 0.5	463	-
<i>Purge</i>	1000	0.5	463	19
<i>Cooldown</i>	7000	0.5 (→ 0)	463 → 293	-
<i>Pressurization</i>	2000	0 → 1	293	54
<i>Idle</i>	5000	1	293	-

Table 5.6: Proposed TPSA cycle performance results

VCM Purity in VCM Stream	95.01	% (<i>v/v</i>)
VCM in N ₂ Stream	7.8	<i>ppm</i> (<i>w/w</i>)
VCM Recovery	99.99+	% (<i>v/v</i>)
N ₂ Recovery	96.50	% (<i>v/v</i>)
VCM Productivity	0.46	<i>mol/(kg_{ads} · h)</i>
N ₂ Productivity	0.66	<i>mol/(kg_{ads} · h)</i>
Energy Consumption	3.62	<i>MJ/kg_{VCM}</i>

Compared to other alternatives presented in the literature, the presented process has both its advantages and disadvantages. The more conventional processes found in the literature include carbon adsorption with steam purge, solvent absorption, and membrane separation. Comparing to carbon adsorption with steam purge, energy wise, there should not be much difference as the energy requirements for heating and cooling the bed would be the same. In terms of capital investment, while direct heating through steam would increase the energy transfer rate and possibly reduce the column length, additional costs would be added to remove the water vapor from the VCM by condensation, and possibly, for further treatment of the resulting liquid stream. One of the most detailed examples of solvent absorption, comes from a patent by Klein¹², in which iso-octane (2,2,4-trimethyl pentane) is used as a solvent for the separation of VCM/inerts. This absorption process requires a high investment cost, high consumption of solvent, and the stripped VCM must be recuperated from the solvent via distillation and then decanted. Despite the high energy consumption and solvent losses through the vent, which can require incineration depending on the current environmental emission regulations, the main advantage of this system lies in the production of a vent gas with a VCM concentration as low as 1 ppm by volume. As for the use of membrane separation systems, the MTR VaporSep® system is the most commercially widespread solution. The performance of this system for the recovery of VCM from PVC reactor vents has already been studied by Lahiere et al.⁸. Unlike the previous systems, this membrane system was designed to recuperate most of the unreacted

monomer. As such, it is not capable of producing an inert vent gas with an admissible VCM concentration to vent to the atmosphere. Although the membrane system benefits from a lower energy requirement, the necessity of an additional purification system, usually incineration, is detrimental.

The proposed TPSA cycle was simulated until a cyclic steady state (CSS) was achieved, which was occurred after 25 cycles. During CSS, the temperature and pressure histories obtained at the entrance, half height, and at the end of the adsorption column are displayed in Figures 5.22 and 5.23. Figures 5.24 and 5.25 show the N_2 and VCM product-rich streams outlet molar flow rate and temperature conditions. From Figure 5.24, it can be observed that during the Feed step, mostly pure nitrogen is being produced at a constant flow rate and temperature. While Figure 5.25 shows that during the Blowdown step, due to the application of a linear depressurization function to the outlet valve, a high purity VCM stream is being produced at a low, controlled molar flow rate, during the Purge step. The N_2 outlet concentration increases as the purge gas is being used to remove any remaining VCM present in the gas phase of the column. A linear depressurization function can be more advantageous for the dimensioning of the support vacuum pumps, as it prevents the high initial flow rates characteristic of valves operating under an exponential function. Due to the column pre-heating, the VCM rich product stream is produced at a temperature range of 383 to 413 K.

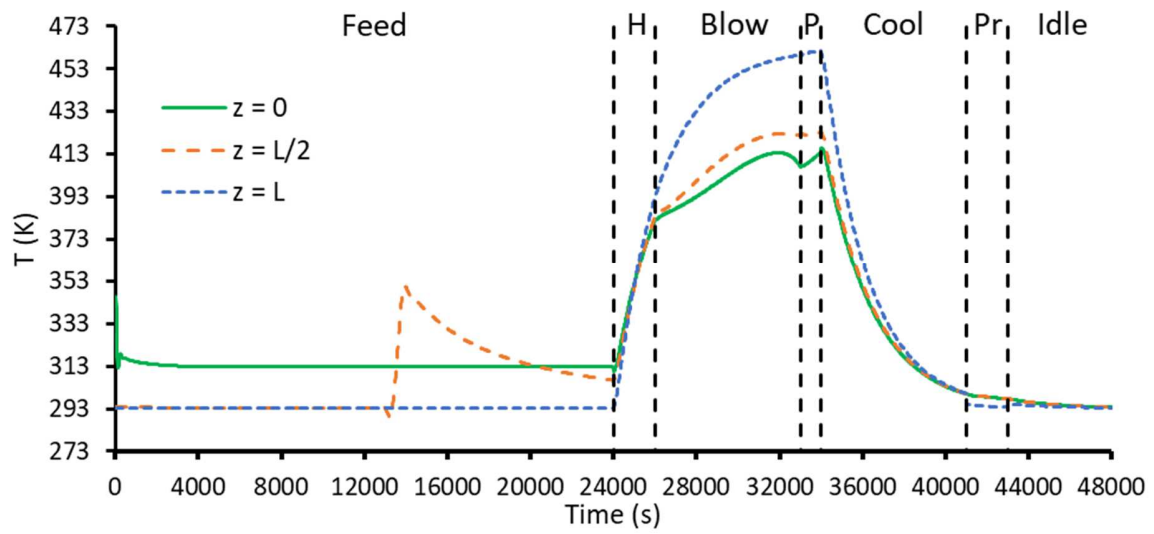


Figure 5.22: Gas Phase Temperature History at the entrance, halfway and end of the adsorption bed at CSS

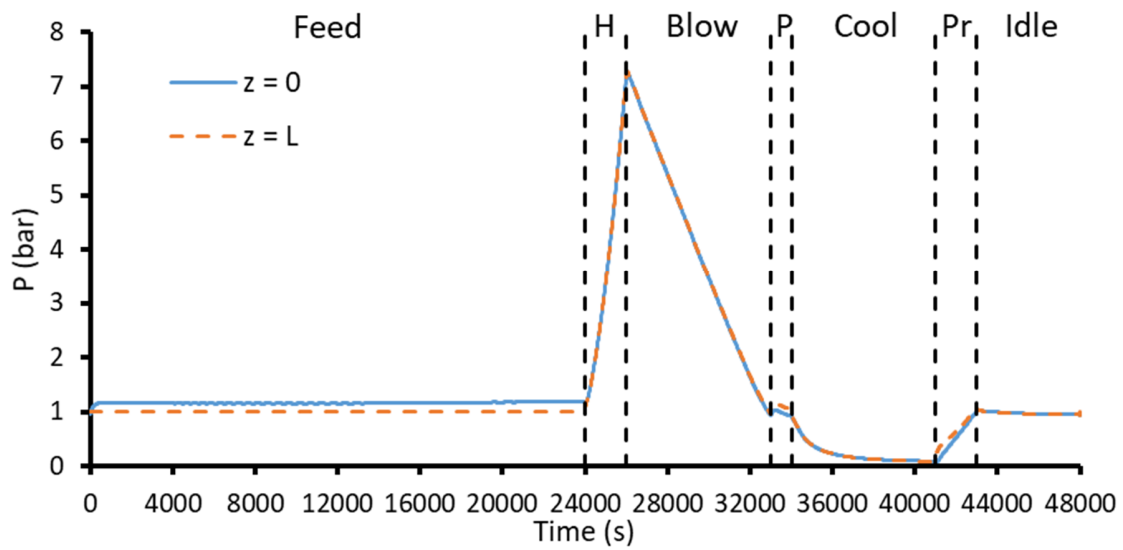


Figure 5.23: Pressure History at the entrance and end of the adsorption bed at CSS

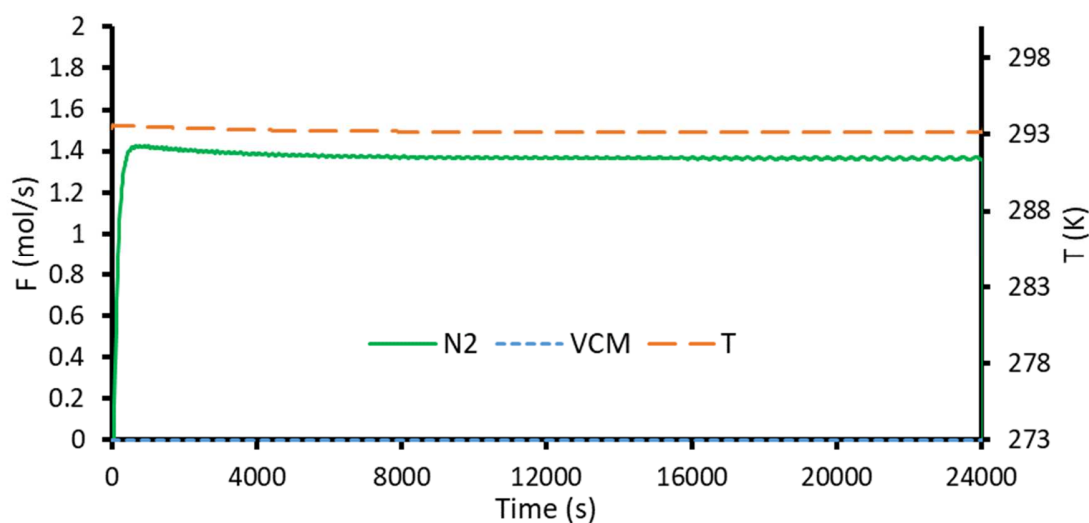


Figure 5.24: Molar Flow Rate and Temperature History during the N_2 production step at CSS

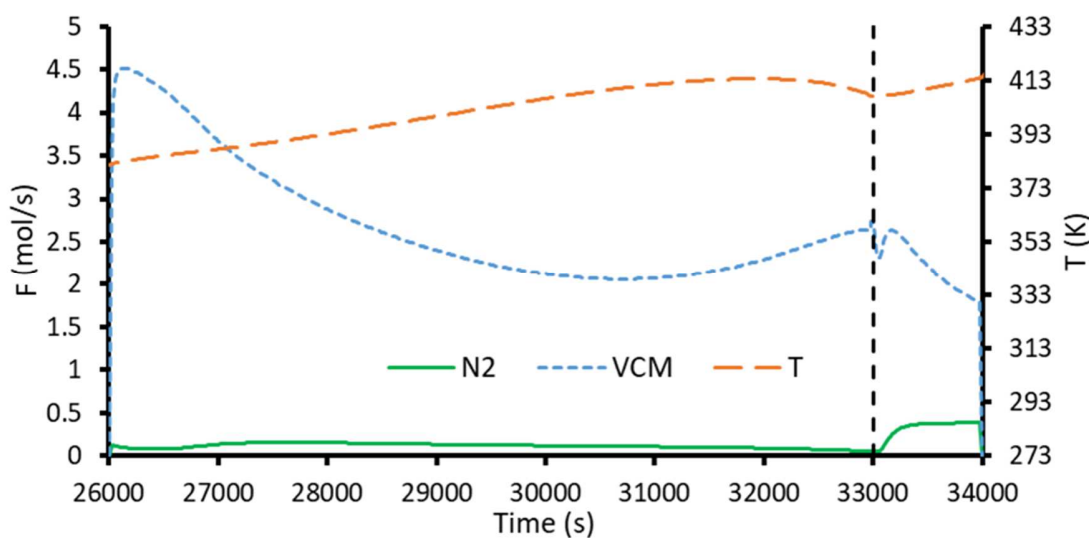


Figure 5.25: Molar Flow Rate and Temperature History during the VCM production step at CSS

From Figure 5.26 to 5.29 are shown the gas-phase and solid-phase concentration profiles, for VCM and N_2 , at the end of each step at CSS. Figure 5.30 shows the temperature profile at the end of each step at CSS. In Figures 5.26 up to 5.30, the representation of the Idle step is purposely left out as no particular change can be observed during that time for the

variables under study. During the Feed step, a steep VCM front is formed, and a corresponding high temperature gradient, of about 70 K, is formed as well. The temperature decay observed in the Feed step originates from both the influence of the external cooling and the lower temperature of the feed stream (313 K). During the Closed Heating step, the temperature increase leads to the desorption of VCM and, consequently, the increase in the gas-phase VCM concentration and pressure inside the column. The duration of this pre-heating step is purposely set to prevent any significant dispersion and progression of the VCM front. During the Blowdown step, most of the desorbed VCM is removed from the column, while a small dispersive concentration front reaches the end of the adsorption bed. Following, the Purge step feeds part of the N₂ product counter-currently back into the adsorption column, to remove most of the remaining gas-phase VCM and further promote the desorption of adsorbed VCM and push back the VCM front for the next cycle. After the end of both the production steps, the column is cooled down to almost 293 K, which leads to an overall decrease in the internal pressure of the column caused by the promoted adsorption of any of the remaining amounts of VCM left in the column. Finally, the column is pressurized back to the feed pressure with a counter-current pressurization using part of the N₂ product. Although not represented, a specific duration of the Idle step is established, to guarantee a continuous feed of the untreated VCM/N₂ feed mixture.

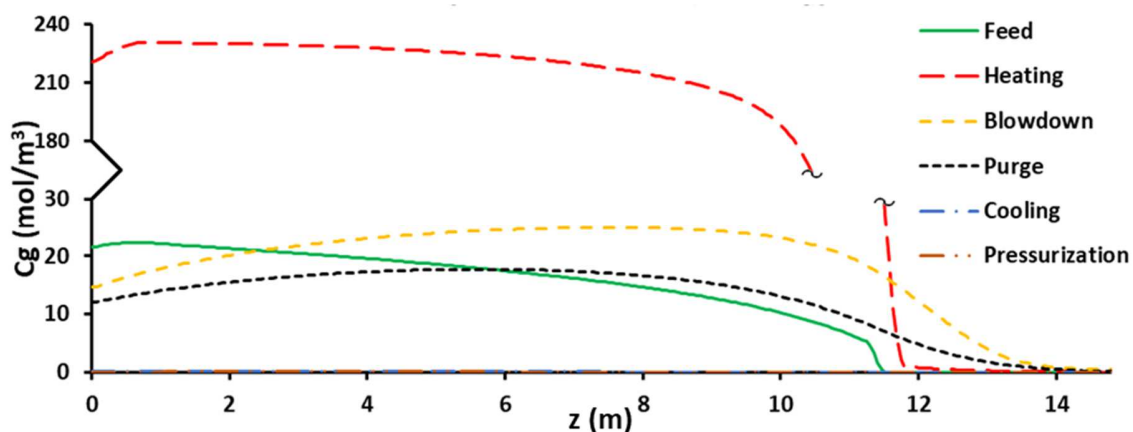


Figure 5.26: VCM Gas-Phase concentration profiles at the end of each step at CSS

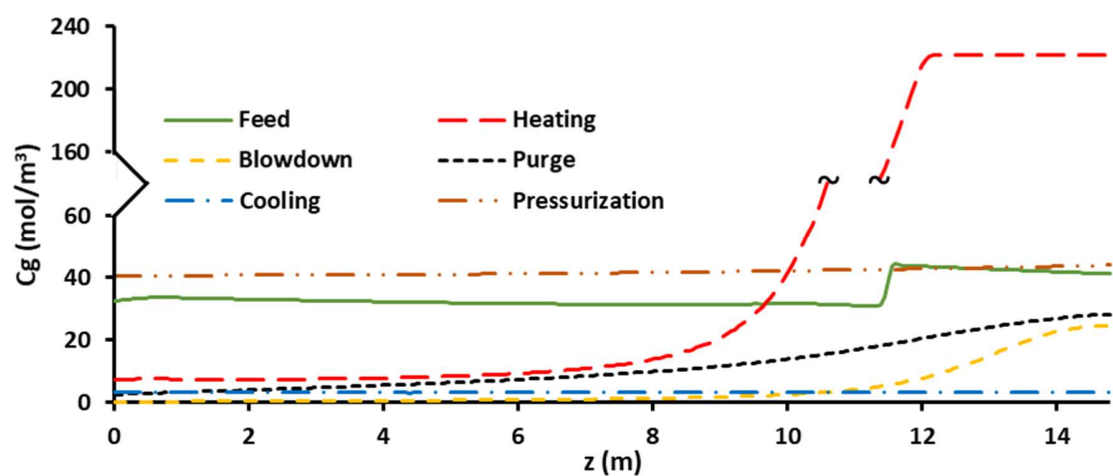
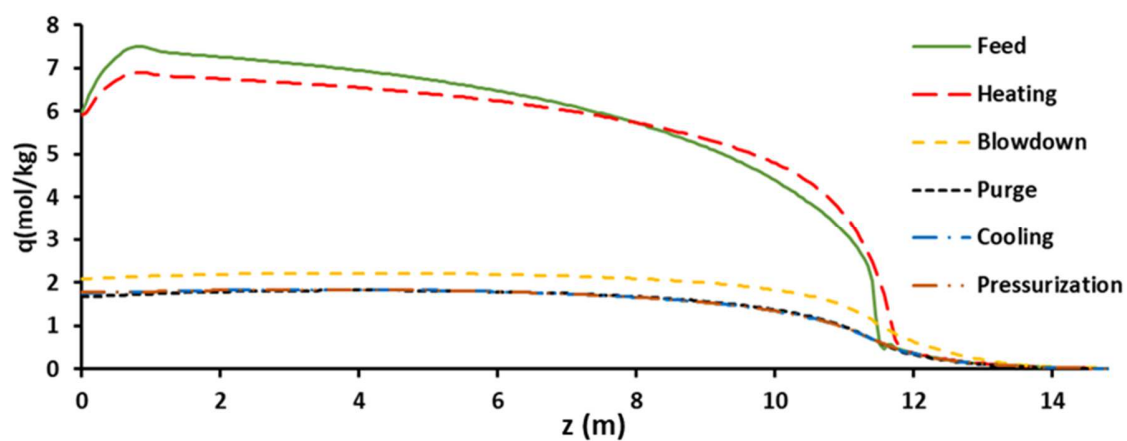
Figure 5.27: N₂ Gas-Phase concentration profiles at the end of each step at CSS

Figure 5.28: VCM Solid Phase concentration profiles at the end of each step at CSS

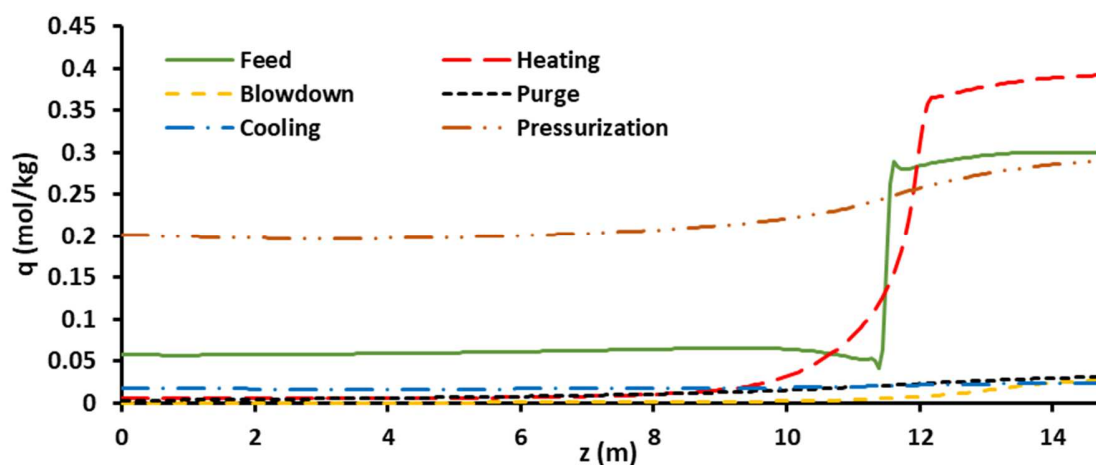


Figure 5.29: N₂ Solid Phase concentration profiles at the end of each step at CSS

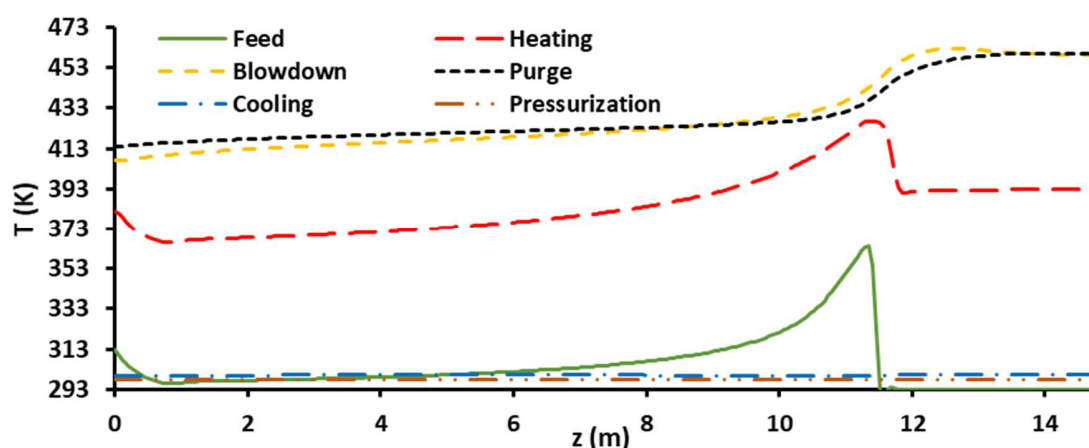


Figure 5.30: Temperature Profiles at the end of each step at CSS

5.5.3. Sensitivity Tests

To better understand the conditions proposed as a result of this research, several additional studies were performed to investigate the robustness and the sensitivity of the proposed system towards alterations in the adsorbate equilibrium, steps configuration and duration, on the performance of the proposed TPSA cycle.

As the adsorption behavior of present study is solely based upon adsorption equilibrium isotherm data collected from the available literature, the author have little to no control

over its reported quality. Additionally, most of the isotherm data collected in this study was not determined using dedicated equipment but assessed by breakthrough experiments. As such, it would be advisable to test the robustness of the present process against variations in the used isotherm fitting parameters. To test this robustness, four simulations were performed where the adsorption capacity (q_{sat}) of the used DSL isotherm model was altered to be lower or higher than the set value. To allow a comparison between the different simulations, the purge inlet flowrate was adjusted for each case to satisfy the outlet VCM (95%(v/v)) purity requirement. Figure 5.31(a) shows a comparison between the original and the modified VCM isotherms at 313 K, as well as the variations to the VCM concentration in the N₂ rich stream as a function of the adsorption capacity. As can be seen from Figure 5.31(b), for adsorption capacities higher than the original measurements, the TPSA cycle is still capable of producing an N₂ vent gas with a VCM contamination lower than the established 8 ppm (w/w) limit. However, for lower adsorption capacities, the resulting VCM content in the N₂ stream tends to increase exponentially beyond the established limit, which results in inadequate separations.

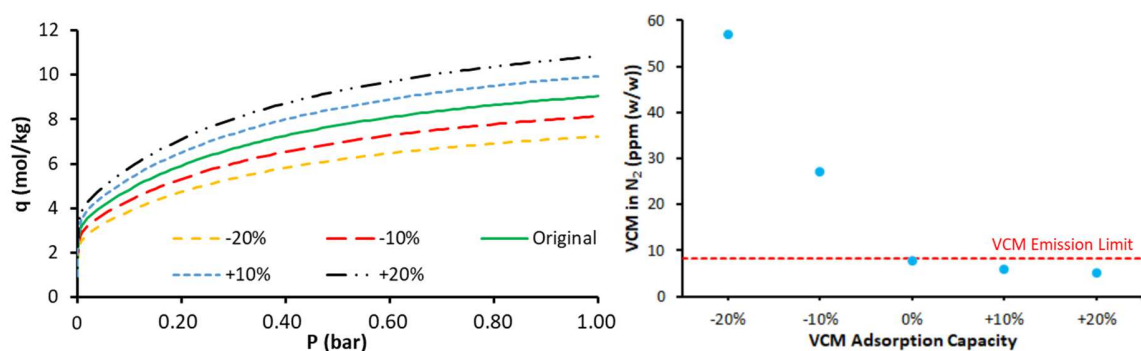


Figure 5.31: (a) Effect of the adsorption capacity variations on the VCM adsorption equilibrium isotherm at 313 K, and (b) VCM concentration of the N₂ rich stream for the VCM isotherm robustness tests

To test the sensitivity of the TPSA cycle and to allow a more thorough discussion on some of the selected steps, several simulation cases were performed. The more relevant cases

were recorded and reported in this study, as shown in Table 5.7, where Case 1 is the original TPSA cycle previously reported.

Table 5.7: Simulation cases configuration and performance results

<i>Case</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>9</i>
$t_{feed} (s)$	24000	24000	24000	24000	24000	24000	24000	24000	24000
$t_{rinse} (s)$	0	0	0	0	0	0	0	0	2000
$t_{heat} (s)$	2000	2000	0	0	2000	2000	2000	2000	2000
$t_{blow} (s)$	7000	7000	9000	2000	7000	7000	7000	7000	8000
$t_{purge} (s)$	1000	1000	1000	8000	0	6000	3000	500	1000
$t_{cool} (s)$	7000	12000	7000	7000	7000	7000	7000	7000	7000
$t_{press} (s)$	2000	2000	2000	2000	2000	2000	2000	2000	2000
$t_{idle} (s)$	5000	0	5000	5000	6000	0	3000	5500	2000
VCM Purity (%)	95.01	95.01	95.01	95.00	96.96	94.96	95.00	95.07	95.32
VCM in N ₂ Stream (ppm)	7.8	8.0	54.5	138.8	1055	82.1	24.2	7.8	6.9
VCM Recovery (%)	99.999	99.999	99.996	99.991	99.927	99.994	99.998	99.999	99.999
N ₂ Recovery (%)	96.495	96.495	96.497	96.491	97.910	96.459	96.488	96.541	96.630
Energy Consumption (MJ/kg _{VCM})	3.62	3.62	-	-	-	-	-	3.61	3.97

Since the conditions of the Idle step are identical to the Cooldown step, Case 2 explores the possibility that the idle time could be better spent on extending the cooling time of the column. As seen in Table 5.7, the performances of both configurations are almost identical, with only a negligible increase in the VCM concentration on the N₂ stream.

One of the downsides of the reported system is that similarly to most TSA units, the time dedicated to the desorption/regeneration of the adsorbent material is too extensive, which can be pretty impactful on the performance of the system. With time, the VCM front tends to disperse along the bed and contaminate the LUB section of the column.

The cause of this problem is twofold; due to the VCMs high adsorption enthalpy, the system needs to supply more thermal energy to regenerate the adsorbent, but at the same time since the heat transfer is performed radially, TSA systems tend to perform more slowly with scale-up, even with the already high column length to radius ratio in place. Additionally, due to the requirement of 95% purity on the VCM stream, a continuous supply of purge gas over long periods would be detrimental.

Indeed, the closed heating step is implemented to try to restrain the dispersion effects on the VCM gas-phase concentration front. In this step, the increase in temperature and consequent desorption of VCM leads to increased pressure inside the column. The higher inner pressure is then used to increase the velocity profile of the blowdown gas for the remainder of the required heating time, which stifles the deformation of the VCM front. Case 3 and 4 were performed to demonstrate the performance of the column without the heating step. In Case 3, the remaining required time is allocated to the blowdown step, while in Case 4, the duration of the purge step is increased. In both cases, the content of VCM on the nitrogen product is higher than the value allowed by the process specifications.

Case 5 removes the Purge step to maximize the N₂ Recovery for this system, showing the baseline that can be achieved following this particular setup. Case 6, 7, and 8 explore the influence of the purge step duration, and consequently, to maintain the N₂ recovery requirement, the purging gas speed in desorbing the VCM. As shown by Figure 5.32, a longer purge step duration lowers the desorption performance, while a higher purge speed does not show significant improvement and may risk the physical integrity of the bottom carbon particles. The maximum outlet purge velocities for Cases 6, 7, and 8 are respectively 0.20 m/s, 0.22 m/s and 0.36 m/s.

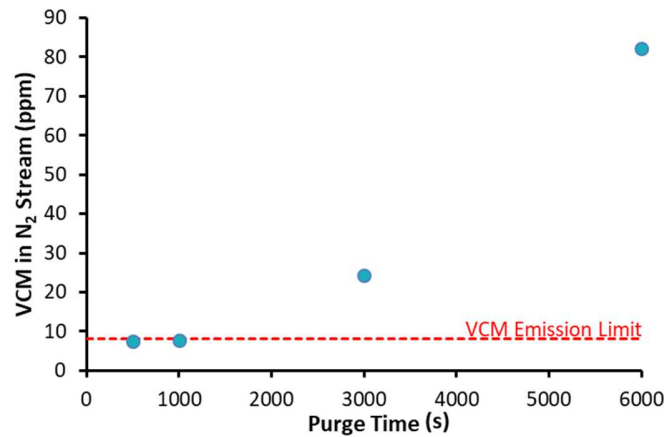


Figure 5.32: Influence of the Purge Time on the VCM concentration in the N₂ rich stream

In Case 9, in order to increase the N₂ recovery and improve the separation performance, a Rinse Step was introduced after the Feed step and as illustrated by Figure 5.33. However, due to VCM's high adsorption affinity, a higher purge speed of nitrogen is required to obtain the VCM purity requirements. This change results in a slight increase in nitrogen recovery and VCM purity at the cost of significantly higher energy consumption.

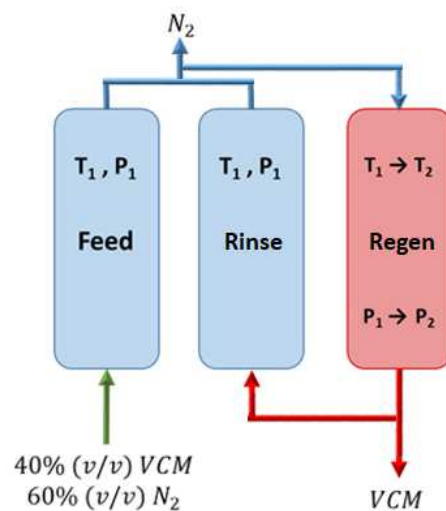


Figure 5.33: Schematic of the TPSA cycle with the implementation of a Rinse step

A final study was also performed to compare the influence of each regeneration method in the performance of the designed TPSA cycle. Based on the used parameters and results obtained in Case 1, two simulations were prepared, one solely based on a TSA cycle, while

the other on a PSA cycle. The cycle specifications for the TSA and PSA cycles and the resulting performance parameters are reported in Table 5.8. For the TSA cycle, the blowdown pressure was set to 1 bar and the purge speed was increased. As seen in Table 5.8, the performance of the TSA cycle is very similar to the original TPSA, except a lower nitrogen purity but with a higher VCM purity. The PSA cycle, on the other hand, has shown to be incapable of performing the separation. Without a temperature-based regeneration, the PSA system cannot regenerate the VCM front, which, over time, results in the almost complete saturation of the carbon bed, as shown by Figure 5.34.

Table 5.8: Performance Comparison between regeneration methods

<i>Case</i>	<i>TPSA</i>	<i>TSA</i>	<i>PSA</i>
t_{feed} (s)	24000	24000	4000
t_{heat} (s)	2000	2000	0
t_{blow} (s)	7000	7000	3000
t_{purge} (s)	1000	1000	500
t_{cool} (s)	7000	7000	0
t_{press} (s)	2000	2000	500
t_{idle} (s)	5000	5000	0
VCM Purity in VCM Stream (%)	95.01	95.37	66.14
VCM in N_2 Stream	7.8 ppm	66 ppm	36 %(v/v)
VCM Recovery (%)	99.999	99.996	17.628
N_2 Recovery (%)	96.495	96.758	92.045
Energy Consumption (MJ/kg _{VCM})	3.62	3.65	0.86

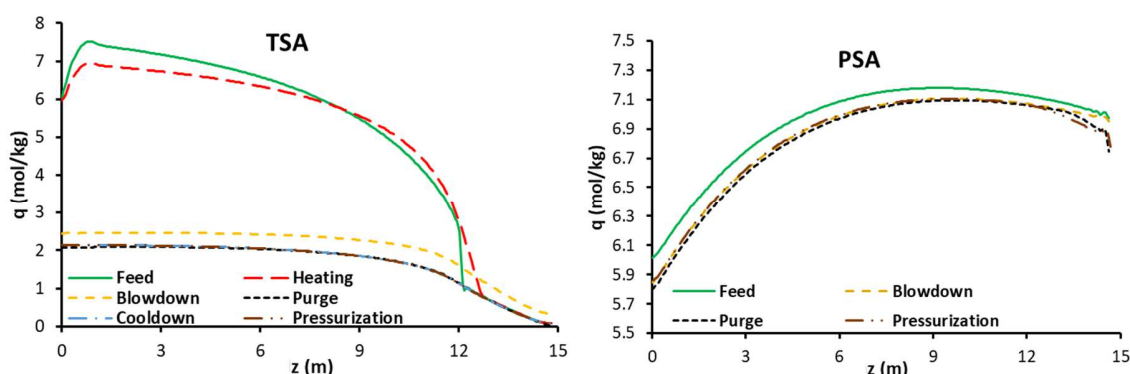


Figure 5.34: Solid Phase VCM concentration profiles at the end of each cycle step at CSS for the reported TSA and PSA systems

5.5.4. MT-TPSA Cycle Design

One of the main limitations pointed out in the previous study was the possibly inappropriate neglect of the radial temperature profiles. Since the present separation is mostly dependent on the performance of the temperature swing process, and the heat transfer mechanism in a TPSA system is implemented radially, if the radial energy transfer is not being precisely simulated, the system's performance may vary greatly. This limitation, together with the feedback received regarding the excessively long column height and the high regeneration temperature of 463 K, led to the research and implementation of an alternative TPSA cycle configuration that could overcome these limitations. Indeed, the proposed 2-dimensional MT-TPSA cycle model circumvents these problems by dramatically increasing the heat transfer surface area, thus shortening the required time for the temperature swing and lowering the load of adsorbent needed, while simultaneously enabling a more accurate study of the radial behavior inside the packed bed.

In the previous single adsorption column TPSA approach, due to the long cycle time duration, mass dispersion effects significantly contributed to the VCM front propagation and impacted the system performance. Due to the reported sharp isotherm shape for VCM, these propagations were difficult to regenerate. However, as seen in Figure 5.35, thorough regeneration can only be accomplished at very high temperatures (> 463 K). If cooling water

were to be used during the Cooldown stage, then, at least, medium pressure steam (> 12 bar) would be necessary for the heating stage. Using a gas phase heating fluid generally results in a lower heat transfer performance¹³, besides the necessary design considerations to accommodate a two-phase heat transfer fluid and the economic disadvantage of acquiring and operating an exclusive steam boiler. Due to the increased surface area, employing an MTA geometry would cut down on the required stage time durations. As such, for a TPSA system following the MTA geometry with Pittsburgh PCB AC, the regeneration temperature was lowered to 393 K, which enables the use of pressurized water as the heating fluid.

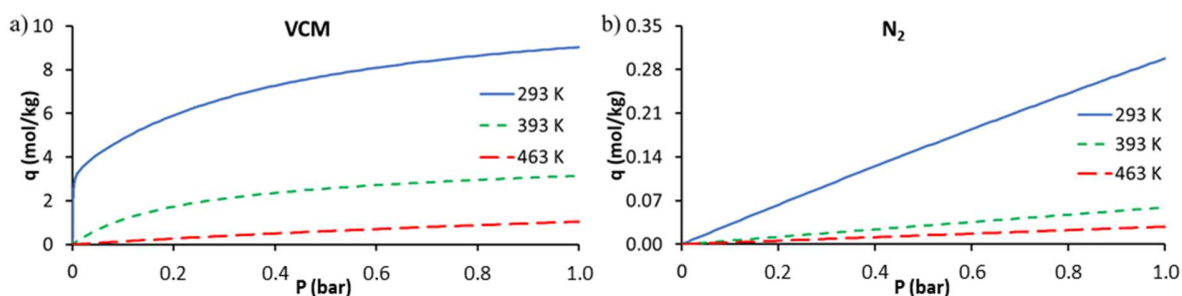


Figure 5.35: DSL isotherm model predictions for VCM (a) and N_2 (b) at 293, 393, and 463 K

As in the previous section, the physical and transport parameters used in this MT-TPSA simulation were calculated based on the process feed conditions established at the beginning of this Chapter and using the estimations described in Chapter 4 or from values available in the literature when applicable. As such, Table 5.9 shows the transport parameter values calculated for a $180 \text{ Nm}^3/\text{h}$ feed stream of a 40/60 % (v/v) VCM/ N_2 mixture at 1.15 bar and 313 K. While Table 5.10 shows the physical and sizing parameters used in the MT-TPSA and fixed-bed simulations. Compared to the literature available on the design of multitubular heat exchangers, a lower inlet velocity was selected to maintain an acceptable pressure drop along the tubes. Additionally, a feasible design for the MT-TPSA system was assured using typical, commercially available tube sizes and shell specifications.

Table 5.9: Transport Parameter values used in the MT-TPSA Simulation calculated at feed conditions

Axial Mass Dispersion	5.93×10^{-3}	m^2/s
Radial Mass Dispersion	1.40×10^{-3}	m^2/s
Axial Heat Dispersion	8.43×10^{-1}	$W/(m.K)$
Radial Heat Dispersion	2.99×10^{-1}	$W/(m.K)$
Mixture Viscosity	6.28×10^{-5}	$Pa.s$
Shell Side Heat Transfer Coefficient	1715	$W/(m^2.K)$
Wall Heat Transfer Coefficient	133	$W/(m^2.K)$
Particle Heat Transfer Coefficient	412	$W/(m^2.K)$
Tube Side Overall Heat Transfer Coefficient	50.5	$W/(m^2.K)$

Table 5.10: Physical and Sizing properties parameters used for the MT-TPSA and Fixed Bed simulations

	MTA	Fixed Bed	
Tube Length	5.4		m
Tube Inner Diameter	29.35×10^{-3}	4.45×10^{-1}	m
Tube Outer Diameter	31.75×10^{-3}	4.47×10^{-1}	m
Tube Pitch	39.69×10^{-3}	-	m
Tube Clearance	7.94×10^{-3}	-	m
Bed Porosity	0.37		-
Tube Thickness	1.20×10^{-3}		m
Number of Tubes	230	-	-
Total Adsorbent Mass	450		kg
Transfer Surface Area	124	15	m^2
Tube Bundle Diameter	0.75	-	m
Shell Diameter	0.8	0.49	m
Baffle Spacing	0.36	-	m
Baffle Cut	25	-	%
Shell Inlet velocity	0.5		m/s

A temperature swing cycle is typically composed of three stages, a Feed, a Heating, and a Cooldown stage. To guarantee a continuous consumption of the feed mixture stream, the duration of each or the sum of the Heating and Cooldown stages, must be proportional to the duration of the Feed stage. While, additionally, to ensure continuous production of VCM, the duration of the Heating stage should also be equal to or higher than the Feed stage. Since the duration of the Heating and Cooldown stage are mostly dependent on the overall radial heat transfer rate to tube volume ratio, which is independent of the tube length, then the Feed stage duration, and the corresponding tube length, should be adjusted to fit whichever of the previously mentioned requirements, as well as, depending on the sizing and flow specifications.

To determine the cycle step durations, and thus estimate the ideal tube length, breakthrough simulations were performed following the parameters given in Tables 5.9 and 5.10. Figure 5.36 shows the binary breakthrough curves, and the temperature history at the outlet, for the adsorption and regeneration of a VCM/N₂ mixture feed following the MT-TPSA configuration.

Based on the specifications listed in Table 5.10, the breakthrough curves were obtained at 1 bar, and under an external cooling of 293 K for a 180 Nm³/h feed stream evenly split over 230 tubes, with an inlet composition of 40/60 %(v/v) VCM/N₂ at 313 K. After complete saturation (8000 s), the bed is regenerated by a co-current blowdown to 0.5 bar, and an indirect heating of 393 K. From this breakthrough simulation, some assumptions on the cycle time step duration can be done. The ideal duration of the Heating stage can be estimated by the time elapsed between the beginning of the regeneration step and the stabilization of both the temperature and VCM molar flow histories. For which, taking the example provided in Figure 5.36, a bed of Pittsburgh PCB carbon saturated in a 40/60 %(v/v) VCM/N₂ mixture should take at least 1000 and at most 2000 seconds, to regenerate under the proposed sizing specifications.

Although not present in the breakthrough simulation, the duration of the Cooldown stage should be shorter than the Heating stage. As both the Heating and Cooldown stages are being simulated under the same transport parameter estimations, and the energy required to change the temperature of the adsorbent material should also be the same in both stages, the Heating stage duration will always be longer due to the higher concentration of gas- and solid-phase adsorbates, which will require thermal energy to simultaneously heat up and desorb.

The Feed stage duration can be estimated depending on the intended number of adsorption units in the MT-TPSA system and by guaranteeing the previous requirements.

Finally, the length of the tube system can be estimated by the duration of the simulated breakthroughs that satisfy the imposed schedule while also taking into account the VCM useful adsorption equilibrium capacity, determined between the equilibrium conditions set for the Feed and Heating stages. However, again due to the strict N₂ purity requirement and the propagation of the VCM front, an additional extension of the tube length should be considered to guarantee the process requirements (LUB).

The MTA design was adopted to enable the development of more compact and swift adsorption separation units, and compensate for the lower overall radial heat transfer characteristic of gas flows. To visualize the impact of the proposed design consideration, an additional breakthrough simulation was used to compare the resulting production flow rates and temperature histories. Figure 5.37 shows the binary breakthrough curves of VCM and N₂, as well as the temperature history of the outlet flow, for a 2D fixed bed model, with a transverse area equivalent to the sum of all the tubes proposed in the MTA design. The breakthrough simulation described in Figure 5.37 is performed under the same feed and operating conditions described for Figure 5.36, and following the specifications listed in Table 5.9 and Table 5.10.

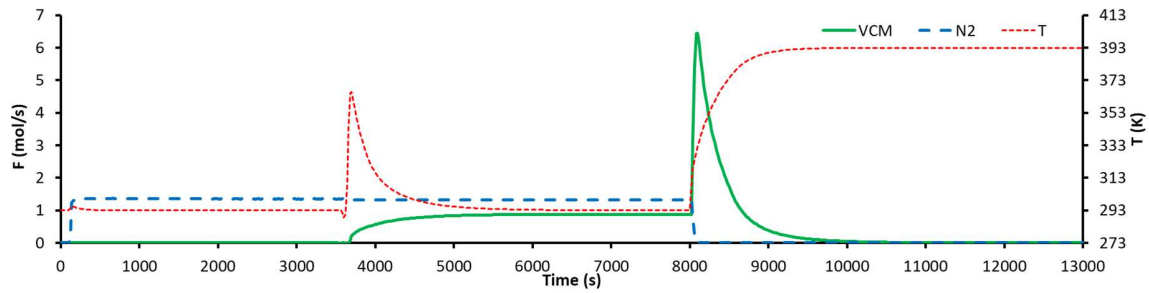


Figure 5.36: VCM and N₂ outlet molar flow rates (F) and temperature (T) history, at the exit of the bed, averaged over the radial direction, using a 2D model for the MTA design, for an inlet 180 Nm³/h flow rate with a 40/60% (v/v) VCM/N₂ gas mixture, at 313 K and 1 bar.

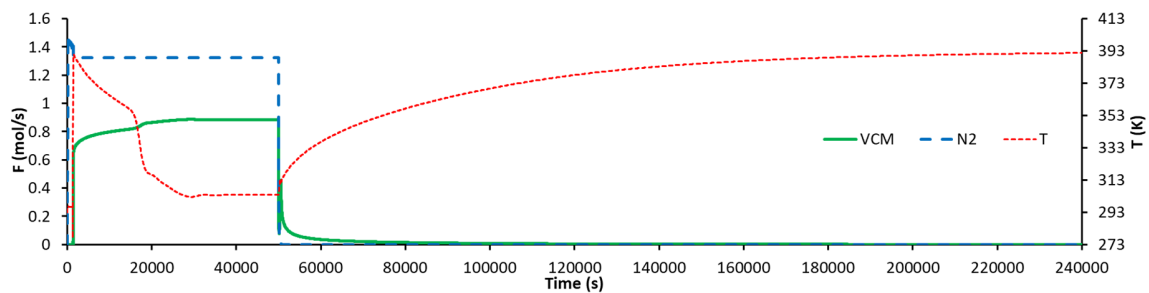


Figure 5.37: VCM and N₂ outlet molar flow rates (F) and temperature (T) history, at the exit of the bed, averaged over the radial direction, using a fixed bed 2D model with equivalent bed diameter, for an inlet 180 Nm³/h flow rate with a 40/60% (v/v) VCM/N₂ gas mixture at 313 K and 1 bar.

As can be observed by comparing the breakthrough simulations from Figures 5.36 and 5.37, the increased surface area of the MTA geometry provides a significant improvement to the heat transport mechanics of the system. When compared to the MTA design, the breakthrough performed under the fixed bed geometry not only requires significantly more time to thoroughly heat up the packed bed, but during the Feed step, the fixed bed system is incapable of completely removing the heat of adsorption. As after the 20000 s mark, the abrupt drop in temperature is caused by the lower temperature feed, as evidenced by the temperature stabilization towards 313 K instead of 293 K.

5.5.5. MT-TPSA Simulation Results

As illustrated by Figure 5.38, the proposed MT-TPSA process consists of six steps: Feed, Rinse, Blowdown, Counter-Current Purge, Cooldown, and a Counter-Current Pressurization. Following the MT-TPSA cycle step schedule and operational specifications proposed in Table 5.11. The present system can be expanded into a three MTA unit system to guarantee continuous feed consumption and production, as exemplified in Figure 5.39. As described in Table 5.12, an MT-TPSA following the proposed cycle conditions will be capable of producing two continuous product streams within the established purity requirements. For this system, a VCM productivity of 2.35 mol/kg_{ads}.h was achieved with a total thermal energy consumption of 4.88 MJ per kilogram of produced VCM. Specifically, 81.8% of the energy consumption comes as the energy required for the heat exchanger, while 9.8 and 8.6 % account for the operation of the gas and liquid pumps, respectively. For thermal energy consumption, the Adsorption Cooling and the Cooling Duties represent the thermal energy removed from the system using cooling water during the Feed and Rinse steps, and the Cooldown and Pressurization steps, respectively. While the Heating Duty represents the thermal energy supplied by the heated pressurized water during the Blowdown and Purge steps, used to regenerate the adsorbent material. Considering that the performance results were obtained at CSS, it can be concluded that only 19.3% of the thermal energy requirement is used to heat up and regenerate the adsorbed VCM effectively. This parameter can be used to quantify the efficiency of the temperature-swing process.

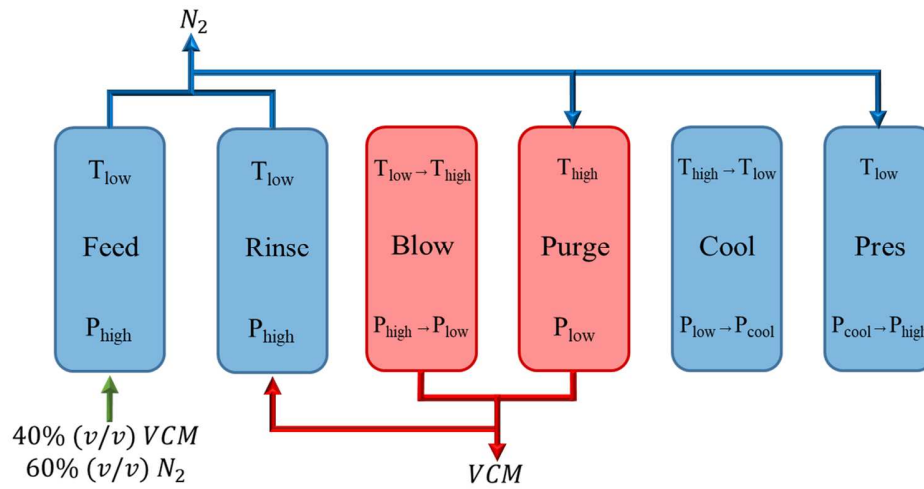


Figure 5.38: Outline of the MT-TPSA process

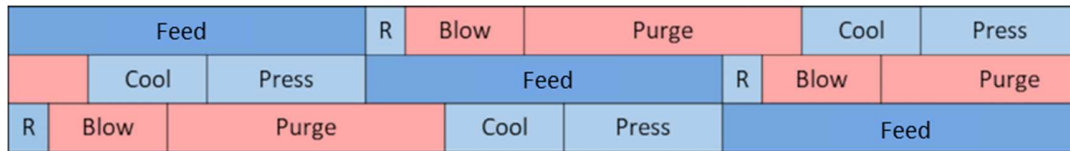


Figure 5.39: Extension of the proposed MT-TPSA schedule to a three-MTA unit system

Table 5.11: Proposed MT-TPSA Simulation Cycle step conditions on the Pittsburgh PCB AC

Steps	Step time (s)	Pressure (bar)	External Temperature (K)	Flow Rate (Nm ³ /h)
Feed	1800	1	293	180
Rinse	200	1	293	180
Blowdown	600	1 → 0.5	293 → 393	-
Purge	1400	0.5	393	11.2
Cooldown	600	0.5 (→ 0.1)	393 → 293	-
Pressurization	800	0.1 → 1	293	4.5

Table 5.12: Detailed TPSA Cycle Performance Results for the 2D and equivalent 1D model on the Pittsburgh PCB MT-TPSA system

	2D	Equivalent 1D	
VCM Purity	95.17	95.18	% (v/v)
VCM in N ₂ Stream	4.1	2.7	<i>ppm</i> (w/w)
VCM Recovery	99.9997	99.9998	% (v/v)
N ₂ Recovery	96.57	96.62	% (v/v)
VCM Productivity	2.35	2.35	$mol/(kg_{ads} \cdot h)$
N ₂ Productivity	3.40	3.40	$mol/(kg_{ads} \cdot h)$
Total Energy Consumption	4.88	4.87	MJ/kg_{VCM}
Adsorption Cooling Duty	0.77	0.77	MJ/kg_{VCM}
Heating Duty	2.01	2.00	MJ/kg_{VCM}
Cooling Duty	1.21	1.21	MJ/kg_{VCM}
Gas Pump Operation		0.48	MJ/kg_{VCM}
Liquid Pump Operation		0.42	MJ/kg_{VCM}

One of the primary objectives of the MT-TPSA cycle design was to lower the adsorbent material requirement and shorten the operational cycle time, creating more efficient separation units than other systems reported in the literature. To verify if this goal was fulfilled, Table 5.13 compares the productivity performance between the present MT-TPSA system and the single fixed bed TPSA system reported earlier in this chapter. As shown by these results, the initial demand has been fulfilled. Even though the fixed-bed design operates at a higher regeneration temperature (463 K), implementing an MTA design has led to a ninefold increase in VCM productivity while maintaining the same purity requirements. However, due to the additional volume occupied by the shell side of the unit, the MT-TPSA system is not as efficient volume-wise as the standard adsorption column, as seen by the unit's recovery capacity.

Table 5.13: VCM Productivity and Recovery Capacity comparison between the MTA and the Fixed Bed design

	MTA Design	Fixed Bed Design	Units
VCM Productivity	0.147	0.016	$kg_{VCM}/(kg_{ads} \cdot h)$
Bed VCM Recovery Capacity	78.67	8.60	$kg_{VCM}/(m_{bed}^3 \cdot h)$
Unit VCM Recovery Capacity	24.35	7.11	$kg_{VCM}/(m_{unit}^3 \cdot h)$

Following the aforementioned setup, a 2D MT-TPSA model was simulated until CSS was achieved. In order to simplify the analysis of the CSS axial behavior, the history and profiles represented in Figures 5.40 to 5.47 have been averaged along the radial direction through a weighted average using the cylindrical geometry. Figures 5.40 and 5.41, report the CSS temperature and pressure changes at the beginning, halfway, and end of the adsorption bed, while Figure 5.42 shows the outlet flow rate histories for both VCM and N₂.

From Figure 5.40, the adsorption enthalpy of the adsorption of VCM during the Feed and Rinse steps can be seen by the temperature spikes of 40 and 16 K registered during the passing of the 40 %(v/v) VCM feed and the 95 %(v/v) VCM product fronts during those steps. During the Blowdown and Purge steps, the difference in the heating rate observed at the end of the column can be attributed to the application of the LUB section, as the lack of adsorbed VCM at the end of the tubes lowers adsorption media heat requirements.

In Figure 5.41, due to the high fluid velocity and the small size of the carbon granulates, increased pressure is observed at the inlet of the tubes. Additionally, an unexpected spike in pressure is again observed at the end of the tubes, most likely caused by the rapid increase in the temperature and consequent VCM desorption coupled with the slower depressurization rate from the linear depressurization scheme used.

From Figure 5.42, it is observed that during the Feed and Rinse steps, mostly pure N₂ is produced, while most N₂ is produced during the Feed step, the N₂ recovery during the Rinse step is essential to ensure a high VCM purity requirement. During the Blowdown step, most

VCM is recovered along with part of the N_2 that remained at the end of the tubes. Additionally, a Purge step is implemented to increase the adsorbent regeneration, and thus the VCM recovery, by purging the tubes with part of the purified N_2 product stream, resulting in an extended production of VCM together with a steady low flow rate of N_2 . Figures 5.43 to 5.47 show the gas and solid concentration, for VCM and N_2 , and temperature profiles at the end of each of the proposed TPSA cycle steps, at CSS.

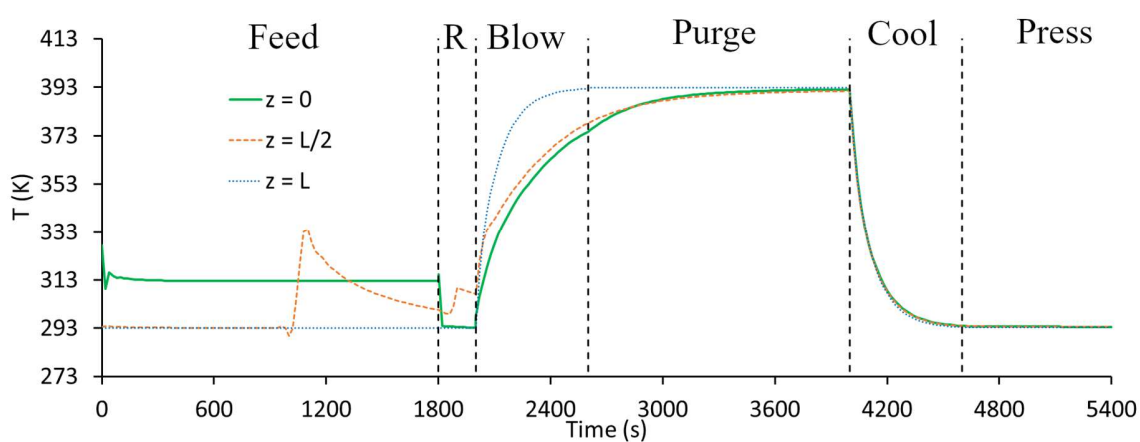


Figure 5.40: Temperature history averaged along the radial direction, during CSS at the start, halfway, and end of the column

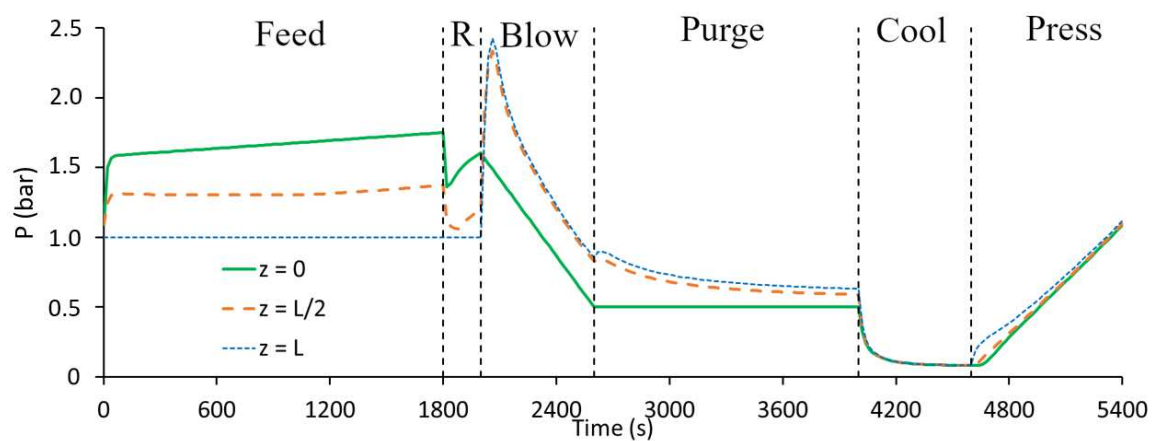


Figure 5.41: Pressure History averaged along the radial direction, during CSS at the start, halfway, and end of the column

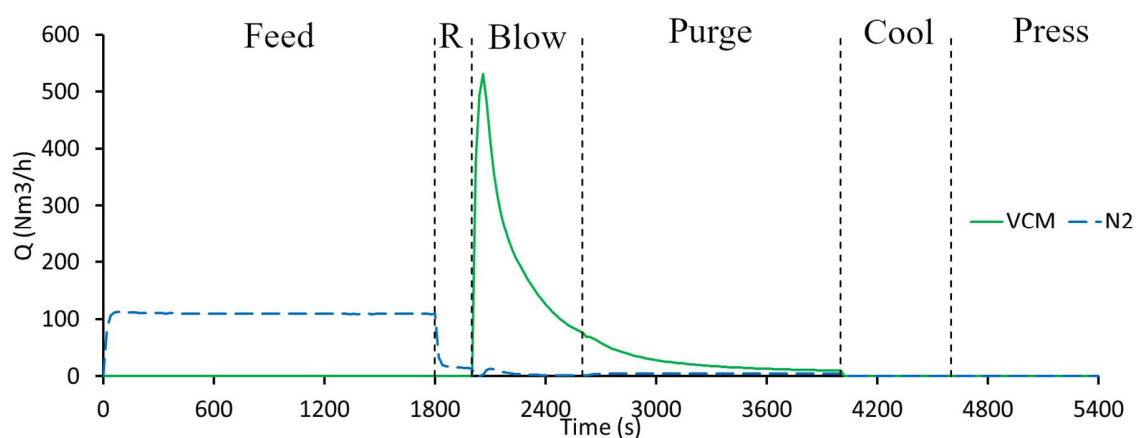


Figure 5.42: Outlet flow rate history averaged along the radial direction, during CSS

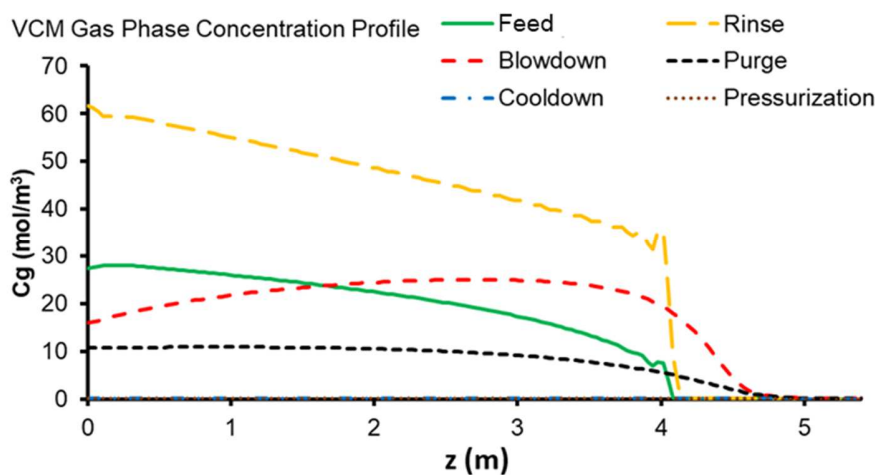


Figure 5.43: VCM gas-phase concentration profile, averaged along the radial direction, at the end of each step

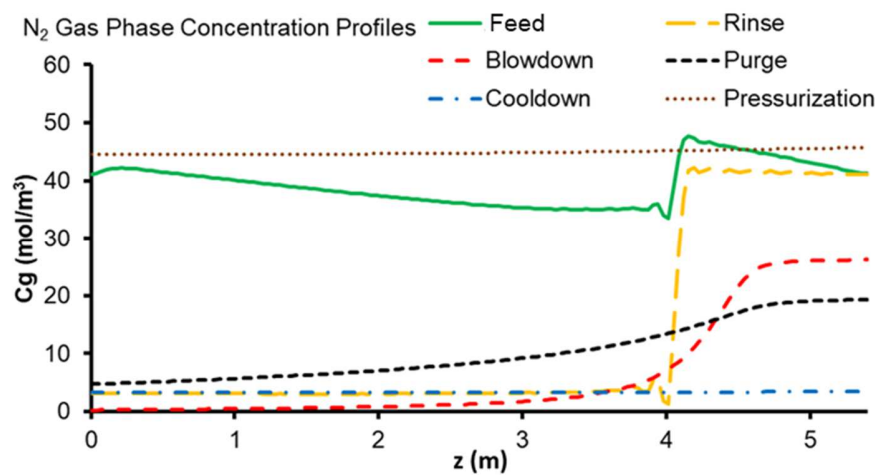


Figure 5.44: N₂ gas-phase concentration profile, averaged along the radial direction, at the end of each step

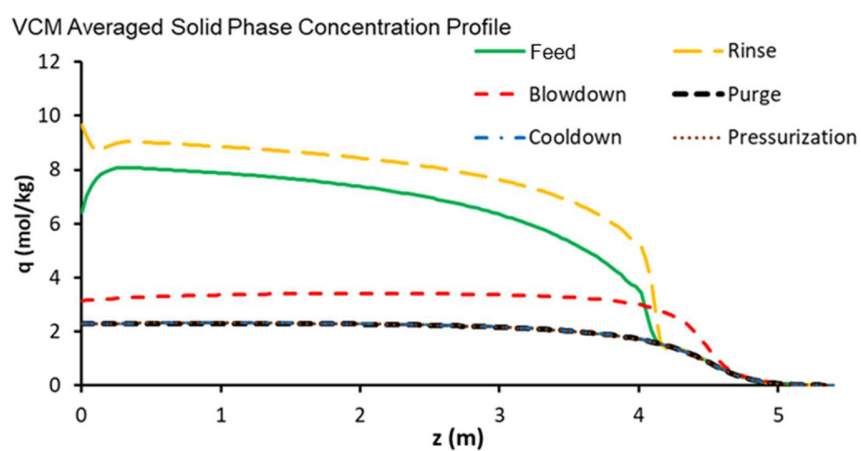


Figure 5.45: VCM Solid-phase concentration profile, averaged along the radial direction, at the end of each step

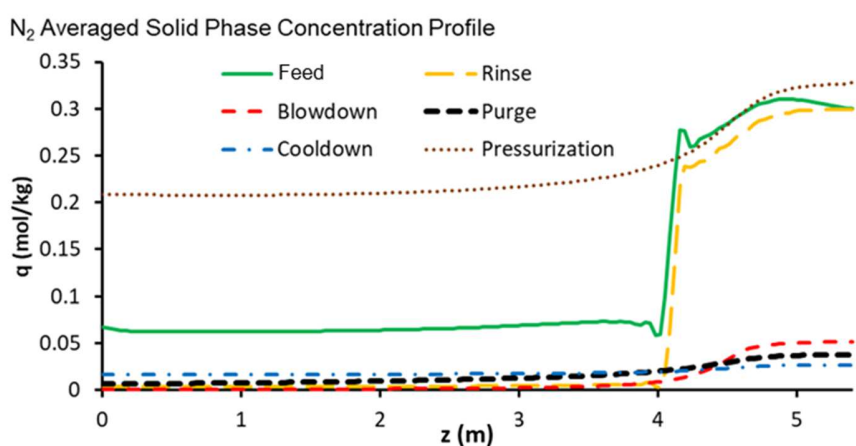


Figure 5.46: N₂ Solid-phase concentration profile, averaged along the radial direction, at the end of each step

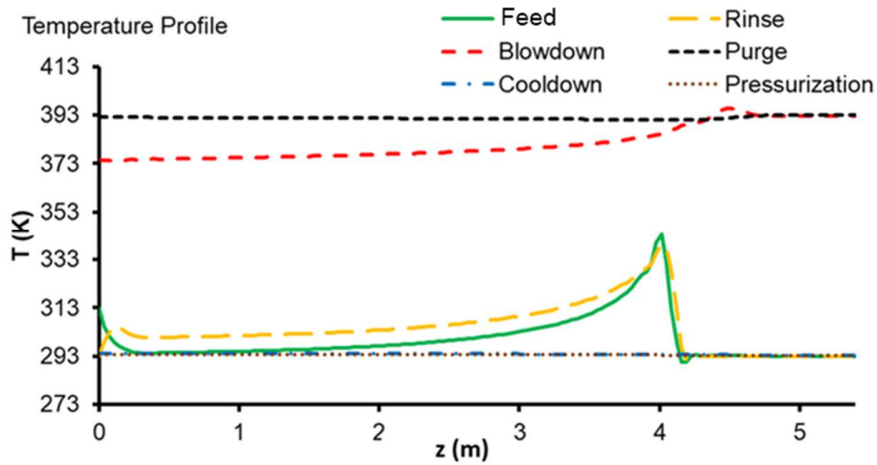


Figure 5.47: Temperature profile, averaged along the radial direction, at the end of each step

At the end of the Feed step, it is observed that the VCM gas-phase concentration front reaches approximately 75 % of the total tube length, which also indicates the length of the bed that is being used to perform the gas mixture separation, while the remaining LUB is used to increase the N_2 product purity. In the Rinse step, part of the product VCM stream is introduced at the start of the tubes and used to clean the remaining adsorbed and gas phase N_2 still present in the adsorption bed, until the newly created 95 % (v/v) VCM concentration front reaches the one developed at the end of the previous Feed step.

From Figures 5.43 and 5.45, it is observed that at the end of the Blowdown step, the VCM gas front still suffers significant dispersion in the axial direction. Two phenomena cause this deformation. Again, the initial rapid heat up observed at the end of the tubes (Figure 5.40), and consequent desorption of VCM, together with the implementation of the slower linear depressurization rate, leads to a local increase in pressure at the VCM front when compared to the downstream LUB zone. If this pressure spike is not evacuated in time, then the gas phase VCM will diffuse towards the opposite direction of the vacuum pumps and risk contaminating the next N_2 production cycle step. At the end of the Blowdown step, further propagation of the VCM front occurs when the axial diffusion of the gas phase VCM overcomes the gas flow imposed by the vacuum pump.

The Purge step is used to further regenerate the adsorption bed, by purging the tubes with part of the purified N_2 stream in countercurrent and extending the heating time by constantly keeping a significant pressure drop profile towards the entrance of the tubes, thus preventing further VCM front dispersion. As such, a balance should be established between both the blowdown and purge step durations, which should be short enough to prevent the propagation of the VCM front and lowering the VCM purity with N_2 purge gas, and long enough to satisfy the required heating time duration. In the present case, to guarantee the N_2 purity threshold, 30 % of the Heating time was used for the Blowdown step, which resulted in the production of 76 % (v/v) of the total VCM product stream, obtaining a VCM purity up to 98 % (v/v). Due to the lower required purity threshold for VCM, a more extensive purge step was used to produce a VCM stream with an average purity of 85 % (v/v), with the outlet VCM gas fraction going down as much as 70 % (v/v). The necessity of the LUB section is evidenced in Figure 5.45 as, due to the highly preferential equilibrium adsorption of VCM over N_2 , the purified N_2 purge gas is unable to regenerate the solid phase VCM present, resulting in the continuous overlap of the VCM solid concentration in this section. After both production steps, the closed Cooldown step lowers the temperature of the tubes, and consequently, the internal pressure profile. The tubes are then pressurized back to the initial conditions of the cycle in the Pressurization step. These steps lead to the adsorption of all remaining gas phase VCM, preventing any contamination of the next N_2 production stream.

5.5.6. Influence of the Radial Behavior

For the design of the present industrial-scale adsorption-based separation system, one of the main challenges encountered concerns the high heat transfer demands created from the VCM high adsorption enthalpy. Coupled with the imposed strict product purity requirements, a more compact and swift design is desirable. Ultimately, to comply with these necessities, a multitubular design was adopted. As stated previously, a multitubular design would solve the heat transfer rate necessity by splitting and packing the adsorbent material into several smaller diameter beds, as opposed to the more common use of one

bed of equivalent diameter, thus increasing the surface area available for heat transfer to the adsorbent volume. However, by reducing the tube radius and operation time, the previously neglected phenomena on the radial direction may gain a bigger influence on the system behavior. As the adsorption phenomenon is greatly influenced by temperature, any thermal, and consequent, mass variations on the radial direction must be thoroughly investigated using a two-dimensional model, with discretization on both axial and radial directions, thus ensuring the precision of the results.

Figure 5.48 shows the development of the gas phase temperature history halfway through the tubes along the radial direction, during the proposed TPSA cycle at CSS. Although the reported averaged temperature history follows a predictable behavior, the radial temperature amplitude shown during each of the main TPSA steps can be significant. During the Feed, Blowdown, and Cooldown steps, maximum temperature variations from the averaged value of 20, 30, and 35 K were registered, respectively.

Equilibrium adsorption-based separations are temperature-sensitive processes. As such, in the presence of temperature variations of the present scale, adsorption equilibrium and gas flow changes in the radial direction are expected. Since the tube system heat transfer occurs between the tube wall and the outermost section of the adsorption media ($r = ID/2$), this section more closely follows the temperature conditions imposed by the shell side heat exchange fluid. Radial thermal transport occurs not only through thermal diffusion but also from convective transport, due to pressure variations caused from the radial temperature profiles, most noticeably in the absence of any imposed convective axial flow, as seen in Figure 5.49.

According to Figure 5.49, during the Feed and Rinse step, the temperature increase caused by the VCM adsorption coupled with the heat removal near the tube wall creates the temperature profile shown in Figure 4.48. The lower temperature in the outermost region of the adsorption media increases the local adsorption equilibrium and creates a pressure drop profile, which leads to the positive displacement from the center of the tube to the outermost region. Since mostly only VCM is adsorbed on the outermost region and since the gas-phase momentum must be conserved, a respective negative displacement of the

non-adsorbed N_2 occurs ahead of the VCM front. At the beginning of the Blowdown step, the heating of the outermost region of the tube leads to the desorption and displacement of VCM from the outermost region to the center of the tubes, as evidenced in Figure 5.49, as well as in Figure 5.50. This leads to an increase in solid-phase VCM concentration at the center of the tubes at the beginning of the Blowdown step. As the Cooldown is a closed step, with no inlet or outlet flow, the VCM solid-phase concentration should slightly increase and then remain mostly constant throughout the step, as seen in the “Averaged” profile in Figure 5.51. However, due to the initial swift decrease in temperature, preferential VCM adsorption occurs on the outermost region of the adsorption bed leading to the displacement and consequent desorption of the VCM from the center of the tubes, resulting in the tilted VCM solid concentration radial profile seen in Figure 5.50. Although, due to the absence of an imposed axial flow, the influence of radial transport is more significant for the moments at the beginning of the Blowdown and Cooling steps. For all cases, it was observed that the mass transport in the radial direction occurs in the same direction as the heat transfer and, as such, positively contributes to expediting the heat transfer performance of the unit. Simplified 2D representations of Figures 5.48 to 5.50 can be found as Figures 5.51 to 5.53, respectively.

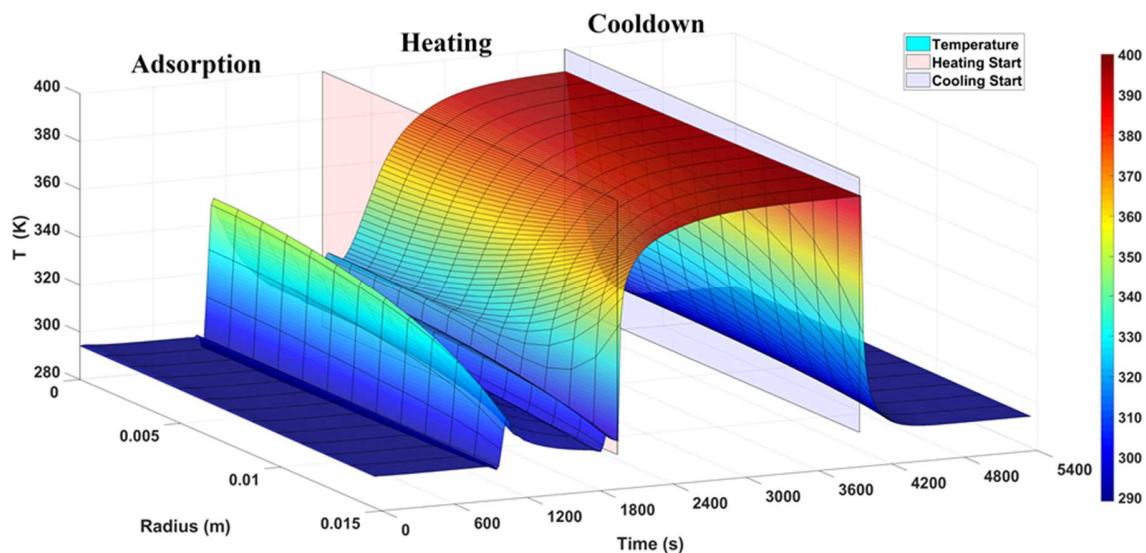


Figure 5.48: Gas Phase temperature history and radial profile halfway through the tube system at CSS

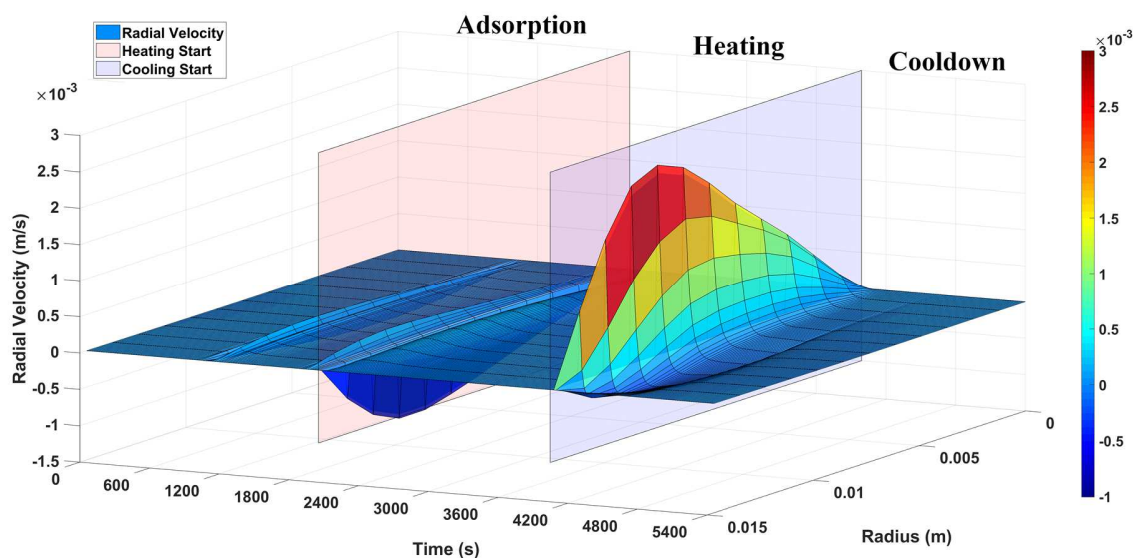


Figure 5.49: Radial Velocity history and radial profile halfway through the tube system at CSS

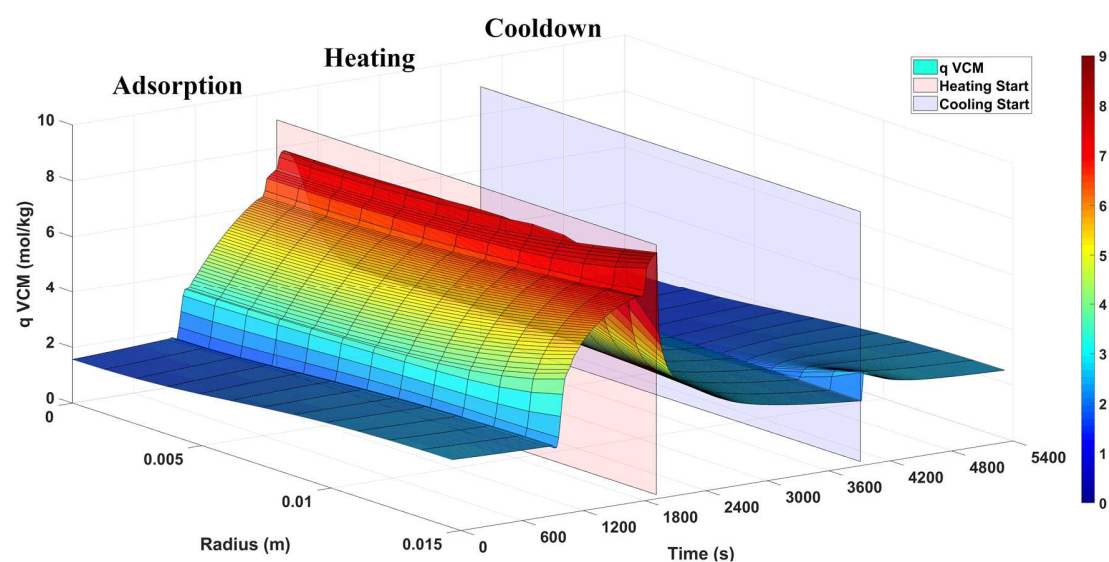


Figure 5.50: VCM solid phase concentration history and radial profile halfway through the tube system at CSS

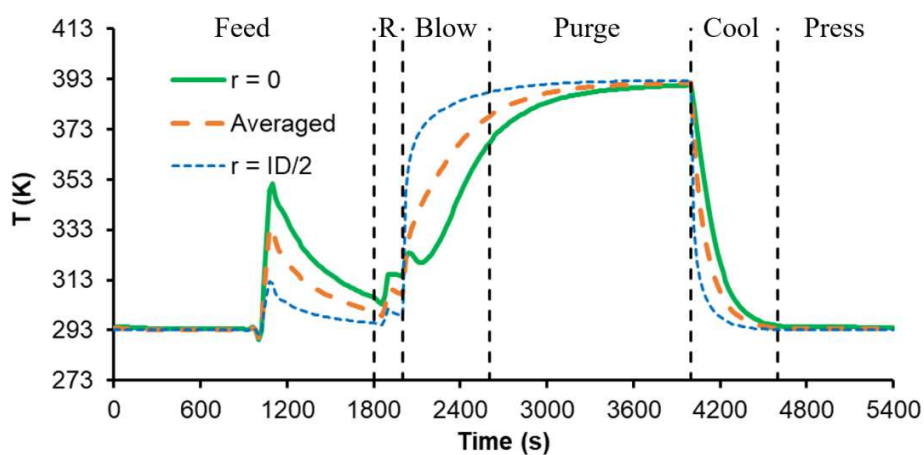


Figure 5.51: Gas Phase Temperature History halfway through the tubes ($z=L/2$) at CSS at the center of the tube ($r=0$), near the wall ($r=ID/2$), and averaged over the radial direction

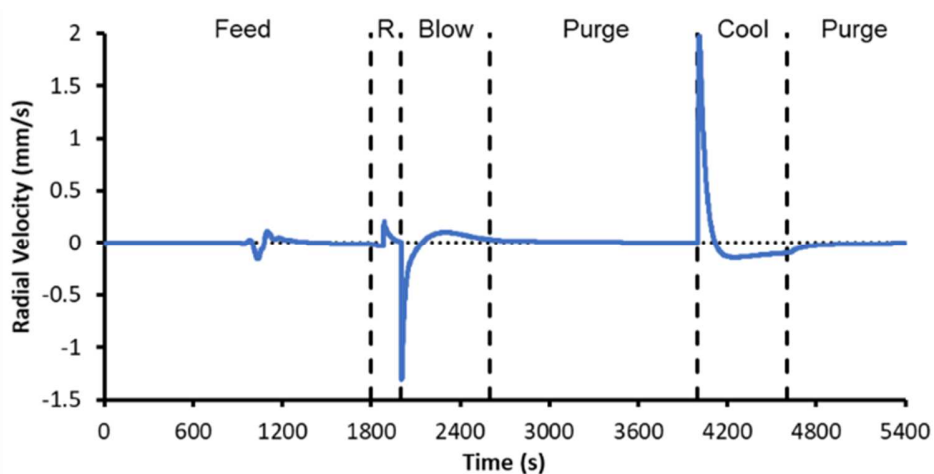


Figure 5.52: Radial Velocity History halfway through the tubes averaged over the radial direction at CSS

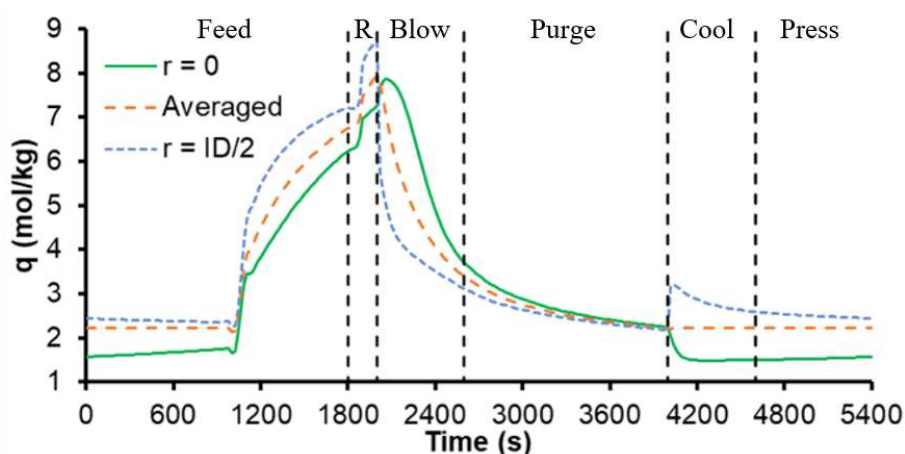


Figure 5.53: Solid Phase Concentration History halfway through the tubes ($z=L/2$) at CSS at the center of the tube ($r=0$), near the wall ($r=ID/2$), and averaged over the radial direction

5.5.7. Equivalent 1D Model

To describe an adsorption separation system with a reported high adsorption enthalpy, and resulting pronounced thermal profiles, requires a mathematical model that can accurately and thoroughly detail the thermal and mass behavior in the system. For this purpose, a 2D model, with both axial and radial discretization, was chosen. Although a 2D model allows for a more thorough analysis of the phenomena in play, it increases computational power and simulation time cost. However, for process designing and optimization, the increased resource costs of 2D simulations are amplified when it is necessary to perform a significant number of cyclic simulations, all under different operating conditions until CSS is achieved. As such, to cut down on the computational and time costs, while continuing to accurately predict the performance of the proposed cyclic adsorption separation system, an equivalent 1D model, which approximates the radial thermal behavior by a lumped contribution of the radial heat dispersion and the wall heat transfer coefficient, was developed. Both models were simulated following the parameters listed in Tables 5.9 and 5.10 and the MT-TPSA cycle setup described in Table 5.11. Figures 5.54, 5.55, and 5.56, respectively, show the comparison between the temperature, pressure, and outlet flow rate histories obtained from both the 2D and equivalent 1D models.

The tube side overall heat transfer coefficient for the equivalent 1D model was calculated from the theoretical sum of the wall and bulk radial diffusion resistances ¹⁴, which provided the best fit for the results obtained from the 2D model. As seen from Figures 5.54 to 5.56, for most of the cycle history, the equivalent 1D model was able to satisfactorily predict the average thermal and mass system's behavior. However, during the initial moments of both the Blowdown and Cooldown steps, the equivalent 1D model fails to predict the system behavior accurately. This discrepancy can be clearly observed in Figure 5.56, where it is seen that during the Blowdown step, although the integral areas of both VCM histories are the same, thus the quantity of produced VCM is also the same, the equivalent 1D model predicts a slower and more spread out outlet flow rate, which can only be correlated to a slower heat transfer. In turn, this can be justified as the derivation used to calculate the lumped heat transfer contribution does not account for heat transfer derived from mass transport. Yet, as shown in Figure 5.52, these are the very same moments that are characterized by a significant radial VCM mass convective flow. Despite the model transient inaccuracies, as the process was designed for an equilibrium adsorption separation and adequate cycle step durations were imposed to guarantee a thorough heating and cooling of the system, the overall performance of the unit can still be predicted, using an equivalent 1D model, to a great degree of accuracy, as seen in Table 5.12.

As such, considering the reliability of the presented results and the successful implementation of the equivalent 1D mathematical model, all the MT-TPSA cycle simulations that somewhat follow the design parameters reported in Table 5.10 will henceforth be using the Equivalent 1D Fixed Bed mathematical model (Chapter 4) to additionally save on computational time and resources.

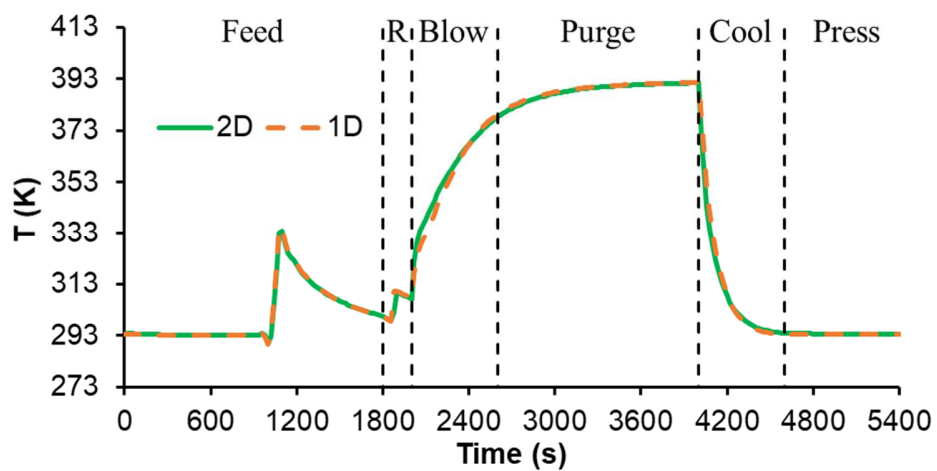


Figure 5.54: Temperature History comparison obtained between the averaged 2D and the equivalent 1D model, halfway through the tube system

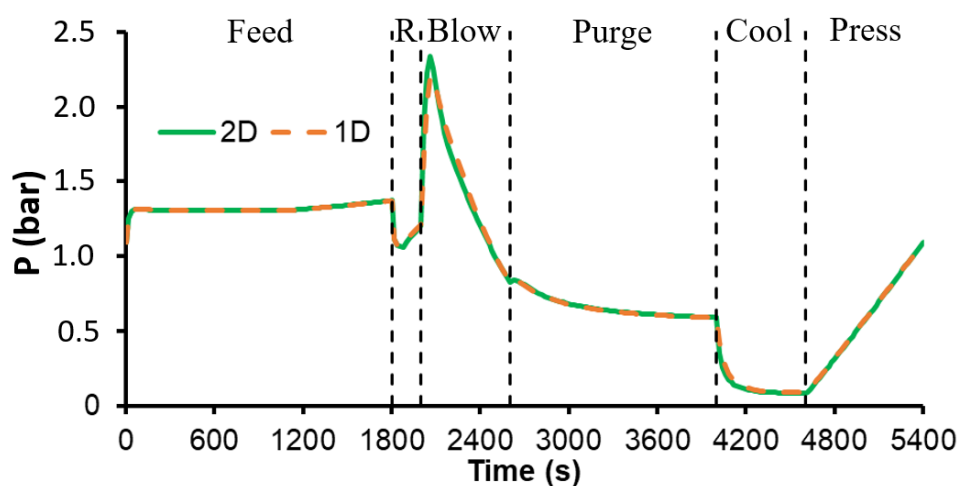


Figure 5.55: Pressure History comparison obtained between the averaged 2D and the equivalent 1D model, halfway through the tube system

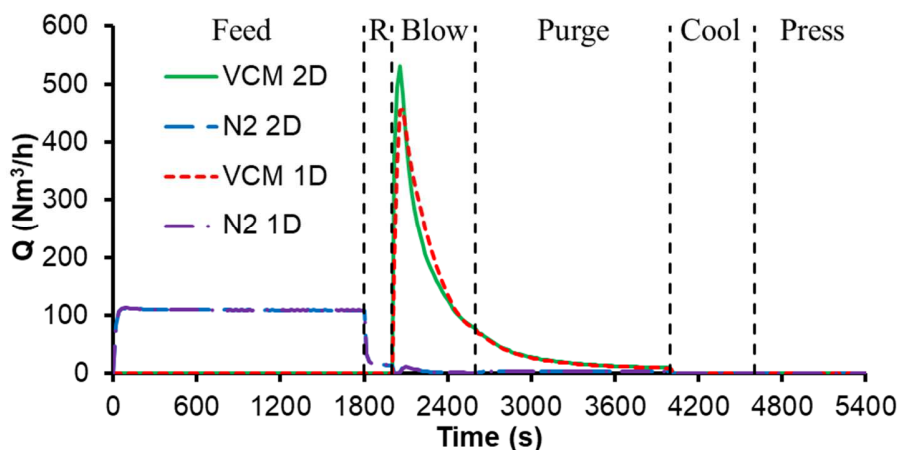


Figure 5.56: Outlet Flow Rate History comparison obtained between the averaged 2D and the equivalent 1D model

5.6. Vinyl Chloride Recovery using Maxsorb Activated Carbon

5.6.1. MT-TPSA Cycle Design

Based on the results of the preliminary work involving the Pittsburgh PCB carbon and the adsorption equilibrium isotherm measurements reported earlier in this chapter, an MT-TPSA system for the separation and recovery of the proposed VCM/N₂ feed mixture on the Maxsorb activated carbon will be developed. For the reasons discussed previously in this chapter, both the MTA design and the Equivalent 1D mathematical model were selected over the standard single fixed bed design and the more detailed 2D fixed bed model. Additionally, although applying a linear depressurization rate led to more even VCM product stream flowrates and was more appropriate to represent the depressurization rates common in industrial settings, it was not without issues. As discussed in Section 5.4.5, the slower linear depressurization scheme has revealed to be incompatible with the rapid desorption of VCM during heating, which leads to a decrease in performance. As such, considering the smaller required adsorbent load reported for the MT-TPSA cycle, an exponential depressurization scheme will be used instead. Contrary to the characterization information reported in Chapter 3, the Maxsorb material used in the development of the industrial scale MT-TPSA cycle comes in the shape of 3 mm pellets as described in the work

of Regufe and al.⁶ Additionally, to account for the capacity loss derived from the pelletization process, an 83% adsorption capacity ratio was assumed for the adsorption of VCM, measured during the adsorption equilibrium isotherm measurements reported earlier in this chapter. To maintain some consistency with the previous work and to validate the performance comparison between the different system, the same unit sizing and regeneration temperature were kept. As such, the proposed MT-TPSA cycle will operate in a temperature range of 303 to 393 K and a pressure range of 1 to 2.5 bar, thus avoiding the use of vacuum pumps. The adsorption temperature was increased to 303 K from the previous 293 K, as 303 K was the lowest temperature that the Rubotherm system could control. The adsorption pressure was also increased to 2.5 bar to maximize the adsorbed VCM during the Feed step, taking into account the adsorption equilibrium isotherms of VCM in the Maxsorb material. By using these operating conditions, the author will also require that the feed mixture must be pressurized up to 2.5 bar and cooled down to 303 K before it is fed into the MT-TPSA system.

Figure 5.57 shows a comparison between the DSL adsorption equilibrium isotherms for VCM (a) and N₂ (b) at 303 and 393 K, which illustrates both the regeneration capacity of the proposed system and as well as the effective VCM adsorption capacity within which the system will operate. By comparing Figures 5.57 (a) and (b), one can calculate that for the feed composition, the Maxsorb material displays a very high VCM/N₂ selectivity of 49 for both the adsorption and regeneration temperatures.

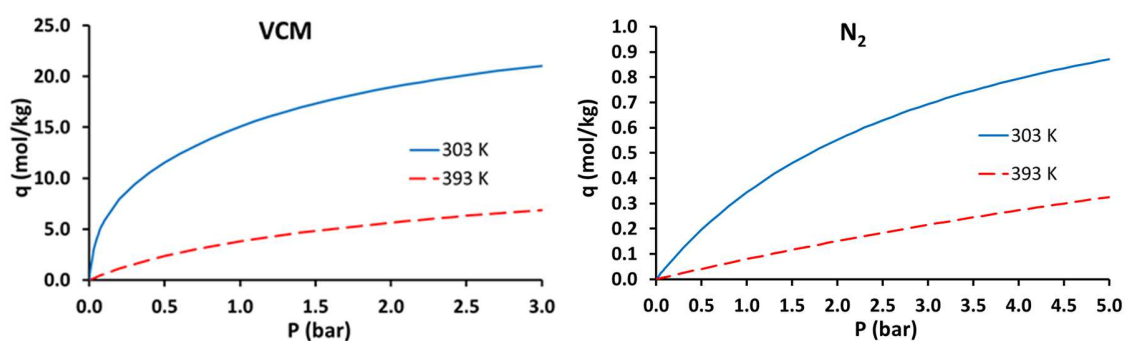


Figure 5.57: DSL isotherm model predictions for VCM (a) and N₂ (b) at 303 and 393 K on the Maxsorb carbon

The simulation of the MT-TPSA system is dependent on the calculation of several transport and sizing parameters. As such, by using the equations and estimations reported in Chapter 4, Tables 5.14 and 5.15 report the transport parameter and physical and sizing parameters used in the design of the MT-TPSA system for the treatment of a 180 Nm³/h feed stream of a 40/60 %(v/v) VCM/N₂ mixture at 303 K and 2.5 bar.

For the proposed MT-TPSA separation unit, the feed stream is split into a tube system with a total of 218 tubes, each with a length of 3 m, which was found to be sufficient to achieve the intended separation. Both the tube sizing and the shell side considerations were kept identical to the previous preliminary work to maintain the validation of the Equivalent 1D model and to facilitate a comparison of the different performances between systems. The reported tube system and the shell side of the unit, will result in a shell diameter of 0.78 m.

Table 5.14: Transport Parameter values used in the MT-TPSA Simulation calculated at feed conditions

Axial Mass Dispersion	9.95 X 10 ⁻⁴	<i>m²/s</i>
Axial Heat Dispersion	8.45 X 10 ⁻¹	<i>W/(m.K)</i>
Mixture Viscosity	1.30 X 10 ⁻⁵	<i>Pa.s</i>
Shell Side Heat Transfer Coefficient	1459	<i>W/(m².K)</i>
Particle Heat Transfer Coefficient	106	<i>W/(m².K)</i>
Tube Side Overall Heat Transfer Coefficient	46.95	<i>W/(m².K)</i>

Table 5.15: Physical and Sizing properties parameters used for the MT-TPSA and Fixed Bed simulations

Tube Length	3.00	<i>m</i>
Tube Inner Diameter	29.35 x 10 ⁻³	<i>m</i>
Tube Outer Diameter	31.75 x 10 ⁻³	<i>m</i>
Tube Pitch	39.69 x 10 ⁻³	<i>m</i>

Tube Clearance	7.94×10^{-3}	<i>m</i>
Bed Porosity	0.37	-
Tube Thickness	1.20×10^{-3}	<i>m</i>
Number of Tubes	218	-
Total Adsorbent Mass	188	<i>kg</i>
Transfer Surface Area	64	<i>m</i> ²
Tube Bundle Diameter	0.73	<i>m</i>
Shell Diameter	0.78	<i>m</i>
Baffle Spacing	0.20	<i>m</i>
Baffle Cut	25	%
Shell Inlet velocity	0.5	<i>m/s</i>

5.6.2. MT-TPSA Simulation Results

Similar to the MT-TPSA system reported in Figure 5.38, the Maxsorb MT-TPSA simulation cycle comprises a Feed, Rinse, Blowdown, Purge, Cooldown, and Counter-Current Pressurizations steps. Following the MT-TPSA cycle step conditions shown in Table 5.16, the proposed MT-TPSA cycle can be expanded to a 2 MTA unit to guarantee a continuous feed consumption, as illustrated in Figure 5.58. As shown in Table 5.17, an MT-TPSA cycle following the specified cycle step conditions is capable of producing a VCM stream with 95.11 %(v/v) purity and an N₂ stream with a VCM contamination lower than the established 8 ppm(w/w) emission limit at 4.78 ppm(w/w). This cycle can reach a VCM productivity of 8.41 mol/(kg_{ads}.h) with a total thermal energy consumption of 3.05 MJ per kilogram of produced VCM. Of the total energy requirements, 81.6 % are used for the operation of the heat exchanger, while 14.1 and 4.3 % are used to operate the gas and liquid pumps. By analyzing the detailed thermal energy consumption, it is concluded that only 27.7 % of the thermal energy is effectively used to heat up and regenerate the adsorbed VCM, while the remaining thermal energy is being used to heat and cool the adsorption material.

Additionally, the productivity by weight and recovery capacity of the Maxsorb MT-TPSA system are reported in Table 5.18. When compared to the results reported for the

preliminary work on Tables 5.12 and 5.13, it can be observed that for the same purity requirements, not only does the Maxsorb MT-TPSA system display higher productivity but also at significantly lower energy consumption, which is a direct consequence of the higher VCM adsorption capacity and the lower adsorption enthalpy of VCM in this material.

Table 5.16: Proposed Maxsorb MT-TPSA Simulation Cycle step conditions

Steps	Step time (s)	Pressure (bar)	External Temperature (K)	Flow Rate (Nm ³ /h)
Feed	1600	2.5	303	180
Rinse	240	2.5	303	180
Blowdown	320	2.5 → 1	303 → 393	-
Purge	760	1	393	9.13
Cooldown	220	1 (→ 0.19)	393 → 303	-
Pressurization	60	0.19 → 2.5	303	150

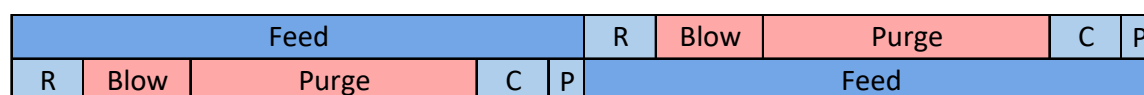


Figure 5.58: Extension of the proposed Maxsorb MT-TPSA schedule to a 2-MTA unit system

Table 5.17: Detailed TPSA Cycle Performance Results for the Maxsorb MT-TPSA system

VCM Purity	95.11	% (<i>v/v</i>)
VCM in N ₂ Stream	4.78	<i>ppm</i> (<i>w/w</i>)
VCM Recovery	99.99+	% (<i>v/v</i>)
N ₂ Recovery	96.57	% (<i>v/v</i>)
VCM Productivity	8.41	<i>mol/(kg_{ads} · h)</i>
N ₂ Productivity	12.18	<i>mol/(kg_{ads} · h)</i>

Total Energy Consumption	3.05	MJ/kg_{VCM}
Adsorption Cooling Duty	0.69	MJ/kg_{VCM}
Heating Duty	1.26	MJ/kg_{VCM}
Cooling Duty	0.54	MJ/kg_{VCM}
Gas Pump Operation	0.43	MJ/kg_{VCM}
Liquid Pump Operation	0.13	MJ/kg_{VCM}

Table 5.18: VCM Productivity and Recovery Capacity for the Maxsorb MT-TPSA

VCM Productivity	0.526	$kg_{VCM}/(kg_{ads} \cdot h)$
Bed VCM Recovery Capacity	224	$kg_{VCM}/(m_{bed}^3 \cdot h)$
Unit VCM Recovery Capacity	69	$kg_{VCM}/(m_{unit}^3 \cdot h)$

To analyze the behavior of the system, the Equivalent 1D MT-TPSA model was simulated following the proposed cycle step conditions until CSS was achieved. For the Maxsorb MT-TPSA cycle, the temperature and pressure histories registered at the entrance, halfway, and end of the tube system are presented in Figures 5.59 and 5.60. From Figure 5.59, even with the lower adsorption enthalpy of VCM on the Maxsorb material, due to the high VCM adsorption, a temperature spike of 35 K was registered during both the Feed and Rinse steps which indicated the timing of the passage of the VCM front during those steps. Since at feed conditions, the Maxsorb material is still far from saturation the temperature spike during the Rinse step is of similar magnitude as the one during the Feed step. Again, due to the lack of gas and solid phase VCM at the exit of the tubes, the temperature variation at this location occurs much more rapidly. From Figure 5.60, it can be observed that due to the use of more reasonably sized adsorbent materials and lower inlet velocities, the system suffers little to no significant pressure drops during the Feed step. Additionally, due to the exponential depressurization scheme, the pressure during the Blowdown step lowers significantly faster, and no pressure increase is ever registered for the duration of the Blowdown step. From Figure 5.61, one can see that during the Feed and Rinse steps, pure

N₂ is continually produced with only a drop on the N₂ outlet volumetric flow rate occurring during the Rinse step due to the lower N₂ feed fraction. During the Blowdown and Purge steps, a continuous but decreasing outlet flow rate of mainly VCM is produced, with a higher fraction of N₂ arising during the Purge step.

Figures 5.62 to 5.65 show the gas and solid phase concentration profiles for VCM and N₂ along the axial direction of the tubes. At the end of the Feed and Rinse steps, Figures 5.62 and 5.64 show that contrary to the results shown during the preliminary work, most of the tube length is partly saturated with VCM. Although partial deformation of the VCM front occurs at the end of the Blowdown step, this is not a critical factor, as can be seen especially from Figure 5.64, at the end of the Purge step, not only does the VCM front slightly recede but the N₂ purge gas has shown to be capable of regenerating the adsorbed VCM, to a sufficient degree. During the Blowdown and Purge steps, despite the temperature over the entirety of the tube system not reaching the target regeneration conditions, the VCM regeneration is sufficient to ensure that the purity requirements are guaranteed. During the Cooldown step, the temperature of the tube system is lowered, and most of the gas phase VCM and N₂ are adsorbed, causing the pressure drop below 1 bar, registered in Figure 5.60. During Pressurization, a counter-current stream of purified N₂ is used to pressurize the column, which leads to the adsorption of any remaining gas-phase VCM and some of the N₂, evidenced by the temperature increase seen in Figure 5.59.

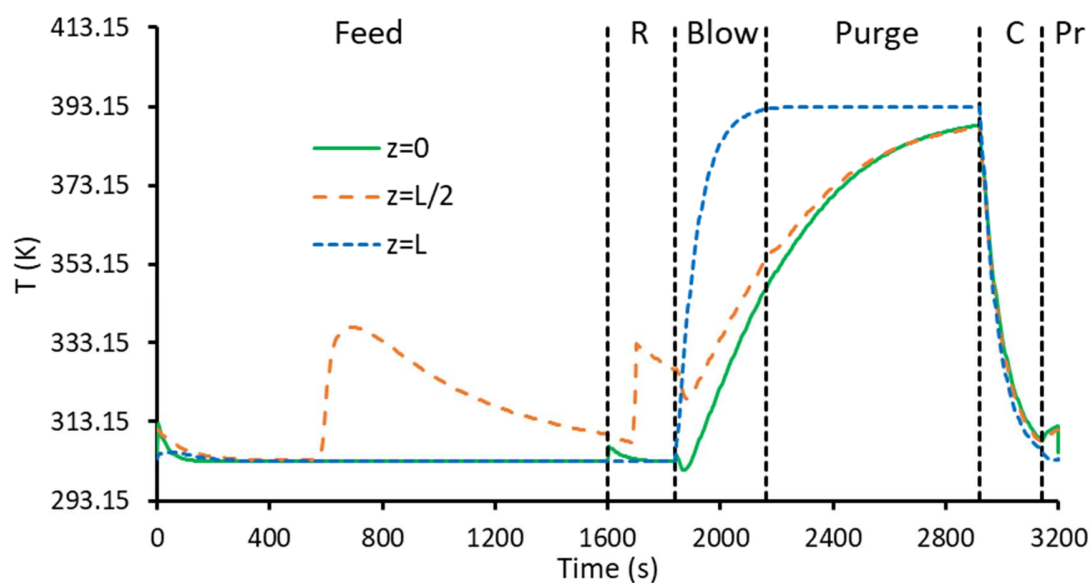


Figure 5.59: Temperature History during CSS at the start, halfway, and end of the column of Maxsorb carbon

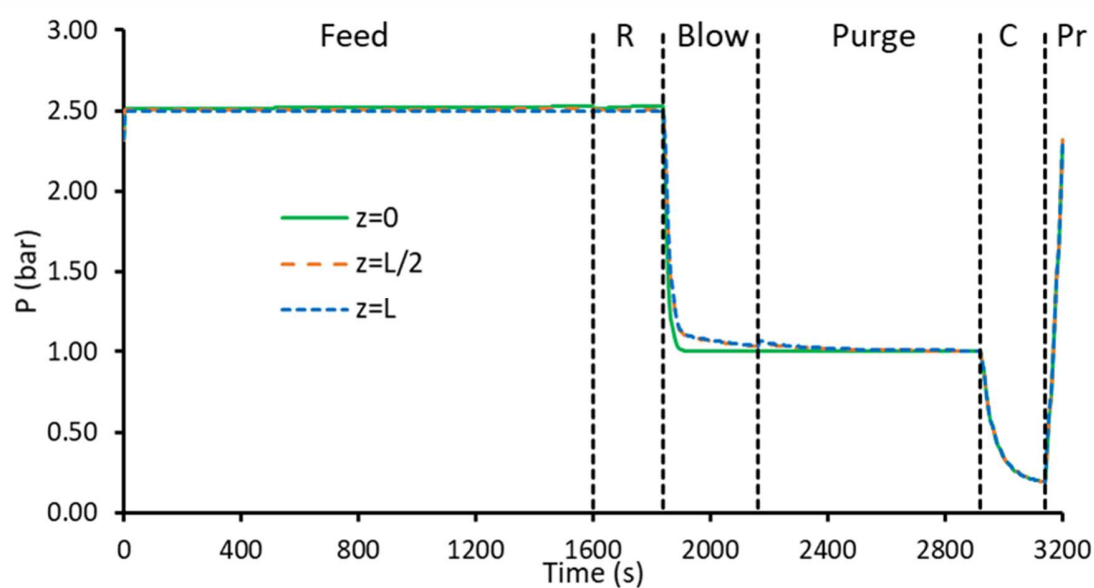


Figure 5.60: Pressure History during CSS at the start, halfway, and end of the column of Maxsorb carbon

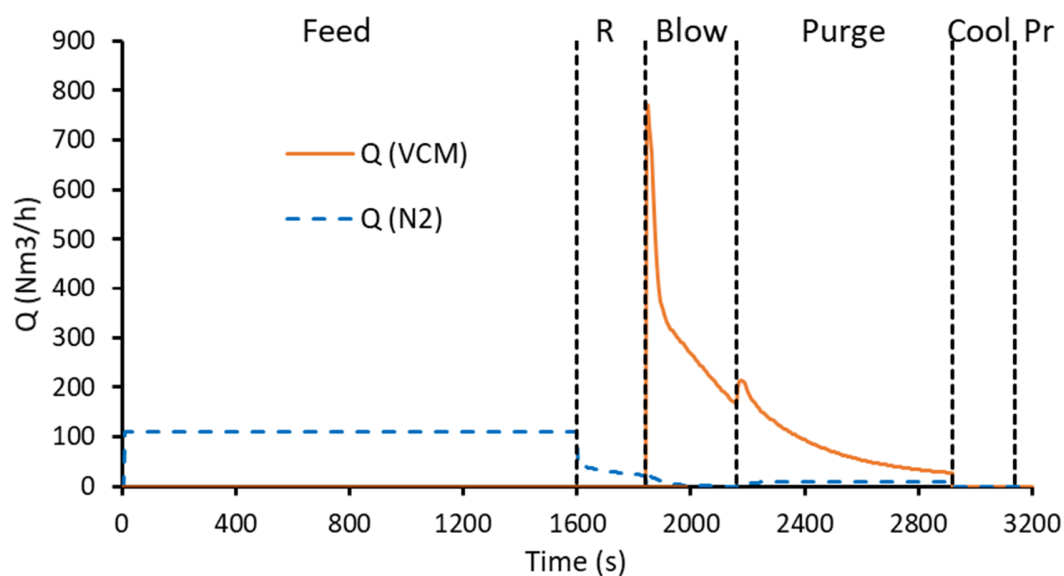


Figure 5.61: Outlet Flowrate History on the Maxsorb carbon during CSS

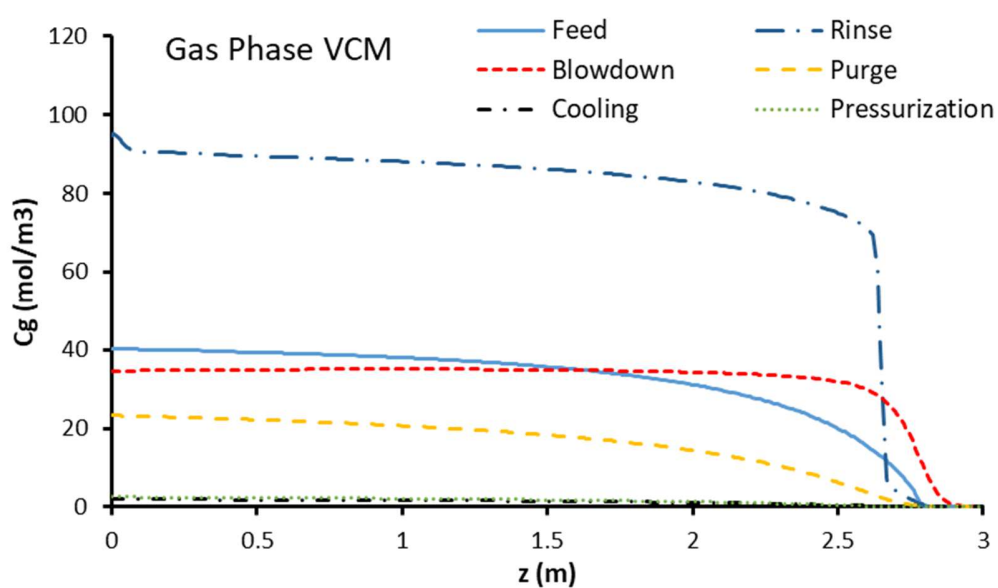


Figure 5.62: VCM Gas-Phase Concentration Profile on the Maxsorb carbon, during CSS, at the end of each step

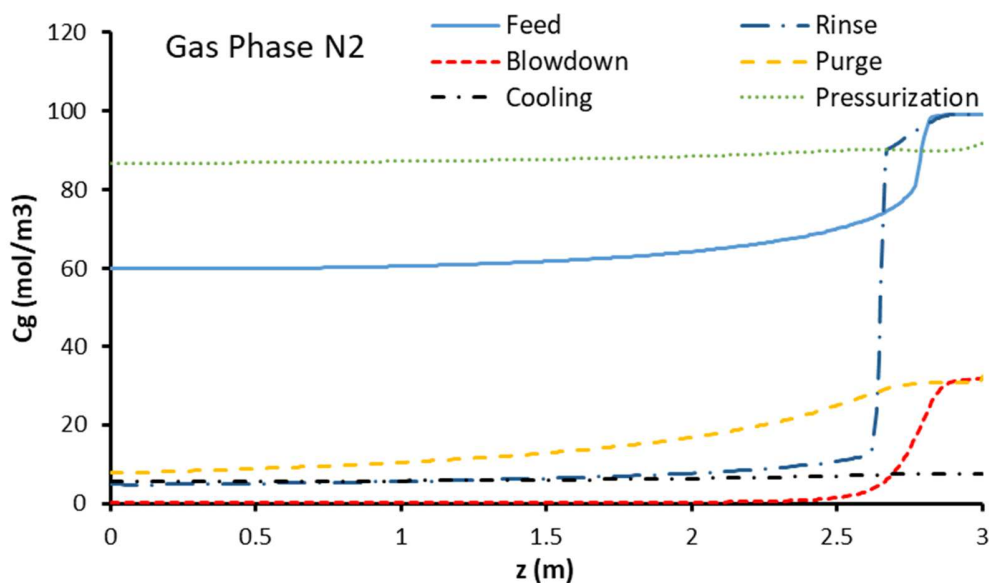


Figure 5.63: N₂ Gas-Phase Concentration Profile on the Maxsorb carbon, during CSS, at the end of each step

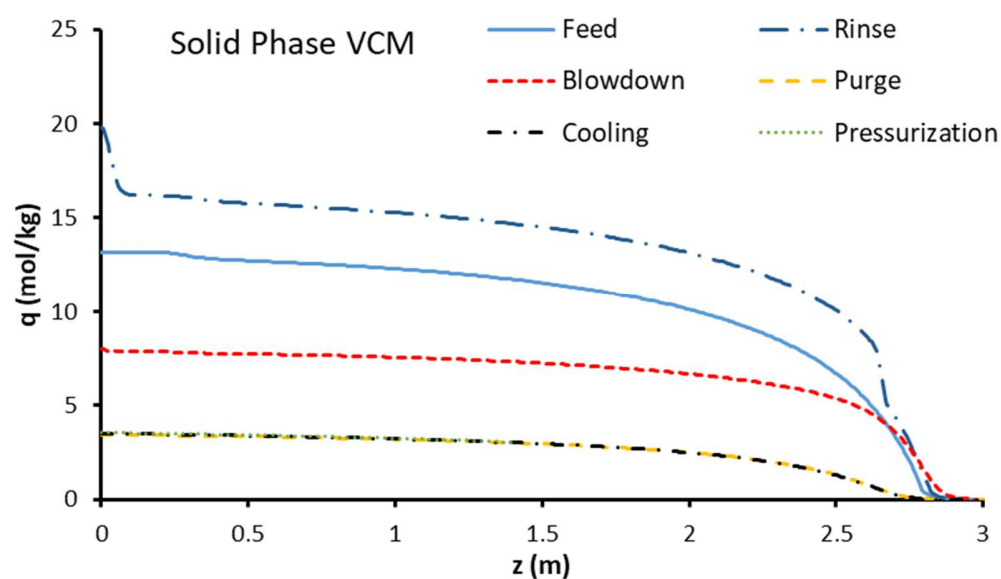


Figure 5.64: VCM Solid-Phase Concentration Profile on the Maxsorb carbon, during CSS, at the end of each step

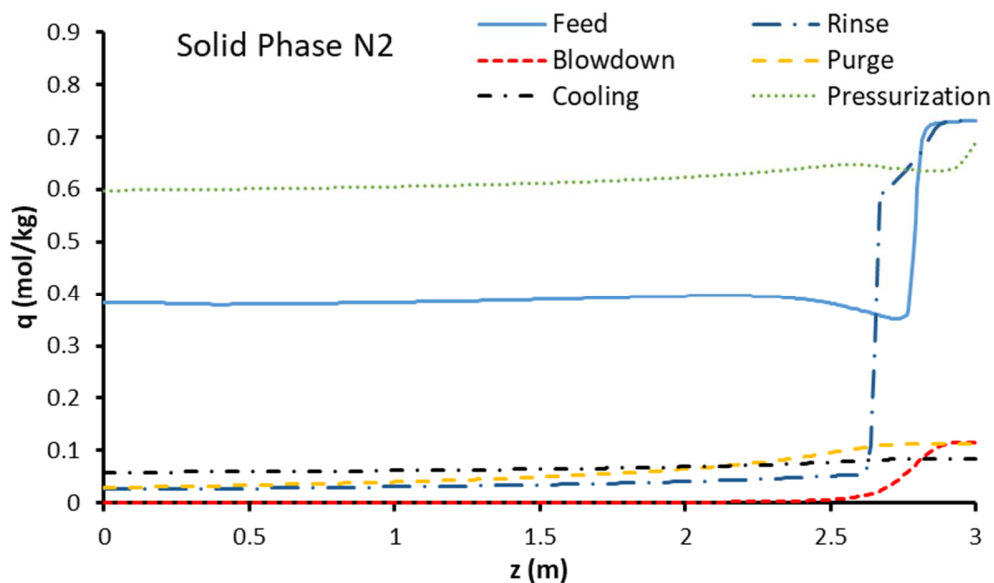


Figure 5.65: N_2 Solid-Phase Concentration Profile on the Maxsorb carbon, during CSS, at the end of each step

5.7. Vinyl Chloride Recovery using Carbotech Activated Carbon

5.7.1. MT-TPSA Cycle Design

Using the Carbotech DGK activated carbon, a VCM separation and recovery unit is henceforth proposed following a MT-TPSA cycle design for the treatment of the VCM/ N_2 feed mixture described at the beginning of this Chapter. Similar to the design proposed for the Maxsorb carbon, the proposed MT-TPSA cycle will be simulated using the Equivalent 1D fixed bed mathematical model and following the boundary and initial conditions stated in Chapter 4. Likewise, an exponential pressurization scheme will be used for the Blowdown step, while the tube sizing and shell design will be kept identical to the previous designs.

The proposed MT-TPSA system will operate in a pressure and temperature range of 0.5 to 2 bar and 303 to 393 K. Due to the faster VCM saturation of the Carbotech DGK carbon, a lower pressure adsorption pressure is required to maximize the capacity of the adsorbent. However, the higher VCM adsorption heat and sharper VCM isotherm shape mean that to achieve an adequate separation, a vacuum pressure of 0.5 bar must be used. The temperature range was kept consistent over all MT-TPSA designs. The choice of these

operating conditions was supported by the VCM, and N₂ pure component isotherm predictions shown in Figure 5.66, where it can be observed that even at a high temperature of 393 K the VCM adsorption isotherm for VCM remains highly non-linear. Unfortunately, by comparing the isotherm predictions of VCM and N₂ at the two operating temperatures, one will find that the VCM selectivity for the feed mixture will increase from 23.2 at the adsorption temperature to 53.6 at the regeneration temperature. In addition to the lower selectivity at feed conditions when compared to the other material, the higher selectivity at the regeneration temperature will lower the performance of the Purge step, which again incentivizes the use of more stringent regeneration conditions.

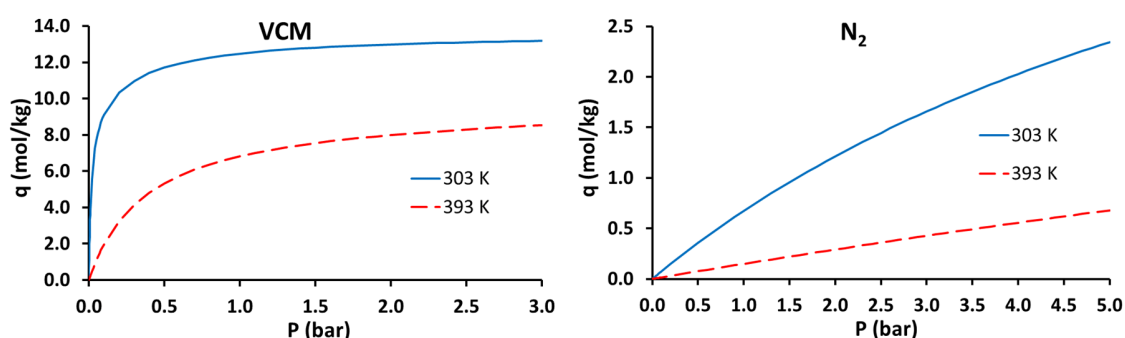


Figure 5.66: DSL isotherm model predictions for VCM (a) and N₂ (b) at 303 and 393 K on the Carbotech DGK carbon

Based on the estimations discussed in Chapter 4, the transport parameters required for the simulation of the proposed MT-TPSA cycle are calculated for feed conditions. As such, for the treatment of a 180 Nm³/h feed stream with a 40/60 % (v/v) VCM/N₂ mixture at 303 K and 2 bar, the resulting transport parameters and physical and sizing properties of the required MT-TPSA cycle system are shown in Tables 5.19 and 5.20. For the proposed feed conditions, the feed stream must be pressurized to 2 bar and cooled down to 303 K before being split into the 256 tube system, resulting in an average inlet velocity of 0.16 m/s. The final MTA unit should have a tube length of 3 meters and a shell diameter of 0.84 m.

Table 5.19: Transport Parameter values used in the Carbotech DGK MT-TPSA Simulation calculated at feed conditions

Axial Mass Dispersion	1.15×10^{-4}	m^2/s
Axial Heat Dispersion	4.37×10^{-1}	$W/(m.K)$
Mixture Viscosity	1.30×10^{-5}	$Pa.s$
Shell Side Heat Transfer Coefficient	1564	$W/(m^2.K)$
Particle Heat Transfer Coefficient	90	$W/(m^2.K)$
Tube Side Overall Heat Transfer Coefficient	48.56	$W/(m^2.K)$

Table 5.20: Physical and Sizing properties parameters used for the Carbotech DGK MT-TPSA simulations

Tube Length	3.00	m
Tube Inner Diameter	29.35×10^{-3}	m
Tube Outer Diameter	31.75×10^{-3}	m
Tube Pitch	39.69×10^{-3}	m
Tube Clearance	7.94×10^{-3}	m
Bed Porosity	0.37	-
Tube Thickness	1.20×10^{-3}	m
Number of Tubes	256	-
Total Adsorbent Mass	362	kg
Transfer Surface Area	77	m^2
Tube Bundle Diameter	0.79	m
Shell Diameter	0.84	m
Baffle Spacing	0.2	m
Baffle Cut	25	%
Shell Inlet velocity	0.5	m/s

5.7.2. MT-TPSA Simulation Results

Following the MT-TPSA cycle step schedule and operating conditions shown in Table 5.21, a Carbotech DGK MT-TPSA cycle system composed of a Feed, Rinse, Blowdown, Purge, Cooledown, and Counter-Current Pressurization steps can be extended to a 2 MTA unit system to guarantee a continuous feed consumption, as shown in Figure 5.67. An MT-TPSA cycle following the proposed operating conditions together with the sizing parameters stated in Table 5.20, will be capable of successfully producing a VCM stream with 95.45 %(v/v) purity and an N₂ stream with a VCM contamination of 4.40 ppm(w/w), which are within the established purity levels. A VCM productivity of 4.38 mol/(kg_{ads}.h) was achieved for a total thermal power consumption 3.21 MJ/kg_{VCM}. Of the reported energy requirements, 80.0 % are used for the operation of the heat exchanger, while 15.6 and 4.4 % are used to operate the gas and liquid pumps. Of the thermal energy requirement, only 27.6 % of the thermal energy is effectively being used to heat up and regenerate the adsorbed VCM. As the focus of the MT-TPSA cycle remains on the productivity of the system, Table 5.23 shows the expected VCM productivity by weight and recovery capacity of the proposed system. When compared to the previous Maxsorb MT-TPSA cycle, the proposed Carbotech cycle has a higher energy consumption, which can be attributed to both the lower VCM productivity and the additional required use of a vacuum pump to adequately regenerate the adsorption bed, which incurs in additional electrical costs. The lower VCM productivity can be attributed to the required higher adsorbent load and partially to the lower adsorption capacity of the Carbotech DGK carbon. Due to the high dependency on the temperature control of both the Maxsorb and Carbotech MT-TPSA cycles and similar specific heats, the efficiency of the thermal regeneration is almost the same.

Table 5.21: Proposed Carbotech DGK MT-TPSA Simulation Cycle step conditions

Steps	Step time (s)	Pressure (bar)	External Temperature (K)	Flow Rate (Nm ³ /h)
Feed	2460	2.0	303	180
Rinse	140	2.0	303	180
Blowdown	220	2.0 → 0.5	303 → 393	-
Purge	1420	0.5	393	5.52
Cooldown	520	0.5 (→ 0.06)	393 → 303	-
Pressurization	160	0.06 → 2.0	303	183

Feed				R	B	Purge		Cool	P
R	B	Purge		Cool	P	Feed			

Figure 5.67: Extension of the proposed Carbotech DGK MT-TPSA schedule to a 2-MTA unit system

Table 5.22: Detailed TPSA Cycle Performance Results for the Carbotech DGK MT-TPSA system

VCM Purity	95.45	% (<i>v/v</i>)
VCM in N ₂ Stream	4.40	<i>ppm</i> (<i>w/w</i>)
VCM Recovery	99.99+	% (<i>v/v</i>)
N ₂ Recovery	96.82	% (<i>v/v</i>)
VCM Productivity	4.38	<i>mol/(kg_{ads} · h)</i>
N ₂ Productivity	6.37	<i>mol/(kg_{ads} · h)</i>
Total Energy Consumption	3.21	<i>MJ/kg_{VCM}</i>
Adsorption Cooling Duty	0.71	<i>MJ/kg_{VCM}</i>
Heating Duty	1.30	<i>MJ/kg_{VCM}</i>
Cooling Duty	0.56	<i>MJ/kg_{VCM}</i>

Gas Pump Operation	0.50	MJ/kg_{VCM}
Liquid Pump Operation	0.14	MJ/kg_{VCM}

Table 5.23: VCM Productivity and Recovery Capacity for the Maxsorb MT-TPSA

VCM Productivity	0.274	$kg_{VCM}/(kg_{ads} \cdot h)$
Bed VCM Recovery Capacity	190.52	$kg_{VCM}/(m^3_{bed} \cdot h)$
Unit VCM Recovery Capacity	60.19	$kg_{VCM}/(m^3_{unit} \cdot h)$

Following the MT-TPSA cycle specifications mentioned previously, the Equivalent 1D MT-TPSA mathematical model was simulated until CSS was achieved. For the Carbotech DGK MT-TPSA cycle, the temperature and pressure histories registered at the entrance, halfway, and end of the tube system are presented in Figures 5.68 and 5.69. As a consequence of the sharp VCM isotherm, a different temperature history is shown in Figure 5.68 during the Feed and Rinse steps. Caused by the reported high adsorption heat, the adsorption of VCM during the Feed step causes a significant temperature spike of 50 K to pass through the adsorption bed. However, since after the Feed step, the Carbotech carbon is almost completely saturated, the Rinse step occurs rather quickly, as the 95 % (v/v) VCM stream rinse is mostly used to push any of the remaining gas-phase N₂, while very little is adsorbed, as confirmed by the much smaller temperature spike of 8 K. During the remaining steps, the temperature and pressure histories behave identically to the case reported for the Maxsorb MT-TPSA cycle. The outlet volumetric flow rates, represented in Figure 5.70, also behave similarly to the Maxsorb system. During the Feed and Rinse steps, mostly pure N₂ is produced, while the purified VCM is produced during the Blowdown and Purge steps. The only exception comes as the major source of N₂ contamination in the VCM stream. As discussed previously, due to the higher VCM selectivity together with the high sharpness of the VCM isotherm at the regeneration temperature, means that the Purge step will not be capable of regenerating the adsorption bed by itself, a statement which is corroborated by the solid phase VCM concentration profiles displayed in Figure 5.73. As such, a larger

portion of the adsorption bed is left unused (LUB) to ensure the N_2 purity requirement, while the purge step N_2 feed is kept at a minimum value to prevent any further dissipation of the VCM front. Which, as seen from Figure 5.70, results in a higher N_2 outlet composition during the Blowdown rather than the Purge step.

Figures 5.71 to 5.74 show the gas- and solid-phase concentration profiles for VCM and N_2 of the tubes packed with Carbotech DGK carbon. As seen in Figure 5.71, to guarantee the N_2 purity requirement, the final 13 % of the adsorption beds are left unused. Simultaneously, the Rinse step has also been accurately modeled as the VCM front at the end of the Rinse step coincides length-wise with the Feed concentration profiles, preventing any contamination of the future cycles. Due to the use of an exponential depressurization scheme and the short Blowdown step time duration, very little dispersion on the VCM front is observed, while a longer Purge step is used to maximize the Heating stage. As can be confirmed by Figure 5.73, the VCM solid phase concentration profile at the end of the purge step shows that the N_2 purge had little effect in the adsorbed VCM quantity, as the reported values in the profile are equal to the VCM equilibrium at 393 K. After both production stages, the tube system is cooled and pressurized back to the feed conditions during the Cooldown and Pressurization steps. At the end of the pressurization step, the overall

temperature increase is still caused by the adsorption of any remaining trace quantities of gas-phase VCM.

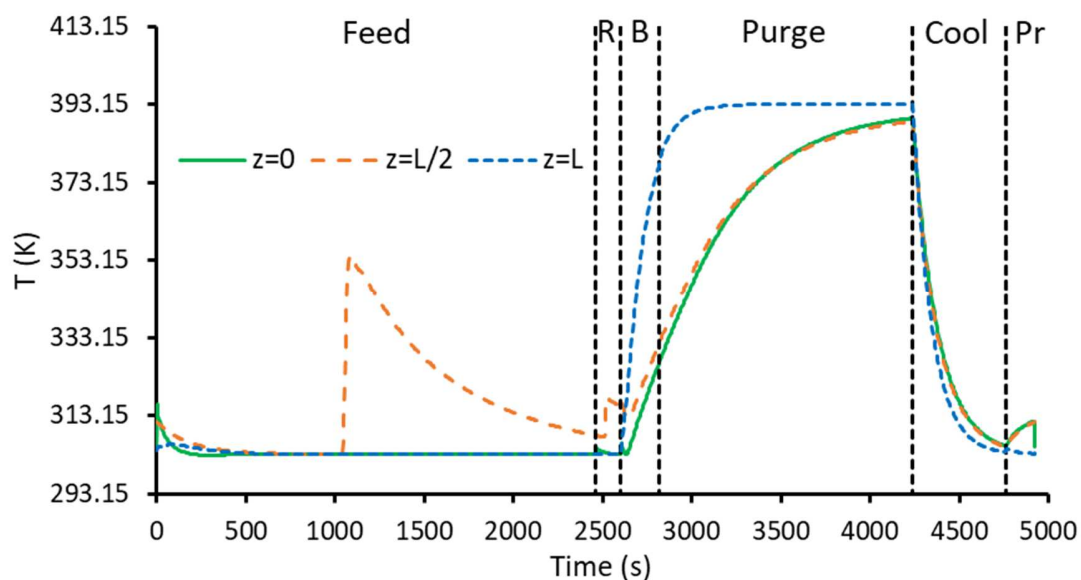


Figure 5.68: Temperature History during CSS at the start, halfway, and end of the column of Carbotech DGK carbon

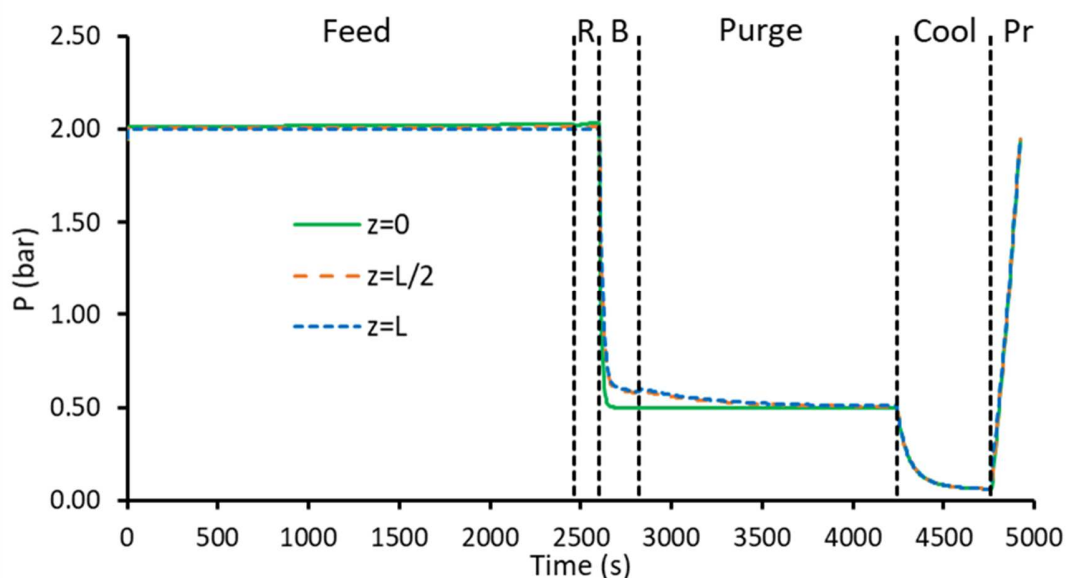


Figure 5.69: Pressure History during CSS at the start, halfway, and end of the column of Carbotech DGK carbon

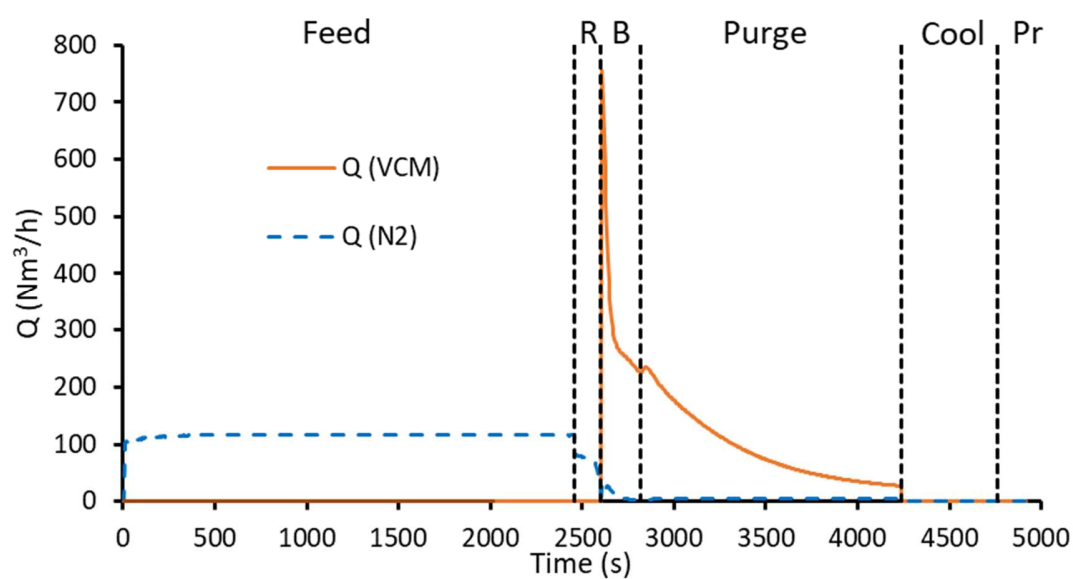


Figure 5.70: Outlet Flowrate History on the Carbotech DGK carbon during CSS

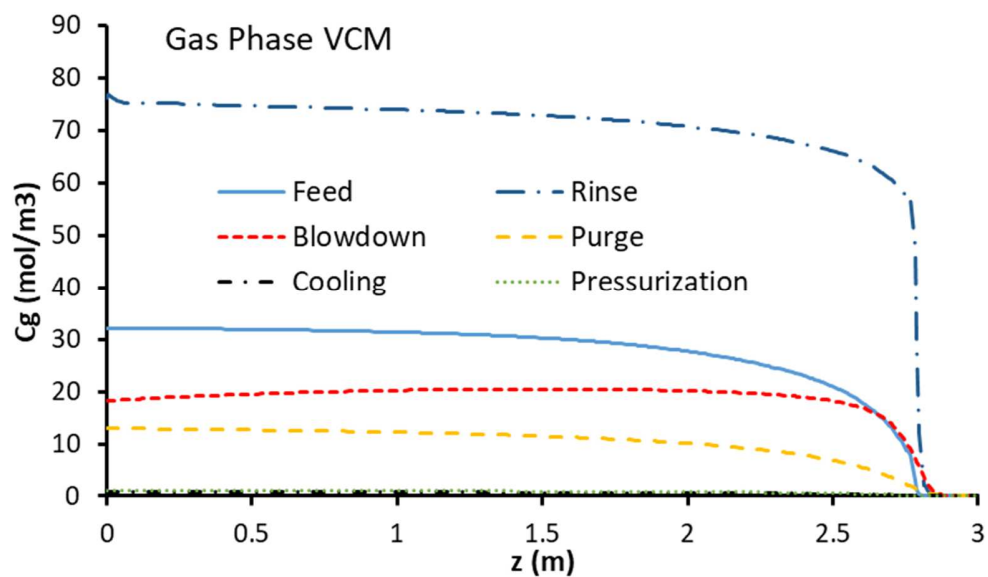


Figure 5.71: VCM Gas-Phase Concentration Profile on the Carbotech DGK carbon, during CSS, at the end of each step

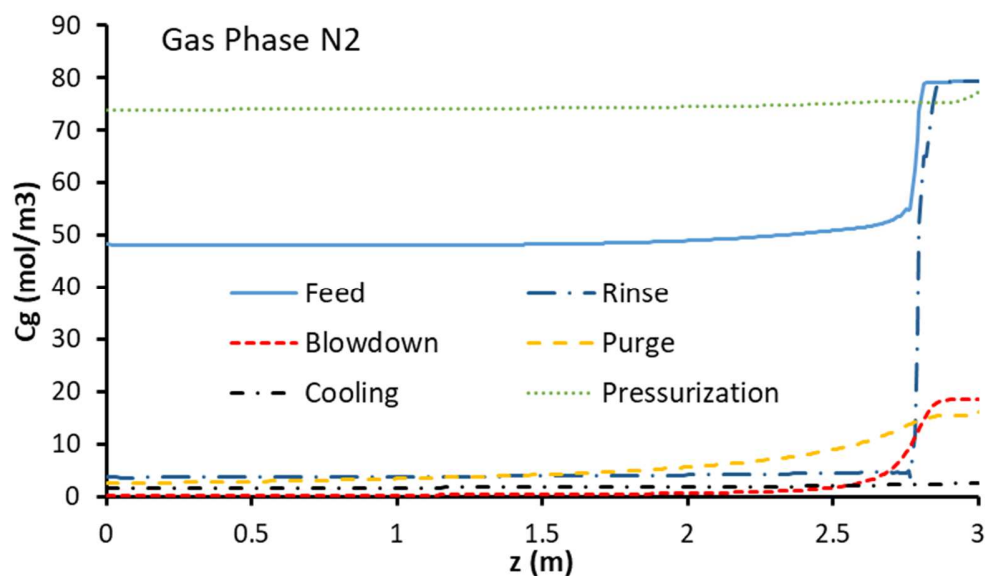


Figure 5.72: N_2 Gas-Phase Concentration Profile on the Carbotech DGK carbon, during CSS, at the end of each step

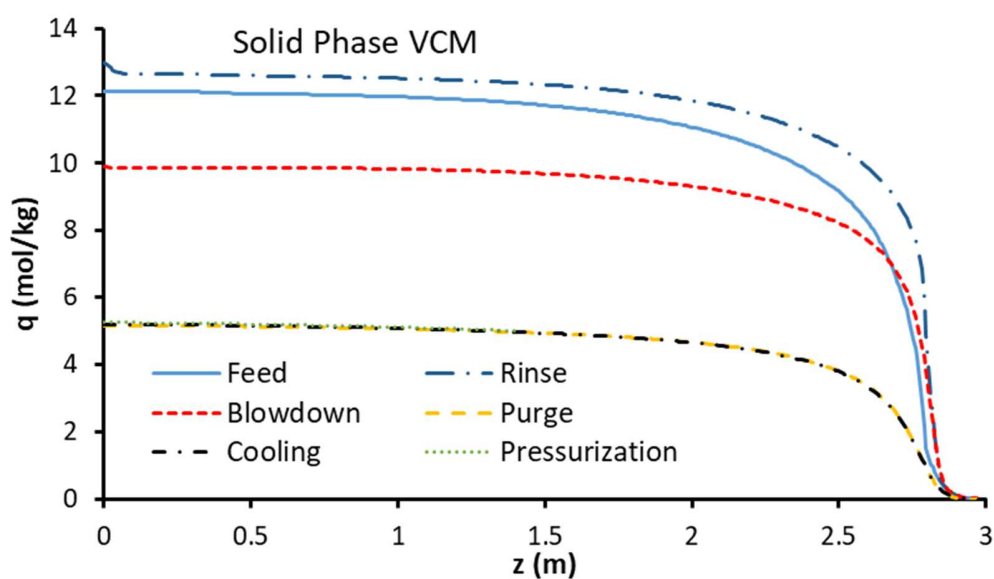


Figure 5.73: VCM Solid-Phase Concentration Profile on the Carbotech DGK carbon, during CSS, at the end of each step

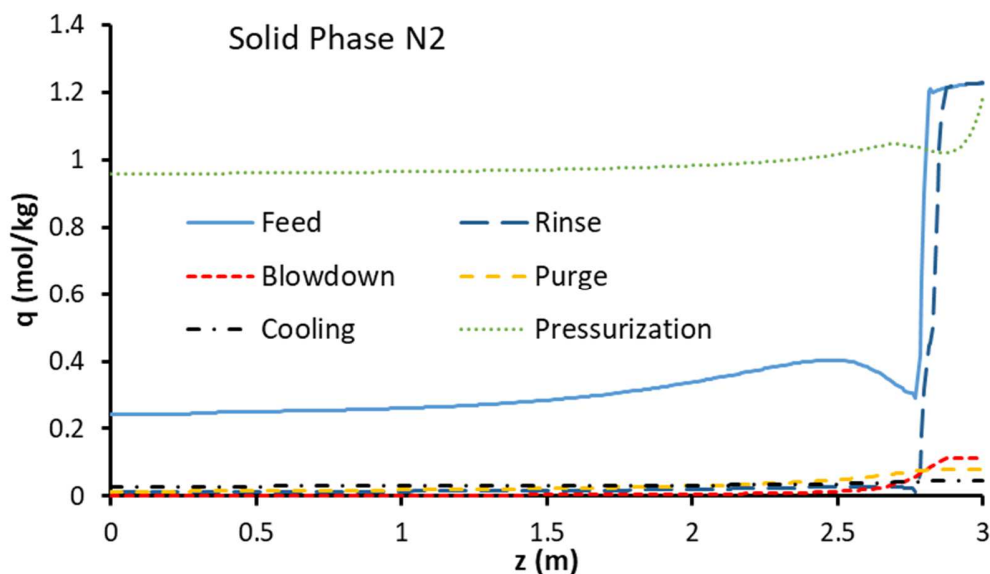


Figure 5.74: N₂ Solid-Phase Concentration Profile on the Carbotech DGK carbon, during CSS, at the end of each step

5.8. Vinyl Chloride Recovery using MIL-100(Fe) MOF

Of all the adsorbent materials scheduled for this work, only the MIL-100(Fe) MOF had some previous research developed by the group that backed the possibility of a favorable adsorption equilibrium separation. As reported in the works of Ribeiro et al.¹⁵ and Narin et al.¹⁶, the MIL-100(Fe) material showed an excellent selectivity and separation performance for the separation and recovery of a propylene/N₂ mixture by pressure swing adsorption (PSA). As such, one of the initial primary objectives of this thesis was to study the possibility of extending the potential of these systems for a similar monomer/N₂ separation, involving, in this case, vinyl chloride. As described in the literature, the advantages of the MIL-100(Fe) reside in its high monomer/N₂ selectivity and almost linear shape isotherms for monomer adsorption at higher temperatures, due to its mesoporous cages, which would enable the use of modest regeneration pressures while still achieving a good working adsorption capacity.

Indeed, from the adsorption equilibrium isotherm measurements reported in Chapter 5.3, the adsorption of VCM in the MIL-100(Fe) was confirmed to follow a more linear isotherm

behavior than the other proposed materials while also still showing favorable selectivity when compared to the adsorption of N_2 . As such, based on the results of the adsorption equilibrium measurements, both PSA and MT-TPSA cycles were deemed as viable separation processes using this material. In this section, the design of both a PSA and a MT-TPSA cycles will be performed for the separation and recovery of a VCM/ N_2 feed mixture following the feed conditions established at the beginning of this chapter, and their performance will be compared.

5.8.1. PSA Cycle Design

In the design of the PSA system, a favorable isotherm shape is of great importance to the viability of the system; as such, to facilitate the VCM regeneration, a higher feed temperature of 343 K was selected. As shown in Figure 5.75, at 343 K while the VCM isotherm is significantly more linear, a high VCM/ N_2 selectivity of 49.4 can still be achieved. The development of the present PSA cycle will follow the 1D fixed bed mathematical model and the Pressure Swing Adsorption Model initial and boundary conditions reported in Chapter 4. An exponential function will describe the valve system responsible for the depressurization of the column. The proposed PSA system will operate at a constant feed and external temperature of 343 K and a pressure range of 0.1 to 7 bar. As such, prior to being fed into the PSA unit, the VCM/ N_2 feed mixture must be separately pressurized and heated up to the adjusted feed conditions of 7 bar and 343 K.

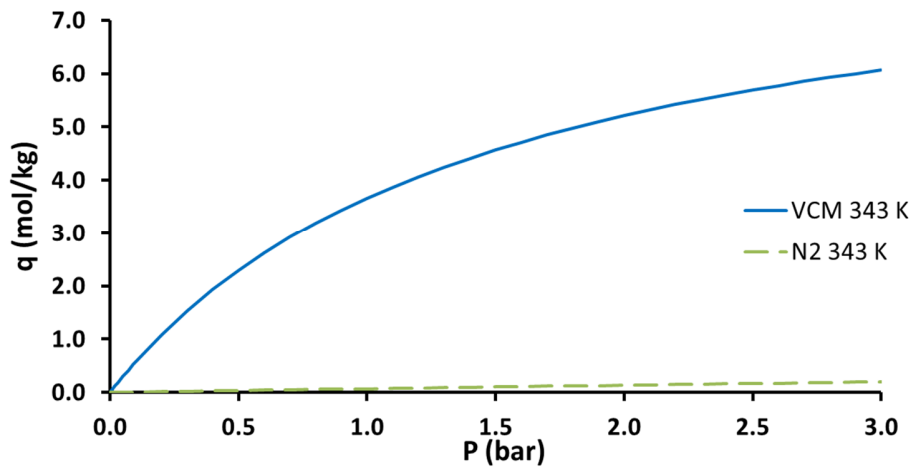


Figure 5.75: DSL isotherm model predictions for VCM and N₂ at 343 K on the MIL-100(Fe)

To simulate the proposed PSA cycle behavior through a mathematical model, transport and physical parameters must be calculated based on the feed conditions. Table 5.24 shows the mass and thermal transport parameters calculated according to the correlations proposed in Chapter 4, while Table 5.25 shows the estimated sizing characteristics for the proposed PSA system. The sizing of the PSA adsorption column was calculated considering the characteristics of the MIL-100(Fe) adsorbent material and the inlet velocity for which the supplied feed conditions would count as a fraction of the minimum fluidization velocity.

Table 5.24: Transport Parameter values used in the MIL-100(Fe) PSA Simulation calculated at feed conditions

Axial Mass Dispersion	4.90×10^{-4}	m^2/s
Axial Heat Dispersion	6.70×10^{-1}	$W/(m \cdot K)$
Mixture Viscosity	1.37×10^{-5}	$Pa \cdot s$
Particle Heat Transfer Coefficient	102	$W/(m^2 \cdot K)$
Wall Heat Transfer Coefficient	160	$W/(m^2 \cdot K)$
External Heat Transfer Coefficient	38.2	$W/(m^2 \cdot K)$

Table 5.25: Physical and Sizing properties parameters used for the MIL-100(Fe) PSA simulations

Column Length	4.50	<i>m</i>
Bed Diameter	0.50	<i>m</i>
Column Diameter	0.51	<i>m</i>
Bed Porosity	0.37	-
Total Adsorbent Mass	300	<i>kg</i>

5.8.2. PSA Simulation Results

The proposed PSA cycle is composed of five steps: Feed, Rinse, Blowdown, Purge, and Counter-Current Pressurization. By following the schedule specified in Table 5.26, the proposed PSA cycle can be extended to a triple column unit, which guarantees a continuous feed consumption and continuous production of both product streams, as illustrated by Figure 5.76. As described in Table 5.27, a MIL-100(Fe) PSA system following the sizing and operating conditions specified in Tables 5.25 and 5.26, will be capable of producing a N₂ stream with a VCM contamination of 6.14 ppm(w/w), lower than the established 8 ppm(w/w) limit for free air release and a VCM stream with 95.40 %(v/v) purity, high enough to be blended with the raw material VCM. A VCM productivity of 3.52 mol/(kg_{ads}.h) was obtained with a total energy consumption of 2.48 MJ/kg_{VCM}. Unlike in the design of the MT-TPSA systems, the energy consumption of a PSA unit is completely dependent on the electrical energy required to operate the gas-phase pressurization and vacuum pumps. However, to effectively compare the energy consumption performance between different systems, the electrical energy consumption has been converted into the reported equivalent thermal energy. A more detailed exposition of the used performance parameters can be seen in Chapter 4. Although the VCM productivity is among the lowest of the proposed systems, with exception of the preliminary test performed using the Pittsburgh PCB activated carbon, the MIL-100(Fe) PSA cycle displays the highest VCM recovery capacity at 71.89 kg_{VCM}/(m³_{unit}.h), which is mainly caused by the absence of the extra volume from the shell side through which the heat exchange fluid flows in the MT-TPSA cycles.

Additionally, considering the total energy consumption of each system, even though the reported PSA cycle uses strict regeneration conditions, the MIL-100(Fe) PSA unit still possesses the lowest total energy consumption.

Table 5.26: Proposed MIL-100(Fe) PSA Simulation Cycle step conditions

Steps	Step time (s)	Pressure (bar)	Flow Rate (Nm ³ /h)
Feed	740	7.0	180
Rinse	500	7.0	85
Blowdown	120	7.0 → 0.1	-
Purge	740	0.1	5.16
Pressurization	120	0.1 → 7.0	171

Feed		Rinse	B	Purge	P
Purge	P	Feed		Rinse	B
Rinse	B	Purge	P	Feed	

Figure 5.76: Extension of the proposed MIL-100(Fe) PSA schedule to a 3 column system

Table 5.27: Detailed PSA Cycle Performance Results for the MIL-100(Fe) system

VCM Purity	95.40	% (<i>v/v</i>)
VCM in N ₂ Stream	6.14	<i>ppm</i> (<i>w/w</i>)
VCM Recovery	99.99+	% (<i>v/v</i>)
N ₂ Recovery	96.78	% (<i>v/v</i>)
VCM Productivity	3.52	<i>mol</i> /(<i>kg_{ads}</i> · <i>h</i>)
N ₂ Productivity	5.10	<i>mol</i> /(<i>kg_{ads}</i> · <i>h</i>)
Energy Consumption	2.48	<i>MJ</i> / <i>kg_{VCM}</i>
VCM Recovery Capacity	71.89	<i>kg_{VCM}</i> /(<i>m_{unit}³</i> · <i>h</i>)

For the MIL-100(Fe) PSA cycle step scheduling and conditions presented in Table 5.26, the 1D fixed bed mathematical model was simulated until CSS was achieved. Figures 5.77 and

5.78 display the CSS temperature and pressure histories at the start, halfway, and end of the adsorption column. In the development of the present PSA cycle, special considerations were taken to facilitate the regeneration of the VCM adsorbed bed. Taking advantage of the shallowing of the VCM isotherms on MIL-100(Fe) at higher temperatures, the feed and external temperatures were purposely set to 343 K. However, for the proposed feed and under moderate regeneration conditions, the intended purity requirements were difficult to achieve without the use of much heavier adsorbent loads. The cause of this difficulty can be seen in Figure 5.77. Due to the high VCM adsorption enthalpy and the poor temperature control typical of PSA systems, during the Feed and Rinse steps, temperature increases up to 408 K were registered, which lead to a further decrease in selectivity. In comparison, during Blowdown and Purge step, the temperature decreases to below 293 K, which, as seen in Figure 5.84, results in a sharp VCM isotherm which increases the difficulty of properly regenerating the bed without a temperature-controlled process. As such, it was verified that a high vacuum was necessary to complete this separation, which comes at the cost of the higher energy consumption seen in Table 5.27.

As shown in Figure 5.78, since at the end of the Pressurization step, the internal pressure does not reach the intended adsorption pressure of 7 bar, then in the following few initial seconds of the Feed step, the feed mixture is used to complete the pressurization process. Figure 5.79 illustrates the outlet product volumetric flow rate for N₂ during the Feed and Rinse steps, and for VCM during the Blowdown and Purge steps. During the Feed and Rinse steps, the N₂ product is being produced at 7 bar and 343 K, while during the Blowdown and Purge steps, the VCM product is being produced at 0.1 bar and an average temperature of 293 K. Although difficult to notice from Figure 5.79, the contamination of the VCM stream occurs predominantly due to the purge with N₂. Figures 5.80 to 5.83 show the CSS gas- and solid-phase VCM and N₂ concentration profiles at the end of each step. As seen in Figure 5.80, the use of a high vacuum not only allows for complete saturation of the packed MIL-100(Fe) but also allows for an extensive regeneration of the adsorbent material. Indeed, as can be confirmed by Figure 5.82, during the Blowdown and Purge steps, not only does the VCM solid-phase concentration drop, but the VCM front also recedes significantly during

the Purge step, while according to the outlet flow histories, most of the VCM is produced during the Blowdown step. As shown in Figure 5.82, a very significant quantity of adsorbed VCM is still regenerated using the Purge step.

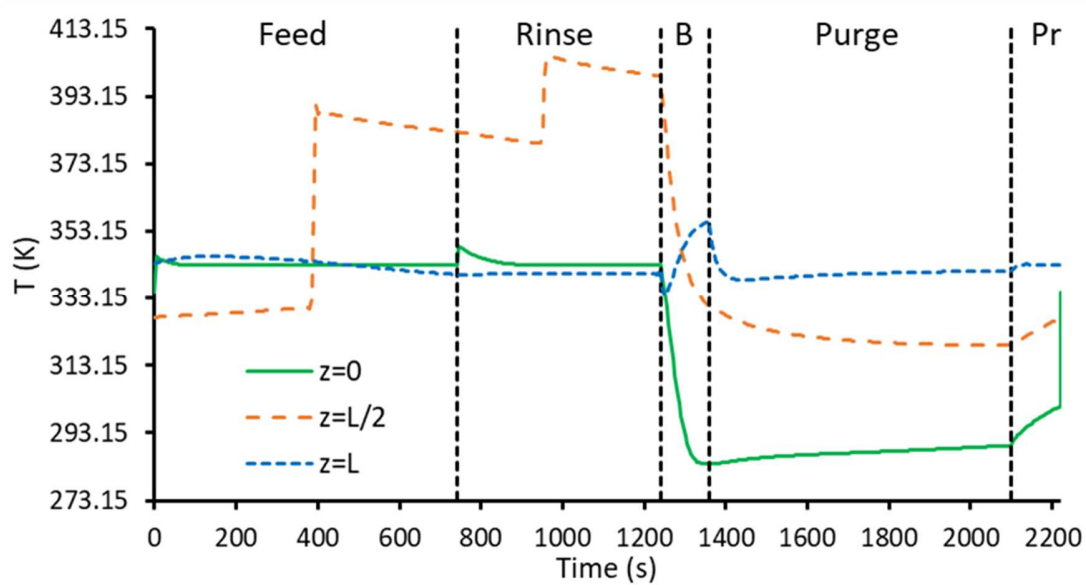


Figure 5.77: Temperature History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF

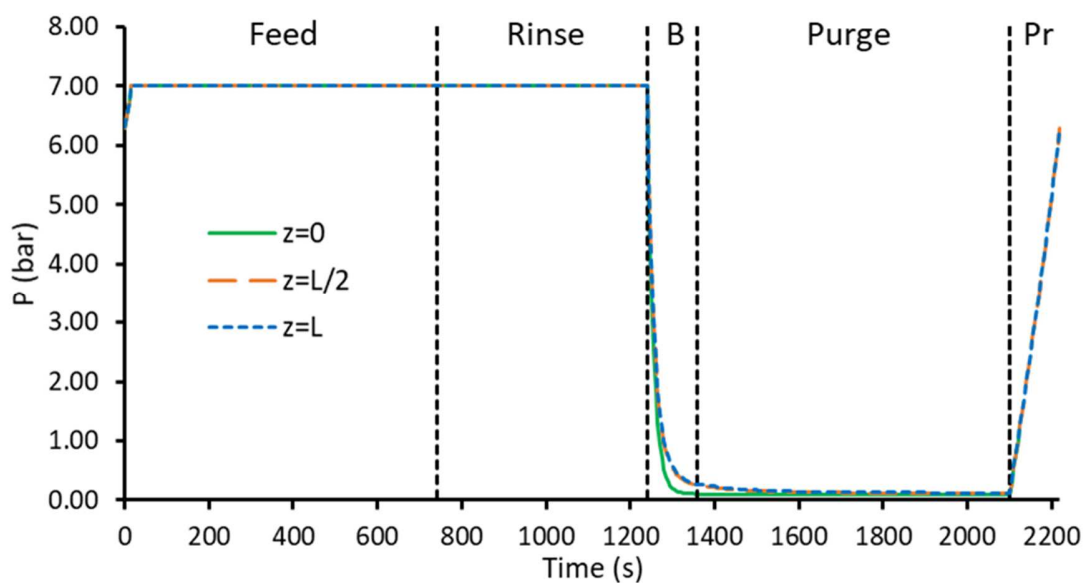


Figure 5.78: Pressure History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF

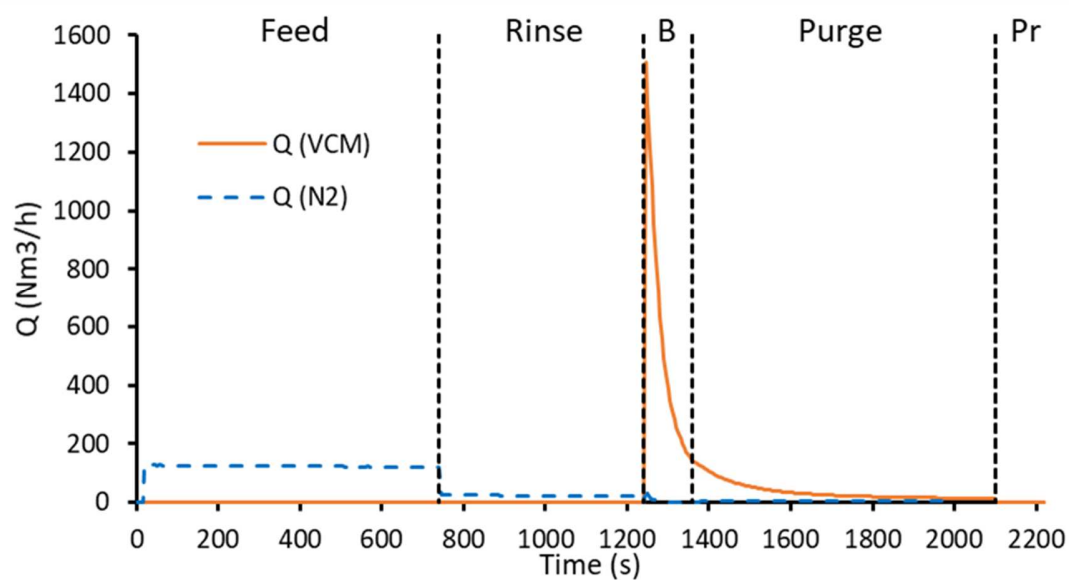


Figure 5.79: Outlet Flowrate History on the MIL-100(Fe) MOF during CSS at the start, halfway, and end of the column

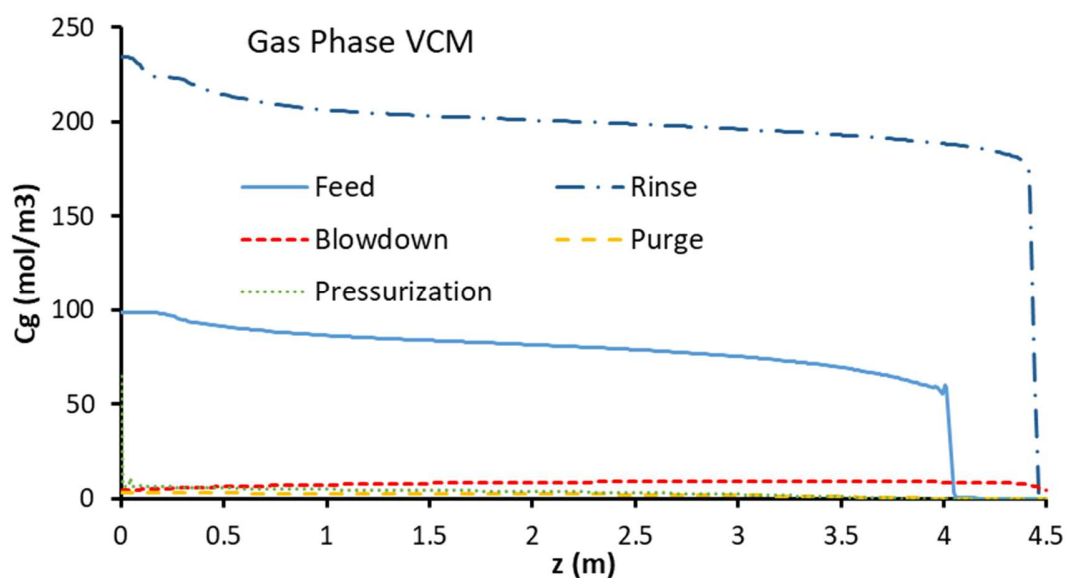


Figure 5.80: VCM Gas-Phase Concentration Profile on the MIL-100(Fe) MOF, during CSS, at the end of each step

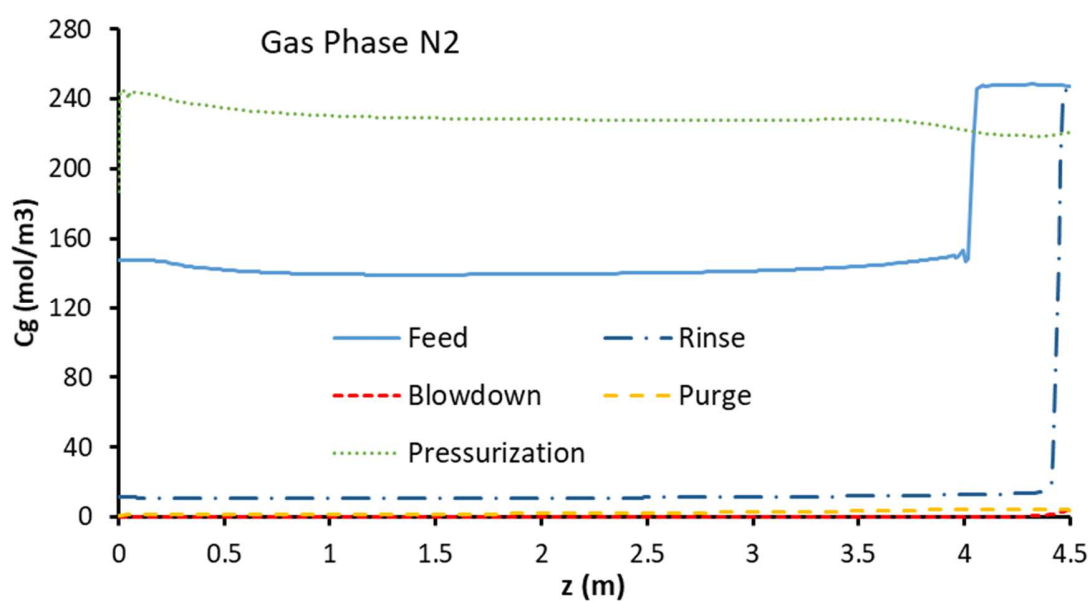


Figure 5.81: N₂ Gas-Phase Concentration Profile on the MIL-100(Fe) MOF, during CSS, at the end of each step

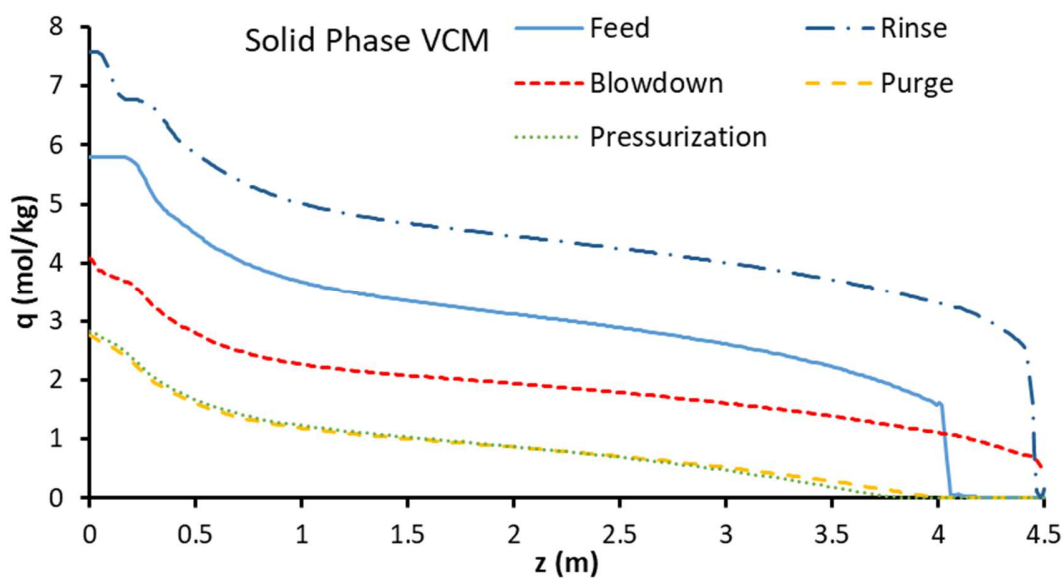


Figure 5.82: VCM Solid-Phase Concentration Profile on the MIL-100(Fe) MOF, during CSS, at the end of each step

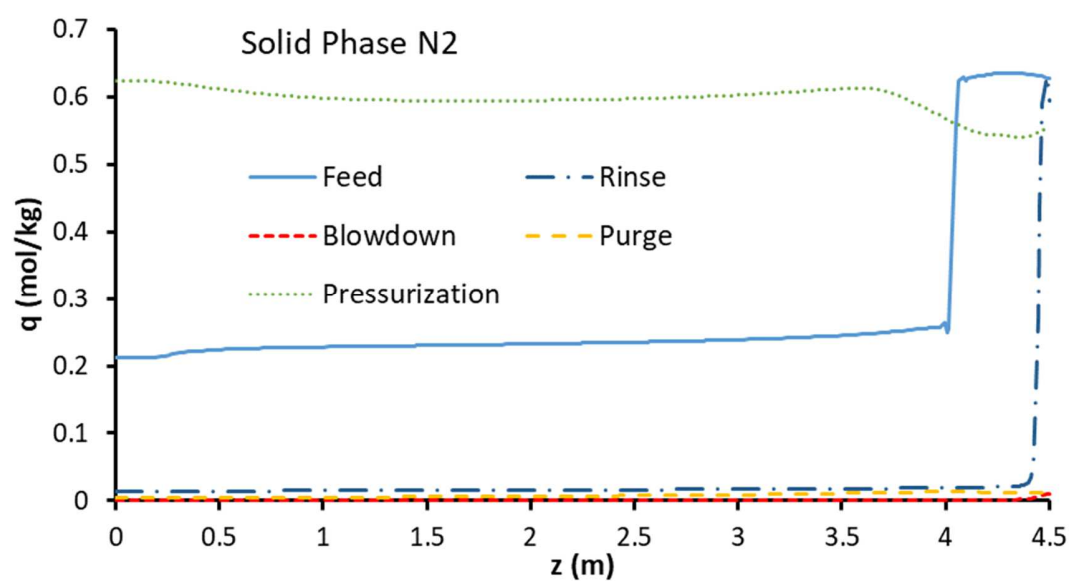


Figure 5.83: N₂ Solid-Phase Concentration Profile on the MIL-100(Fe) MOF, during CSS, at the end of each step

5.8.3. MT-TPSA Cycle Design

Similar to the previous MT-TPSA designs, the MIL-100(Fe) MT-TPSA cycle will be simulated using the Equivalent 1D fixed bed mathematical model and following the initial and boundary conditions established in the MT-TPSA cycle in Section 4.7.3. Likewise, an exponential depressurization will be used for the Blowdown step, while the tube sizing and shell design will be kept identical to the previous designs. Taking into account the results of the adsorption equilibrium measurements, the present MT-TPSA system will operate between a temperature and pressure range of 303 to 393 K and 1 to 3 bar. The temperature range is kept the same through all of the MT-TPSA simulations to facilitate comparison, while the higher regeneration pressure was selected as the VCM should be easily regenerated due to its linear isotherm shape at higher temperatures. The predicted shape of the VCM and N₂ isotherms on the MIL-100(Fe) material at the adsorption and regeneration temperatures can be visualized in Figure 5.84. By comparing the predicted VCM and N₂ isotherms, it can be calculated that, for feed conditions, the VCM/N₂ selectivity tends to decrease with temperature. At 303 K, high selectivity of 50.0 can be obtained, while at 393 K, this selectivity is lowered to 29.7. Therefore, the selectivity at 393 K is still high, and indicates that within this temperature range, adequate regeneration should be quite feasible.

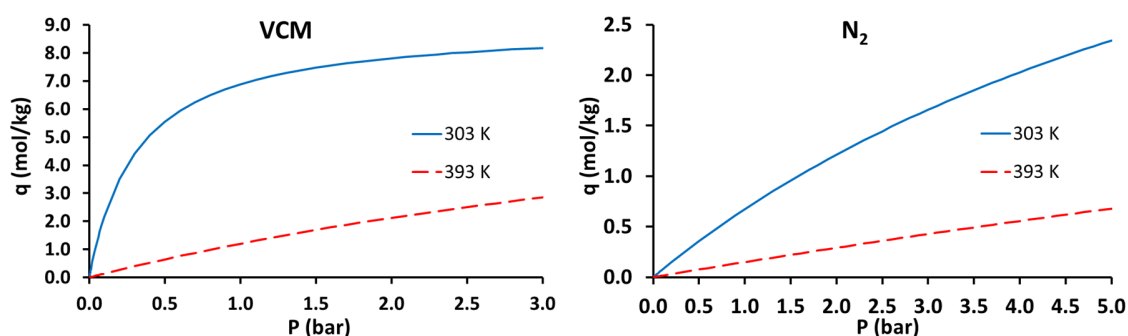


Figure 5.84: Langmuir isotherm model predictions for VCM (a) and N₂ (b) at 303 and 393 K on the MIL-100(Fe) MOF

The transport parameters necessary for the simulation of the proposed MT-TPSA cycle were calculated for the feed conditions using the correlations displayed in Section 4.8. As such,

for the treatment of a 180 Nm³/h feed stream with a 40/60 %(v/v) VCM/N₂ mixture at 303 K and 3 bar, the resulting transport parameters and physical and sizing properties of the required MT-TPSA cycle system are shown in Tables 5.28 and 5.29. The feed stream must be separately cooled and pressurized before being fed into the MTA units to accomplish the specified feed conditions. From Table 5.29, it can be seen that the proposed MTA unit shall be composed of a tube bundle of 161 tubes, within which an average inlet velocity of 0.17 m/s will be registered for feed conditions. The MTA unit will have a tube length of 4 m and a shell diameter of 0.69 m for a total mass of adsorbent of 148 kg.

Table 5.28: Transport Parameter values used in the MIL-100(Fe) MT-TPSA Simulation calculated at feed conditions

Axial Mass Dispersion	1.21 X 10 ⁻³	<i>m²/s</i>
Axial Heat Dispersion	1.10	<i>W/(m.K)</i>
Mixture Viscosity	1.30 X 10 ⁻⁵	<i>Pa.s</i>
Shell Side Heat Transfer Coefficient	1619	<i>W/(m².K)</i>
Particle Heat Transfer Coefficient	136	<i>W/(m².K)</i>
Tube Side Overall Heat Transfer Coefficient	48.33	<i>W/(m².K)</i>

Table 5.29: Physical and Sizing properties parameters used for the MIL-100(Fe) MT-TPSA simulations

Tube Length	4.00	<i>m</i>
Tube Inner Diameter	29.35 x 10 ⁻³	<i>m</i>
Tube Outer Diameter	31.75 x 10 ⁻³	<i>m</i>
Tube Pitch	39.69 x 10 ⁻³	<i>m</i>
Tube Clearance	7.94 x 10 ⁻³	<i>m</i>
Bed Porosity	0.37	-
Tube Thickness	1.20 x 10 ⁻³	<i>m</i>
Number of Tubes	161	-

Total Adsorbent Mass	148	kg
Transfer Surface Area	64	m ²
Tube Bundle Diameter	0.64	m
Shell Diameter	0.69	m
Baffle Spacing	0.27	m
Baffle Cut	25	%
Shell Inlet velocity	0.5	m/s

5.8.4. MT-TPSA Simulation Results

Following the schedule specifications listed in Table 5.30, the proposed MIL-100(Fe) MT-TPSA cycle, composed of a Feed, Rinse, Blowdown, Purge, Cooldown, and a Counter-Current Pressurizations steps, can be extended to a 2-MTA unit system, thus guaranteeing a continuous feed consumption, as seen in Figure 5.85. For the adjusted feed conditions, an MTA unit, with the physical and sizing characteristics listed in Table 5.29 and following the MT-TPSA cycle step schedule and operating conditions proposed in Table 5.30, will be capable of producing a VCM stream with 95.62 %(v/v) purity and an N₂ stream with a VCM contamination of 6.92 ppm(w/w), thus accomplishing the purity requirements set out for this separation. Due to the significantly shorter cycle time, when compared to the other MT-TPSA systems, a very high VCM productivity of 10.70 mol/(kg_{ads}.h) is reached for total energy consumption of 3.68 MJ/kg_{VCM}, which is relatively higher than the value registered for the Maxsorb MT-TPSA cycle. Of the total energy consumption, 82.3 % are used for the operation of the heat exchanger, while 13.9 and 3.8 % are used to operate the gas and liquid pumps. The higher energy consumption could be partially due to the lower thermal efficiency of the MIL-100(Fe) MT-TPSA process, where only 19.8 % of the thermal energy consumption is effectively used to regenerate the adsorbed VCM. Still, a significant part of this difference should be caused by the lower VCM adsorption capacity of the MIL-100(Fe). Despite the thermal energy consumption of the Maxsorb MT-TPSA (218 MJ) being higher than the MIL-100(Fe) (137 MJ), the VCM produced during the Maxsorb cycle (88 kg) is almost double of the MIL-100(Fe) cycle (45 kg). Finally, by analyzing the results in Table 5.32,

it is concluded that although the productivity of the MIL-100(Fe) MT-TPSA cycle is the highest among the reported VCM/N₂ separation systems, due to the higher adsorbent density, the recovery capacity of the Maxsorb MT-TPSA system is actually higher, but by a small margin. In other words, although the MIL-100(Fe) system requires less adsorbent material, the final MTA system unit would need more available industrial area.

Feed					R	Blow	Purge	C	P
R	Blow	Purge	C	P	Feed				

Figure 5.85: Extension of the proposed MIL-100(Fe) MT-TPSA schedule to a 2-MTA unit system

Table 5.30: Proposed MIL-100(Fe) MT-TPSA Simulation Cycle step conditions

Steps	Step time (s)	Pressure (bar)	External Temperature (K)	Flow Rate (Nm ³ /h)
Feed	820	3.0	303	180
Rinse	80	3.0	303	170
Blowdown	220	3.0 → 1.0	303 → 393	-
Purge	300	1.0	393	11.34
Cooldown	140	1.0 (→ 0.34)	393 → 303	-
Pressurization	80	0.34 → 3.0	303	68

Table 5.31: Detailed MT-TPSA Cycle Performance Results for the MIL-100(Fe) system

VCM Purity	95.62	% (<i>v/v</i>)
VCM in N ₂ Stream	6.92	<i>ppm</i> (<i>w/w</i>)
VCM Recovery	99.99+	% (<i>v/v</i>)
N ₂ Recovery	96.96	% (<i>v/v</i>)
VCM Productivity	10.70	<i>mol/(kg_{ads} · h)</i>
N ₂ Productivity	15.56	<i>mol/(kg_{ads} · h)</i>
Total Energy Consumption	3.68	<i>MJ/kg_{VCM}</i>

Adsorption Cooling Duty	0.60	MJ/kg_{VCM}
Heating Duty	1.53	MJ/kg_{VCM}
Cooling Duty	0.90	MJ/kg_{VCM}
Gas Pump Operation	0.51	MJ/kg_{VCM}
Liquid Pump Operation	0.15	MJ/kg_{VCM}

Table 5.32: VCM Productivity and Recovery Capacity for the MIL-100(Fe) MT-TPSA

VCM Productivity	0.669	$kg_{VCM}/(kg_{ads} \cdot h)$
Bed VCM Recovery Capacity	227.30	$kg_{VCM}/(m_{bed}^3 \cdot h)$
Unit VCM Recovery Capacity	66.83	$kg_{VCM}/(m_{unit}^3 \cdot h)$

For the MIL-100(Fe) MT-TPSA cycle step scheduling and conditions presented in Table 5.30, the Equivalent 1D MT-TPSA mathematical model was simulated until CSS was achieved. Figures 5.86 and 5.87 represent the temperature and pressure histories at the entrance, halfway, and end of the tube system. During the Feed and Rinse steps, temperatures spikes of 35 and 10 K were registered indicating the passing of the 40 and the 95 % VCM fronts. During the Blowdown and Purge steps, the temperature of the gas rapidly increases by the influence of the heat exchange fluid, especially near the end of the tube system where no adsorbed VCM is present. Despite the overall temperature inside the tube system does not reach the target regeneration temperature during the Blowdown and Purge steps, the reported VCM regeneration is sufficient to guarantee the VCM purity requirement. As seen in Figure 5.88, during the Feed step, a constant N₂ volumetric flow rate of 112 Nm³/h is being produced, which suffers a drop during the Rinse step. Created by the exponential depressurization valve system, a decreasing VCM flow rate is produced during the Blowdown and Purge steps. Only a small increase in VCM production occurs at the start of the Purge step. Contamination of the VCM stream occurs spontaneously at the start of the Blowdown step, due to the small presence of N₂ at the end of the tube system and continuously throughout the Purge step. Although no outlet is produced during the

Cooldown and Pressurization steps, during the Closed Cooldown step, the heat exchange fluid is switched to cooling water, and the entire tube system is cooled down, promoting the adsorption of any of the remaining VCM and thus lowering pressure inside the tubes to 0.34 bar. Afterward, part of the N₂ product is used to increase the pressure back to the initial 3 bar, during the Pressurization step.

Figures 5.89 to 5.92 represent the CSS gas- and solid-phase concentration profiles for VCM and N₂ at the end of each step along the axial direction of the tube system. As seen from Figure 5.89, most of the tube length is being actively used to adsorb VCM, with only the final 6% of the tube length used to guarantee the N₂ purity requirement. Due to the sharper VCM isotherm shape at lower temperatures, the Rinse step is accomplished relatively quickly; as shown in Figures 5.90 and 5.91. The rinse step is capable of pushing most of the gas-phase N₂ out of the adsorbent, while not requiring the recycling of large quantities of VCM, as confirmed by the low solid phase VCM concentration increase. Although the end of the Rinse step does not coincide with the VCM front created during the Feed step, its performance is sufficient to guarantee the required VCM and N₂ purity limit. Perhaps the most pertinent observation, due to the smoothing of the VCM isotherm at high temperatures, the regeneration of the adsorbed VCM through the Purge step can be thoroughly accomplished. As confirmed by Figure 5.91, during the Purge step, not only is there an overall decrease in the VCM solid phase concentration, but the VCM front itself is significantly pushed back, similar to the behavior displayed in the MIL-100(Fe) PSA cycle.

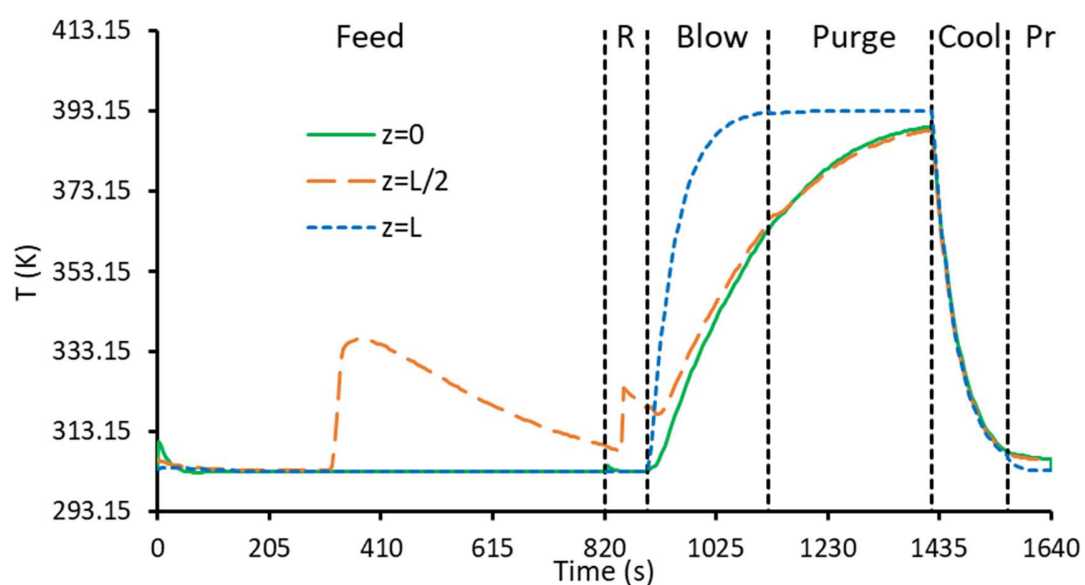


Figure 5.86: Temperature History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF

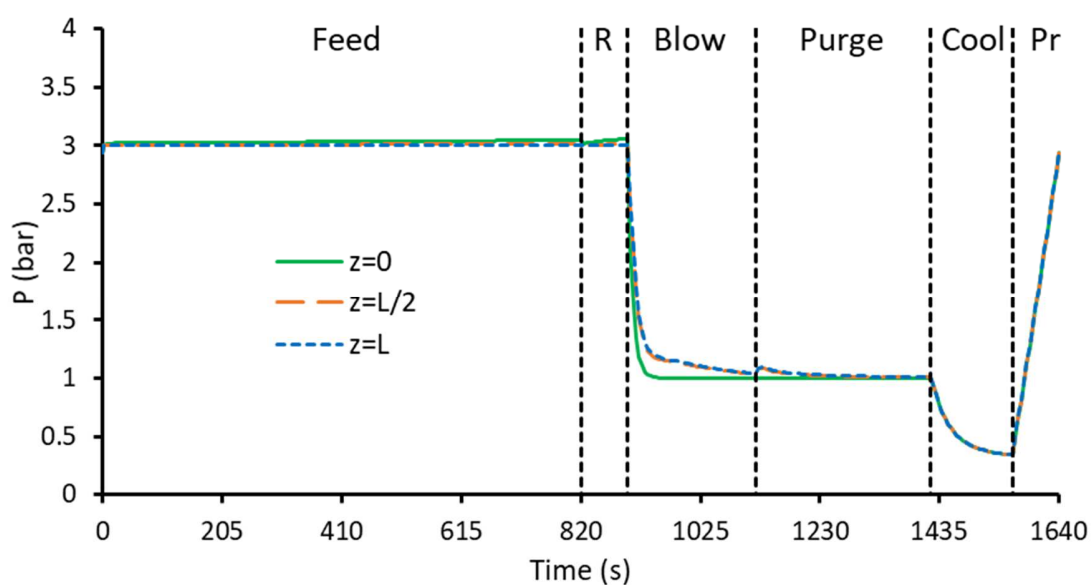


Figure 5.87: Pressure History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF

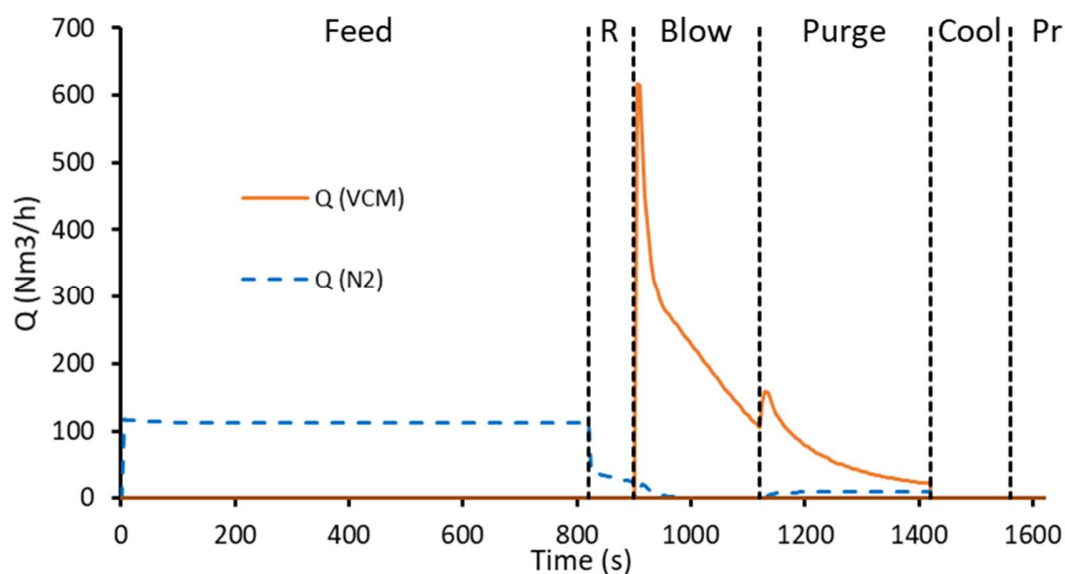


Figure 5.88: Outlet Flowrate History on the MIL-100(Fe) MOF during CSS at the start, halfway, and end of the column

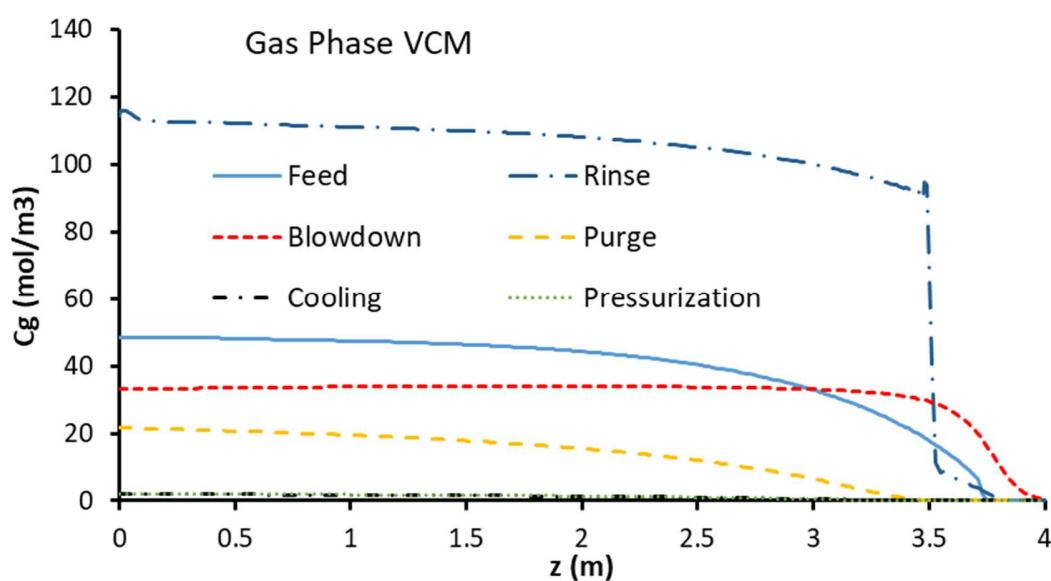


Figure 5.89: VCM Gas-Phase Concentration Profile on the MIL-100(Fe) MOF, during CSS, at the end of each step

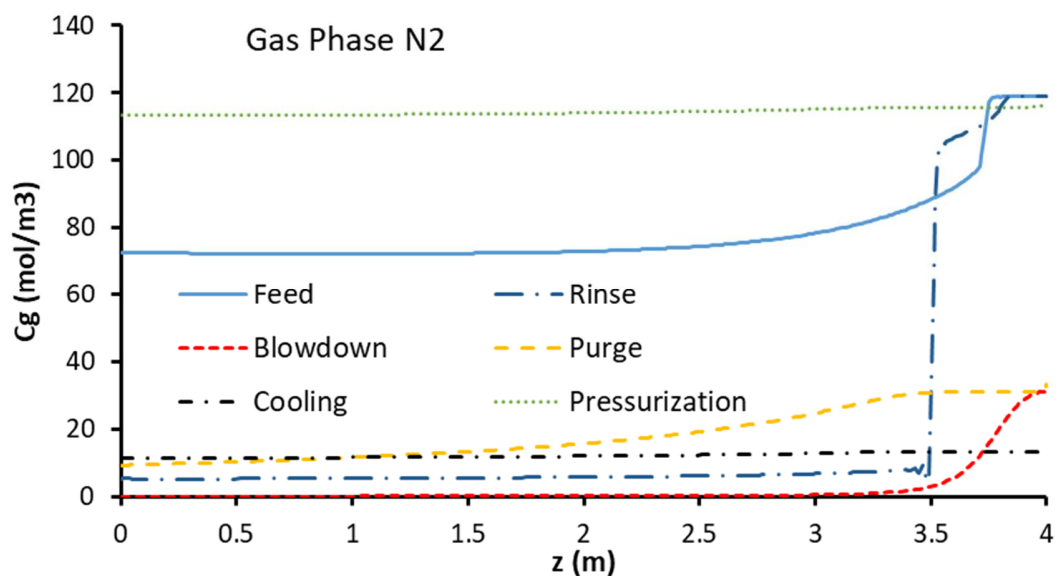


Figure 5.90: N₂ Gas-Phase Concentration Profile on the MIL-100(Fe) MOF, during CSS, at the end of each cyclic time step

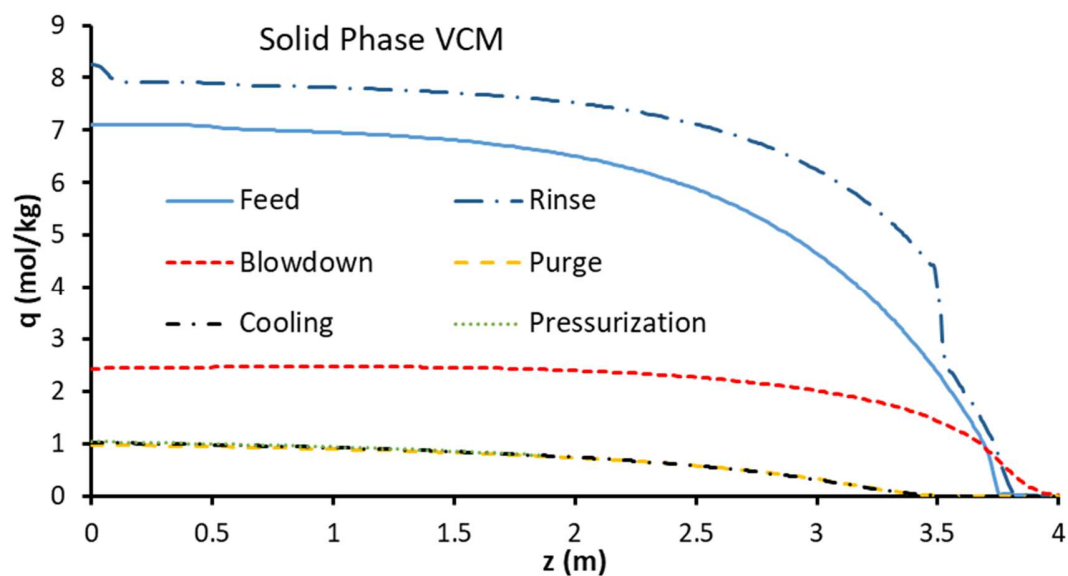


Figure 5.91: VCM Solid-Phase Concentration Profile on the MIL-100(Fe) MOF, during CSS, at the end of each step

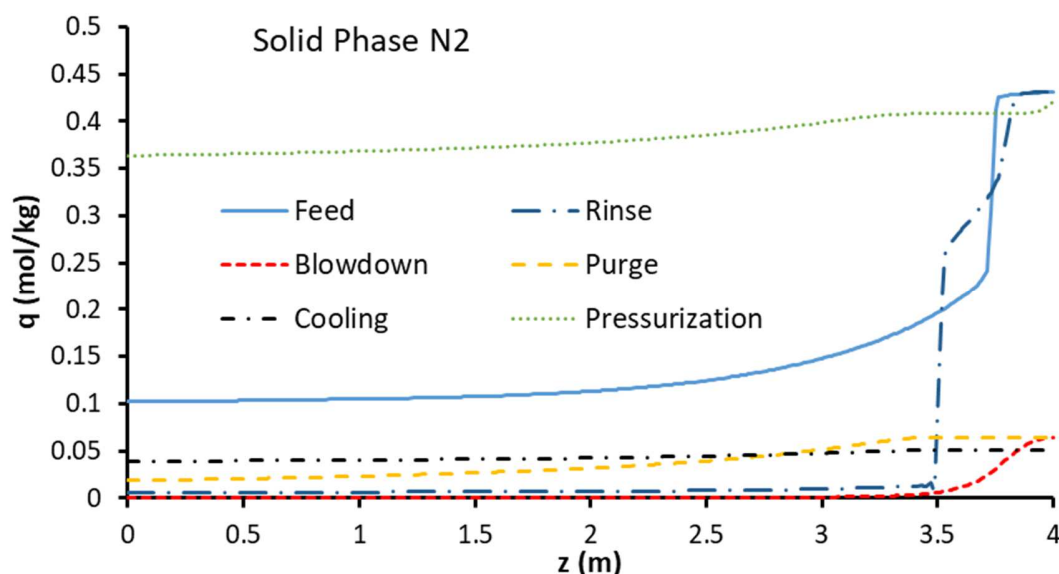


Figure 5.92: N₂ Solid-Phase Concentration Profile on the MIL-100(Fe) MOF, during CSS, at the end of each step

5.9. Conclusions

Using adsorption equilibrium data collected from the literature, a preliminary two-column six-step TPSA cycle was designed for a 40/60 % vinyl chloride/nitrogen separation on Pittsburgh PCB activated carbon. The main goal of the present separation was producing a nitrogen stream with a vinyl chloride contamination lower than the established 8 ppm(w/w) limit for free air release and a vinyl chloride stream with a high enough purity (95 %) to be blended with the raw material vinyl chloride and recycled into the polymerization process. The proposed TPSA cycle operated between a 0.5 to 1 bar and 293 to 463 K range and produced a vinyl chloride stream with 95.01 % purity and a nitrogen stream with a vinyl chloride contamination of 7.8 ppm(w/w). A vinyl chloride productivity of 0.46 mol/kg_{ads}.h was obtained for total thermal energy consumption of 3.62 MJ/kg_{VCM}.

Based on received feedback, an alternative higher productivity system was developed in a triple multitubular adsorber unit following a six-step MT-TPSA cycle. The proposed MT-TPSA cycle was design for the same separation requirements but operated in a 0.5 to 1 bar and

293 to 393 K range and was capable of producing a VCM stream with a 95.17 % purity and a nitrogen stream with a VCM contamination of 4.1 ppm(w/w) with a total adsorbent load of 1350 kg. A vinyl chloride productivity and recovery capacity of 2.35 mol/kg_{ads}.h and 24.35 kg_{VCM}/(m³_{unit}.h) were obtained for total thermal energy consumption of 4.88 MJ/kg_{VCM}. The development of a multicomponent two dimensional (axial + radial directions) fixed bed mathematical model allowed for a more thorough study of both the systems' thermal and mass behavior, as well as the impact of radial transport in the system performance and adsorption phenomena. Also, the viability of accurately recreating the radial behavior using an equivalent one-dimensional fixed bed mathematical model was successfully confirmed for the present conditions.

For the first time, pure component adsorption equilibrium isotherms for vinyl chloride were measured, using a gravimetric method, over powdered Maxsorb carbon, granulated Carbotech DGK carbon, and granulated MIL-100(Fe) MOF, in a range of 0 to 2.5 bar and 303 to 373 K. Pure component isotherms were also obtained for nitrogen over the granulated Carbotech DGK carbon and MIL-100(Fe) MOF, in a range of 0 to 5 bar, and 303 to 373 K. For each material, the Langmuir and Dual Site Langmuir isotherm models were accurately fitted to the measured experimental results.

For each of the three materials, a six-step MT-TPSA cycle was designed for a vinyl chloride/nitrogen separation following the same purity requirements as the previous preliminary work. Additionally, due to the favorable shape of the measured VCM adsorption isotherm on MIL-100(Fe), a five-step PSA process was also designed for the same separation. All the MT-TPSA cycles were operated within a temperature range of 303 to 393 K and were designed using the same tube sizing considerations as the ones defined during the initial Pittsburgh PCB MT-TPSA cycle. The PSA cycle was carried out at a constant feed and external temperature of 343 K. The performance of each process was evaluated and compared based on the products' purity, recovery, productivity, recovery capacity, and energy consumption.

For the Maxsorb MT-TPSA cycle, a two multitubular adsorber system, designed for a pressure operating range of 1 to 2.5 bar, was capable of producing a vinyl chloride stream

with a 95.11 % purity and a nitrogen stream with vinyl chloride contamination of 4.78 ppm(w/w), using a total adsorbent load of 376 kg. A vinyl chloride productivity and recovery capacity of 8.41 mol/(kg_{ads}.h) and 69 kg_{VCM}/(m³_{unit}.h) were achieved for total thermal energy consumption of 3.05 MJ/kg_{VCM}.

For the Carbotech DGK MT-TPSA cycle, a two multitubular adsorber system, designed for a pressure operating range of 0.5 to 2 bar, was capable of producing a vinyl chloride stream with a 95.45 % purity and a nitrogen stream with vinyl chloride contamination of 4.40 ppm(w/w), using a total adsorbent load of 724 kg. A vinyl chloride productivity and recovery capacity of 4.38 mol/(kg_{ads}.h) and 60.19 kg_{VCM}/(m³_{unit}.h) were achieved for total thermal energy consumption of 3.21 MJ/kg_{VCM}.

For the MIL-100(Fe) PSA cycle, a triple adsorption column system, designed for a pressure operating range of 0.1 to 7 bar, was capable of producing a vinyl chloride stream with a 95.40 % purity and a nitrogen stream with vinyl chloride contamination of 6.14 ppm(w/w), using a total adsorbent load of 900 kg. A vinyl chloride productivity and recovery capacity of 3.52 mol/(kg_{ads}.h) and 71.89 kg_{VCM}/(m³_{unit}.h) were achieved for total thermal energy consumption of 2.48 MJ/kg_{VCM}.

For the MIL-100(Fe) MT-TPSA cycle, a two multitubular adsorber system, designed for a pressure operating range of 1 to 3 bar, was capable of producing a vinyl chloride stream with a 95.62 % purity and a nitrogen stream with vinyl chloride contamination of 6.92 ppm(w/w), using a total adsorbent load of 296 kg. A vinyl chloride productivity and recovery capacity of 10.70 mol/(kg_{ads}.h) and 66.83 kg_{VCM}/(m³_{unit}.h) were achieved for total thermal energy consumption of 3.68 MJ/kg_{VCM}.

Although all the proposed adsorption-based separation systems were capable of accomplishing the intended purity requirements, by comparing the remaining performance parameters, two systems stand out as possible solutions for the present separation.

Between the MT-TPSA systems, the two multitubular adsorber Maxsorb MT-TPSA system displays the highest overall performance. Due to its high adsorption capacity and relatively lower adsorption enthalpy for VCM, the Maxsorb MT-TPSA system displays the lowest

energy consumption of all the reported temperature-swing processes. Also, despite the MIL-100(Fe) MT-TPSA system having higher productivity, when converted to the unit recovery capacity, the results for both systems end up being very similar. Assuming that the adsorbent cost should be higher for the MIL-100(Fe) MOF rather than the Maxsorb carbon, the higher adsorbent load for the Maxsorb system should also not be a contrary factor.

The second potential separation unit is, indeed, the MIL-100(Fe) PSA system. Although this system reports much lower productivity, higher adsorbent load, and requires high vacuum, the simpler and less expensive design, together with the overall lower total thermal energy consumption, may make this design more economically advantageous.

On the other hand, if one considers that the thermal duties of the cooling stages can be more cheaply accounted for due to the use of a water cooling tower, then the necessary thermal energy consumptions can be reduced to the energy needed to supply heat during the heating stages and the electrical energy costs. Following this logic, the consumption of energy required of the Maxsorb MT-TPSA cycle can be reduced to 1.82 MJ/kg_{VCM}, which, in turn, could be even further reduced if the MT-TPSA system was to be integrated into the PVC plant heat integration plan, as opposed to the static electrical energy consumption reported for the PSA system.

As an add-on separation unit, the increased simplicity and lower economic upkeep of the MIL-100(Fe) PSA system should quickly compensate for its higher acquisition cost, making it the ideal separation system for the present separation. If the vinyl chloride/nitrogen separation unit could be efficiently integrated into the plant's heat integration plan, preferentially during the plant's design, then the Maxsorb MT-TPSA system would undoubtedly provide the best solution.

A performance comparison summary between all the adsorption-based separation units developed for the separation and recovery of a vinyl chloride/nitrogen mixture is shown in Table 5.33.

Table 5.33: Performance comparison between all the developed technologies for vinyl chloride recovery

Pittsburgh PCB		Maxsorb	Carbotech	MIL-100(Fe)		
TPSA	MT-TPSA	MT-TPSA	MT-TPSA	PSA	MT-TPSA	
Temperature and Pressure						
293 – 473	293 – 393	303 – 393	303 – 393	343	303 – 393	K
0.5 – 1	0.5 – 1	1 – 2.5	0.5 – 2	0.1 – 7	1 – 3	bar
Productivity						
2.9 x 10 ⁻²	1.5 x 10 ⁻¹	5.3 x 10 ⁻¹	2.7 x 10 ⁻¹	2.2 x 10 ⁻¹	6.7 x 10 ⁻¹	kg _{VCM} /(kg _{ads} . h)
7	24	69	60	72	67	kg _{VCM} /(m ³ _{unit} . h)
9	79	224	191		227	kg _{VCM} /(m ³ _{bed} . h)
Energy Requirements						
3.62	4.88	3.05	3.21	2.48	3.68	MJ/kg _{VCM}

5.10. References

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Chapter 6

Light Olefin / Nitrogen Separation and Recovery



6.1. Introduction

In this chapter, the focus will be given to the development of light olefin/nitrogen adsorption-based separation systems applied to the recovery of light olefins from polymer degassing vents and similar sources in the polyethylene and polypropylene industries.

The composition and properties for the propylene/nitrogen feed mixture were chosen according to the information collected from the literature.^{1,2} While, due to the similarities in the manufacturing process, the ethylene-rich stream will follow similar specifications as the propylene stream, except for the capacity, which will be updated to take into account the higher capacity of the polyethylene plants, as reported in the literature.³ As shown in Figure 6.1, the developed light olefin recovery unit must be capable of treating a 5400 Nm³/h (C₂H₄/N₂) or a 3600 Nm³/h (C₃H₆/N₂) feed flowrate of a 30/70 % (v/v) light olefin/nitrogen mixture, supplied at 1 bar and 323 K. The unit must also be capable of producing a pure nitrogen stream with a light olefin contamination lower than the 20 ppm (v/v) limit for free air release established by the Environmental Protection Agency⁴ and a light olefin stream with a minimum purity requirement of 95 % (v/v) in nitrogen.

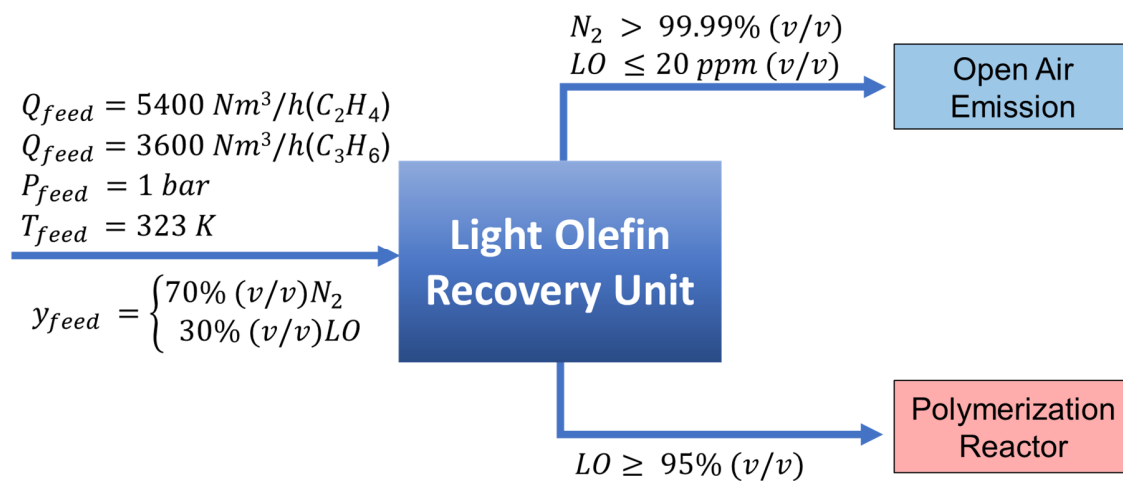


Figure 6.1: Schematic of the Light Olefin (LO) and Nitrogen feed stream conditions and the separation requirements for the developed separation and recovery unit.

Adsorption equilibrium experimental data for ethylene and propylene were obtained by gravimetric methods, and dynamic single and multicomponent breakthrough experiments

were performed on granules of the MIL-100(Fe). Using the collected data, a PSA and an MT-TPSA cycle will be designed for the separation and recovery of each light olefin/nitrogen mixture on MIL-100(Fe), and a comparison of their performances will be made.

6.2. Adsorption Equilibrium Measurements

Unlike the approach taken for vinyl chloride, previous research had already been performed by the group on propylene/nitrogen separation. Based on the work developed by Ribeiro¹ and Narin² et al., the MOF material MIL-100(Fe) showed an adequate selectivity and separation performance for a propylene/nitrogen mixture by Pressure Swing Adsorption (PSA). As previously discussed in Chapter 5, one of the main advantages of the MIL-100(Fe) material is the reported high linearity of the equilibrium isotherms at higher temperatures facilitating the development of more affordable pressure swing systems. Together with the favorable adsorption equilibrium data obtained from the literature for ethylene^{5,6} and propylene⁷, the author decided that MIL-100(Fe) would be an appropriate adsorbent material for the present propylene/nitrogen separation requirements and would have the potential for the development of other light olefins/nitrogen recovery units.

Using the magnetic suspension balance setup, previously discussed in Chapter 3.3, single component equilibrium isotherms for the adsorption of ethylene and propylene on MIL-100(Fe) were obtained for a pressure range of 0 to 5 bar, and at a temperature of 303, 323, and 373 K. Prior to any measurements, the MIL-100(Fe) sample was activated in situ at 433 K and under constant vacuum overnight or until no significant mass loss were observed for more than 1 hour. The measured single component adsorption equilibrium data is presented in Figures 6.2 and 6.3 for ethylene and propylene, respectively. All the experimental equilibrium data is represented by points, while the lines represent the Langmuir isotherm fitting used to model the experimental results. Table 6.1 shows the fitting parameters used for the Langmuir isotherm model.

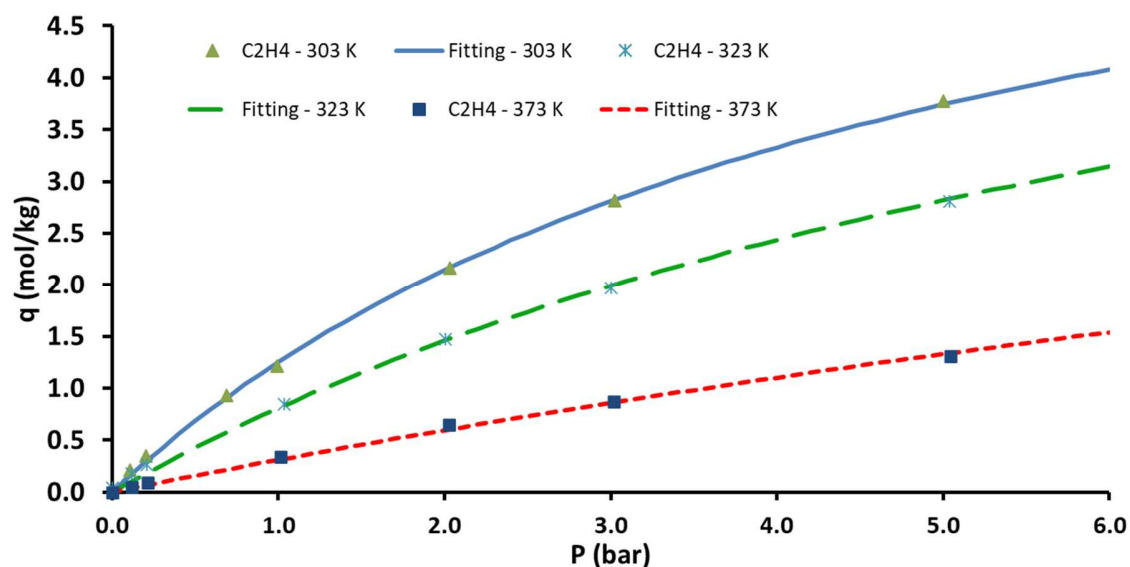


Figure 6.2: Adsorption Equilibrium experimental data and model for ethylene in MIL-100(Fe) at 303, 323, and 373 K

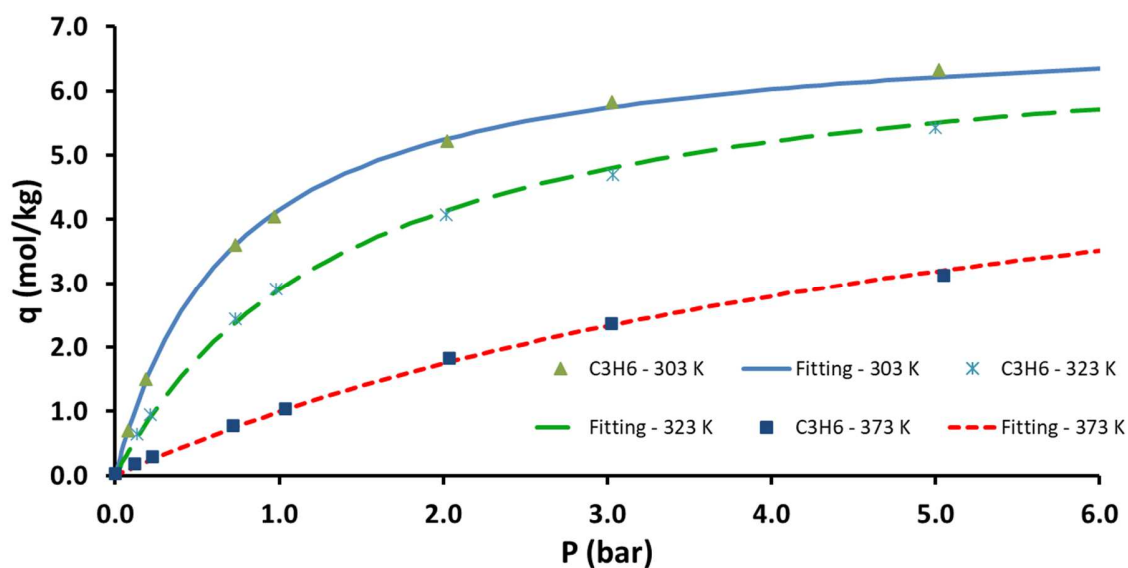


Figure 6.3: Adsorption Equilibrium experimental data and model for propylene in MIL-100(Fe) at 303, 323, and 373 K

Table 6.1: Langmuir isotherm fitting model parameters for the adsorption of ethylene and propylene in MIL-100(Fe)

Isotherm Parameters	Ethylene	Propylene	Units
q_{sat}	7.45	7.09	mol/kg
b_0	5.58×10^{-5}	1.42×10^{-5}	bar^{-1}
$-\Delta H_{ads}$	20648	29001	J/mol

6.3. Isosteric Heat of Adsorption

Similar to the discussion presented in Section 5.4, the isosteric heat of adsorption for ethylene and propylene was calculated as a function of the loading for the MIL-100(Fe) sample, as shown in Figures 6.4 and 6.5. The points represent the values calculated using the experimental data, while the straight line is the enthalpic parameter used in the Langmuir fitting. The isosteric heat of adsorption values were calculated for the experimental loading data of the highest measured temperature, which could be compared to the measured loadings for the other temperatures.

Also as previously discussed for the case of MIL-100(Fe), even though the heterogeneous structure of the material is known, the variations of the isosteric heat for ethylene and propylene remain mostly constant, due to the preferential adsorption of these monomers on the iron(III) sites, rather than in the organic ligands. The preferential adsorption is caused by the formation of electrostatic interactions between the double bond of ethylene and propylene and iron (III) charge. For this reason, the Langmuir model is sufficient to accurately model the variation of the isosteric heat at the measured pressure range.

For MIL-100(Fe), the most robust interactions are established with vinyl chloride (as seen in Chapter 5.4), followed by propylene, ethylene, and nitrogen, as shown by the present results.

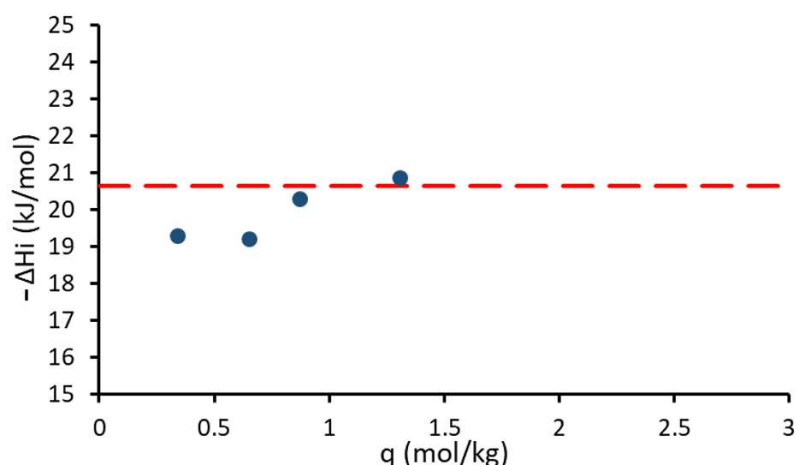


Figure 6.4: Isosteric heat of adsorption versus loading on MIL-100(Fe) granulates for C_2H_4

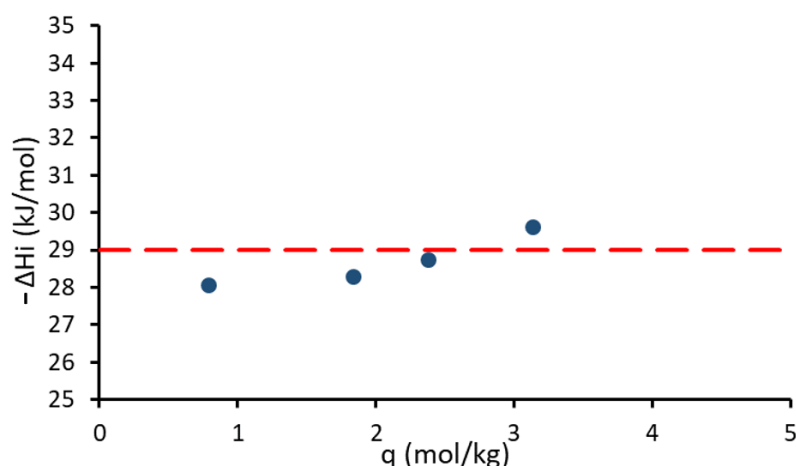


Figure 6.5: Isosteric heat of adsorption versus loading on MIL-100(Fe) granulates for C_3H_6

6.4. Fixed Bed Breakthrough Experiments

To determine the adsorption kinetics and validate the multicomponent isotherm models described in section 6.2, single and multicomponent fixed bed breakthrough experiments were performed using the single column bench-scale PSA unit described in Chapter 3. The validation of the equilibrium and kinetic parameters is performed by simulating the fixed bed behavior of the bench-scale PSA unit using the 1D Fixed Bed model described in Chapter 4 for the Danckwerts boundary conditions. The mass and thermal transport parameters used in the simulation of the breakthrough experiments were calculated at feed conditions using the correlations presented in Section 4.8 and were kept constant throughout the

simulation. The adsorption equilibrium isotherm model parameters used in these simulations are listed in Table 6.1 for ethylene and propylene, and Table 5.2 for nitrogen.

For these experiments, a stainless steel column with an internal diameter of 21 mm and a wall thickness of 2.1 mm was used. Using a fresh sample of granulated MIL-100(Fe), the adsorption column was filled until a bed length of 0.747 m was achieved, which required a total mass of 117 g of fresh adsorbent. At the top and bottom of the column, a glass wool and a metal mesh are used to hold the adsorbent bed in place and to prevent the loss of any powdered debris into the system. After being closed, the adsorption column is introduced into the convection oven and fitted to the PSA system, additionally, three thermocouples are introduced into the adsorption column by specially made lateral entrances, which will measure the temperature inside the adsorption bed, as seen in Figure 3.8. At 0.07 m from the outlet of the column, the top thermocouple is used to measure the temperature at the wall, while at 0.32 and 0.57 m from the outlet, the middle and bottom thermocouples, respectively, measure the local temperature inside the packed bed. The adsorption bed is then activated in situ, under a constant He flow rate of 0.5 SLPM; the temperature of the convection oven is increased gradually (0.5 K/min) until a temperature of 433 K is registered inside the adsorption bed. The activation of the sample is then performed overnight, for a minimum duration of 18 hours, while a water trap is left open after the outlet of the column. After the activation is complete, the bed is cooled down, and the dehydrated sample is weighted to reveal a 24.5 % mass loss, which results in an adsorbent sample with a dry weight of 88 g. A summary of the fixed bed characteristics and estimated transport parameters are shown in Table 6.2.

Table 6.2: Characteristics and estimated transport parameters of the fixed bed adsorption column used in the Breakthrough experiments

Bed Diameter	0.021	m
Bed Length	0.747	m
Bed Porosity	0.37	-
Adsorbent Weight	0.117	kg

Dry Adsorbent Weight	0.088	kg
Bulk Density	340	kg/m ³
Wall Density	8238	kg/m ³
Wall Heat Capacity	500	J/(kg K)
Wall Heat Transfer Coefficient	60	W/(m ² K)
Wall Overall Heat Transfer Coefficient	20	W/(m ² K)

Once the adsorption column has been adequately activated and cooled down, the single column fixed bed will be used to carry out single, binary, and pseudo-binary breakthrough curves for the ethylene, propylene, and nitrogen gases and respective mixtures at 323 K and 2 bar. The experimental conditions of all the breakthrough curves performed in this work are shown in Table 6.3.

Table 6.3: Experimental operating conditions used in the breakthrough experiments

<i>Run</i>	<i>Step</i>	<i>Feed composition</i>	<i>Feed Flow rate (SLPM)</i>	<i>Initial State</i>
<i>Single C₂H₄</i>	Adsorption	C ₂ H ₄	1	He
	Desorption	He	1	C ₂ H ₄
<i>Single C₃H₆</i>	Adsorption	C ₃ H ₆	1	He
	Desorption	He	1	C ₃ H ₆
<i>Single N₂</i>	Adsorption	N ₂	1	He
	Desorption	He	1	N ₂
<i>Binary C₂H₄/N₂</i>	Adsorption	C ₂ H ₄ /N ₂	0.3/0.7	He
	Desorption	He	1	C ₂ H ₄ /N ₂
<i>Binary C₃H₆/N₂</i>	Adsorption	C ₃ H ₆ /N ₂	0.3/0.7	He
	Desorption	He	1	C ₃ H ₆ /N ₂
<i>Pseudo-Binary C₂H₄/N₂</i>	Adsorption	C ₂ H ₄	1	N ₂
	Desorption	N ₂	1	C ₂ H ₄
<i>Pseudo-Binary C₃H₆/N₂</i>	Adsorption	C ₃ H ₆	1	N ₂
	Desorption	N ₂	1	C ₃ H ₆

As discussed previously, the breakthrough curve experiments not only allow for the determination of any kinetic limitations to the adsorption process but also add tremendous value to the validation of the single and multicomponent equilibrium models, as well as the fixed bed mathematical model used to correlate the behavior of the breakthroughs. The following Figures 6.6 to 6.33 show the molar flowrate breakthrough curves and temperature histories at 0.07, 0.32, and 0.57 m from the bed outlet, obtained for the breakthrough experiments described in Table 6.3. As previously explained in Chapter 3.4, the top thermocouple (the one at 0.07 m from the bed outlet) measured the temperature at the wall of the column. All experimental data is represented by points in these graphics, while the simulation results are plotted as lines.

Figures 6.6 to 6.17 show the breakthrough curves and temperature histories obtained from the single component breakthrough experiments for the adsorption and desorption of ethylene, propylene, and nitrogen. As demonstrated by the presented results, the single component breakthroughs are adequately predicted by the fixed bed simulations, which validate the pure component adsorption equilibrium isotherm fitting proposed in the previous section. Additionally, as seen in Figures 6.6, 6.8, 6.10, 6.12, 6.14, and 6.16, no kinetic limitations or delays were observed between the experimental and simulated breakthrough curves. As such, it can be concluded that any separation involving ethylene, propylene, or nitrogen in MIL-100(Fe) will be entirely adsorption equilibrium-based under similar conditions. From Figures 6.7, 6.11, and 6.15, increasing temperature spikes of 1.5, 13, and 37 K can be observed for the adsorption of nitrogen, ethylene, and propylene, respectively, which are in agreement with the increasing adsorption enthalpy determined by the Langmuir isotherm fittings.

Figures 6.18 to 6.25 represent the binary breakthrough curves and temperature histories obtained for the adsorption and desorption of the 30/70 %(v/v) ethylene/nitrogen and propylene/nitrogen mixtures. While Figures 6.26 to 6.33 represent the pseudo-binary breakthrough curves and temperature histories obtained for the adsorption of ethylene and propylene over a bed initially filled with nitrogen and the desorption using flowing nitrogen of a bed filled with ethylene or propylene. From these figures, a good correlation between

the experimental and simulated curves can be observed, which leads to the conclusion that the extended Langmuir fitting model can also accurately predict the multicomponent behavior of nitrogen, ethylene, and propylene on MIL-100(Fe). Important information can be retrieved from the multicomponent breakthroughs, the binary breakthroughs are indirectly simulating the fixed bed behavior under a “Feed” step, while the pseudo-binaries of ethylene and propylene over nitrogen and nitrogen over ethylene and propylene are, respectively, simulating the behavior of fixed bed during the “Rinse” and “Purge” steps.

In the pseudo-binary breakthroughs, the adsorption of ethylene and propylene over nitrogen created a roll-up effect that was not recreated during the simulation; however, since the breakthrough times are still being accurately predicted this discrepancy was ignored.

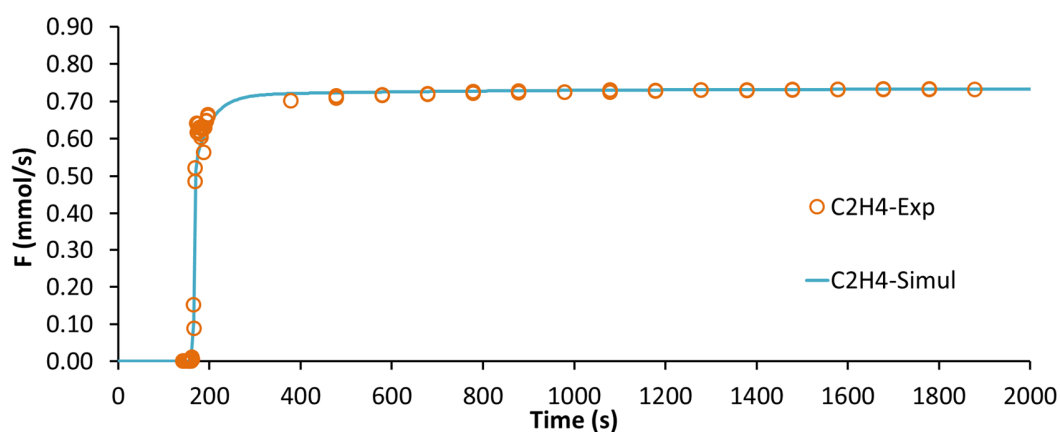


Figure 6.6: Breakthrough Curve for the adsorption of C_2H_4 in a bed initially filled with He at 323 K and 2 bar

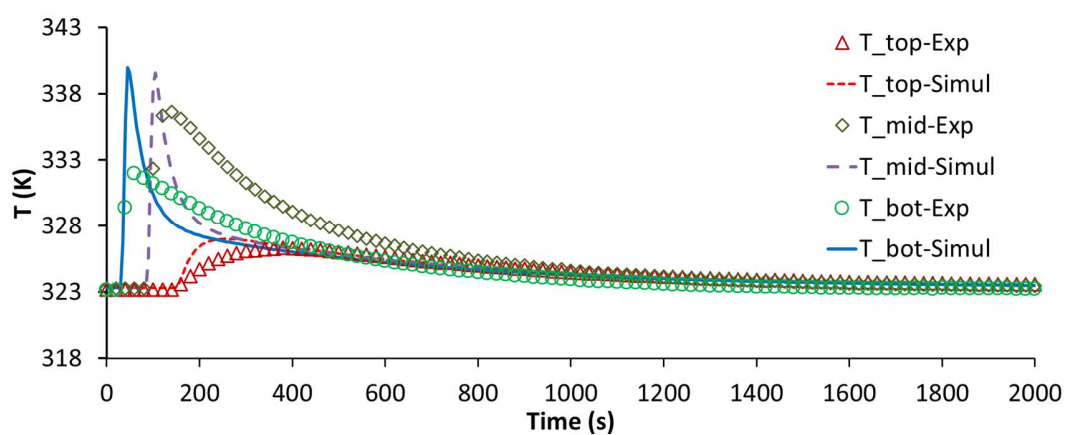


Figure 6.7: Temperature Histories at 0.07, 0.32 and 0.57 m from the outlet for the adsorption of C_2H_4 in a bed initially filled with He at 323 K and 2 bar

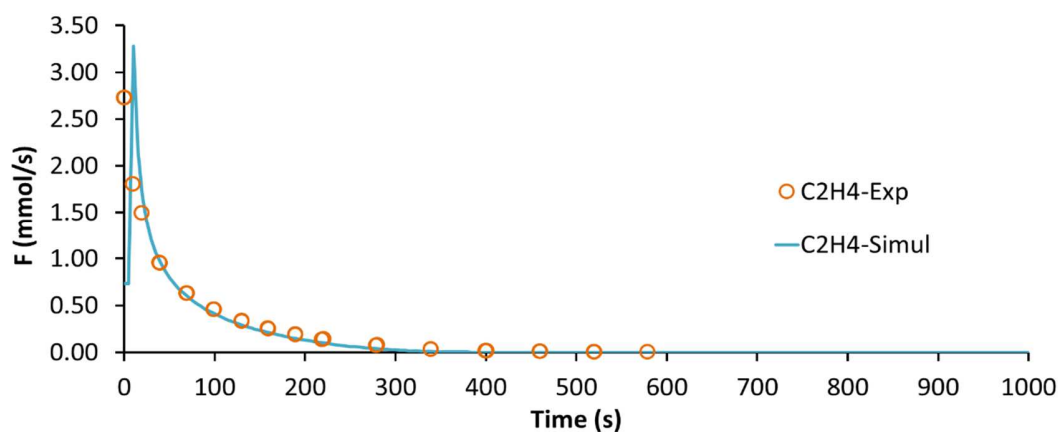


Figure 6.8: Breakthrough Curve for the desorption of the previous C_2H_4 by flowing He at 323 K and 2 bar

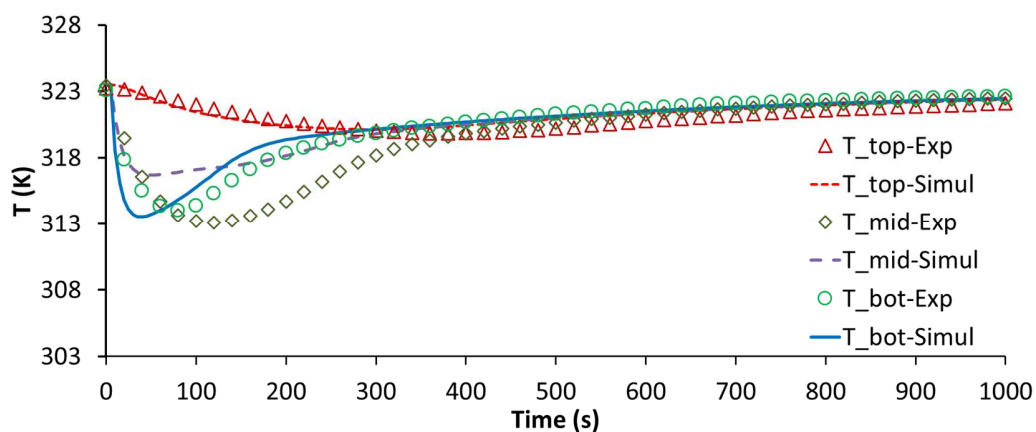


Figure 6.9: Temperature Histories at 0.07, 0.32 and 0.57 m from the outlet for the desorption of the previous C_2H_4 by flowing He at 323 K and 2 bar

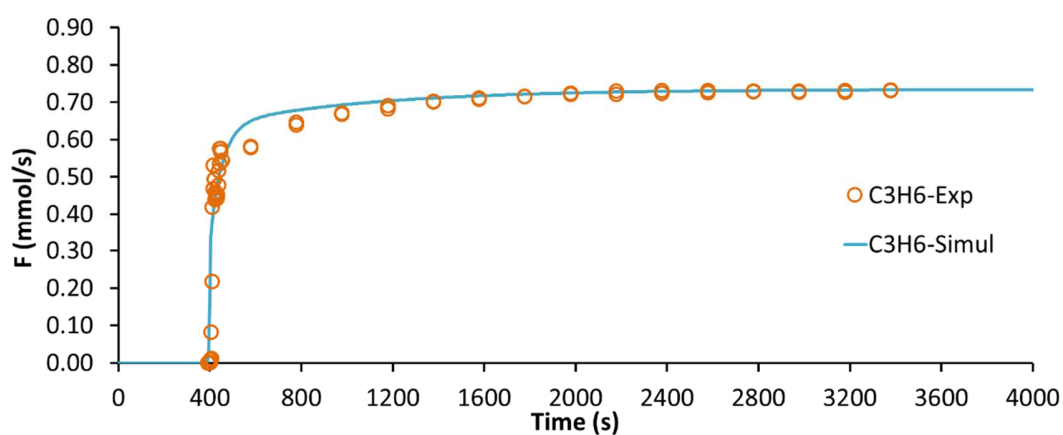


Figure 6.10: Breakthrough Curve for the adsorption of C_3H_6 in a bed initially filled with He at 323 K and 2 bar

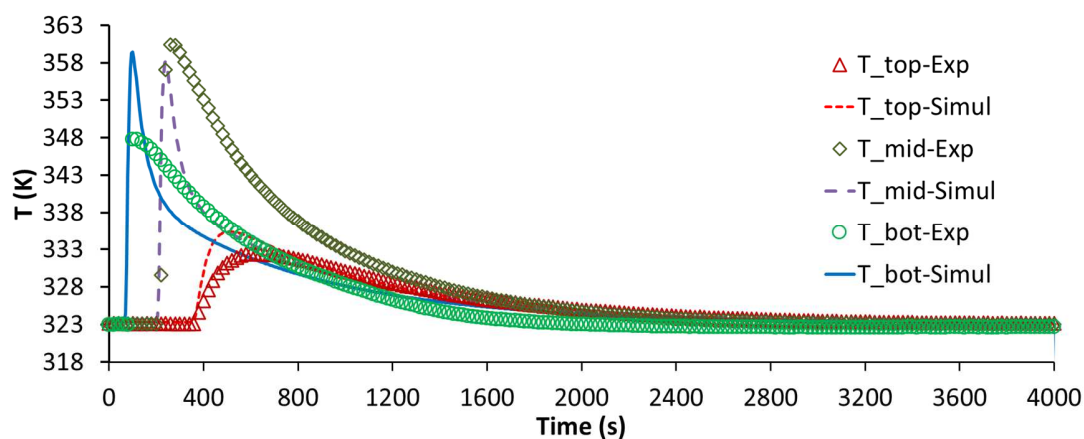


Figure 6.11: Temperature Histories at 0.07, 0.32 and 0.57 m from the outlet for the adsorption of C_3H_6 in a bed initially filled with He at 323 K and 2 bar

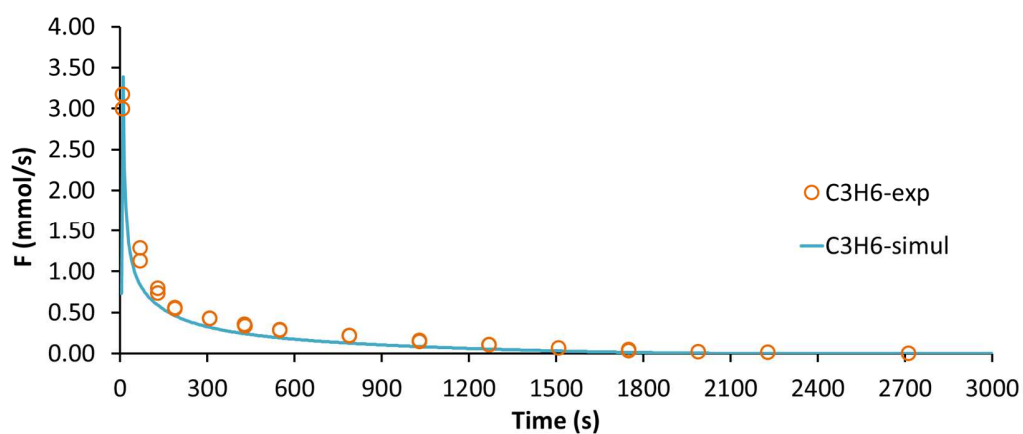


Figure 6.12: Breakthrough Curve for the desorption of the previous C_3H_6 by flowing He at 323 K and 2 bar

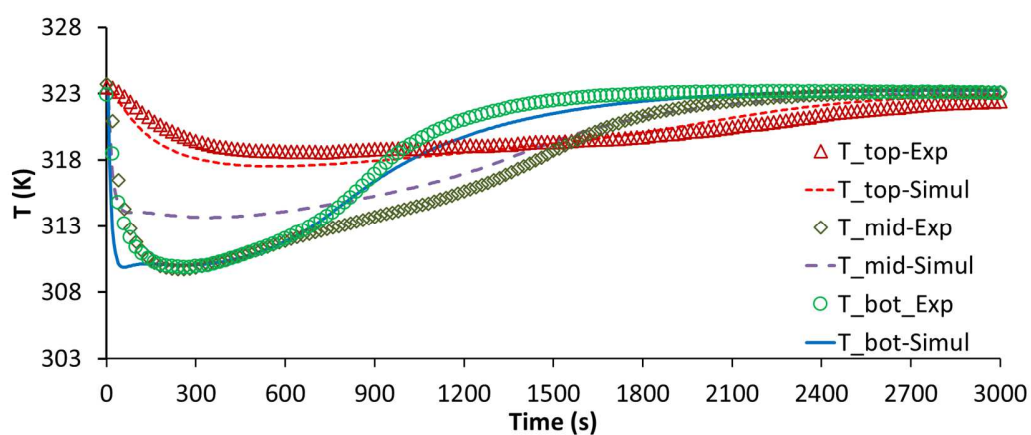


Figure 6.13: Temperature Histories at 0.07, 0.32 and 0.57 m from the outlet for the desorption of the previous C_3H_6 by flowing He at 323 K and 2 bar

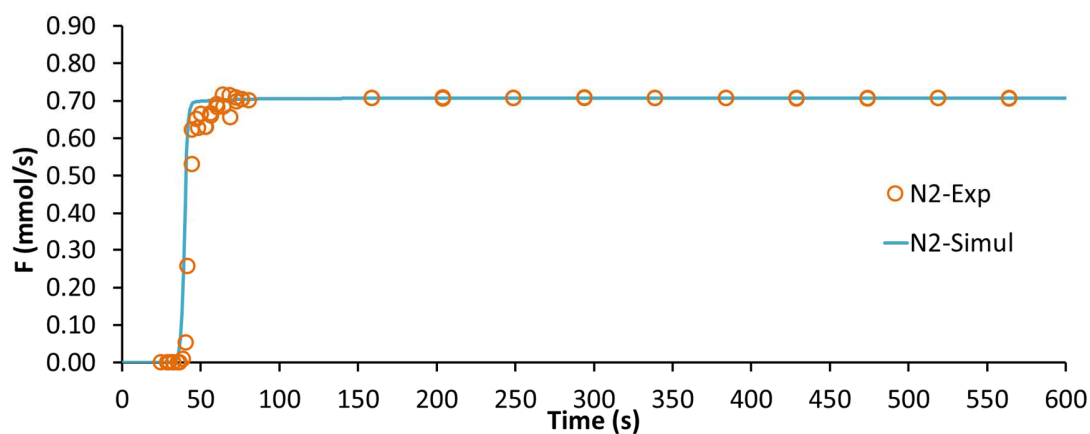


Figure 6.14: Breakthrough Curve for the adsorption of N_2 in a bed initially filled with He at 323 K and 2 bar

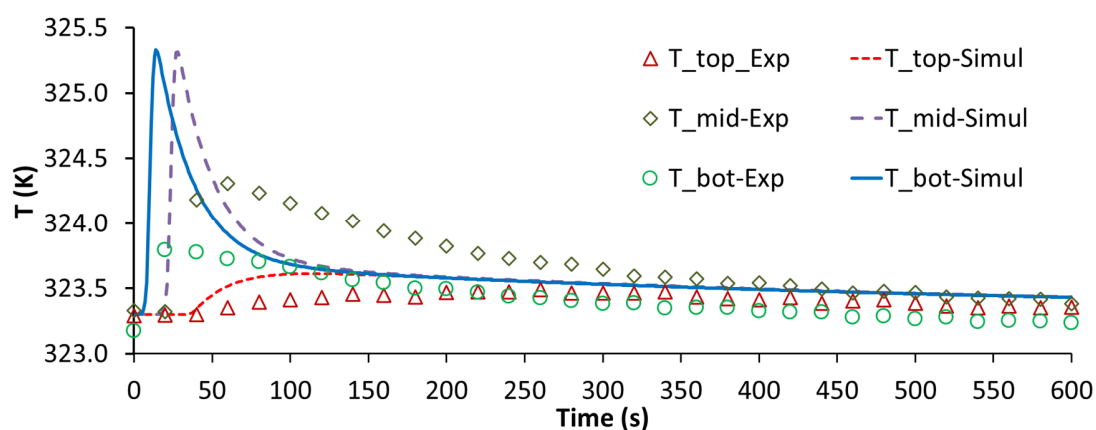


Figure 6.15: Temperature Histories at 0.07, 0.32 and 0.57 m from the outlet for the adsorption of N_2 in a bed initially filled with He at 323 K and 2 bar

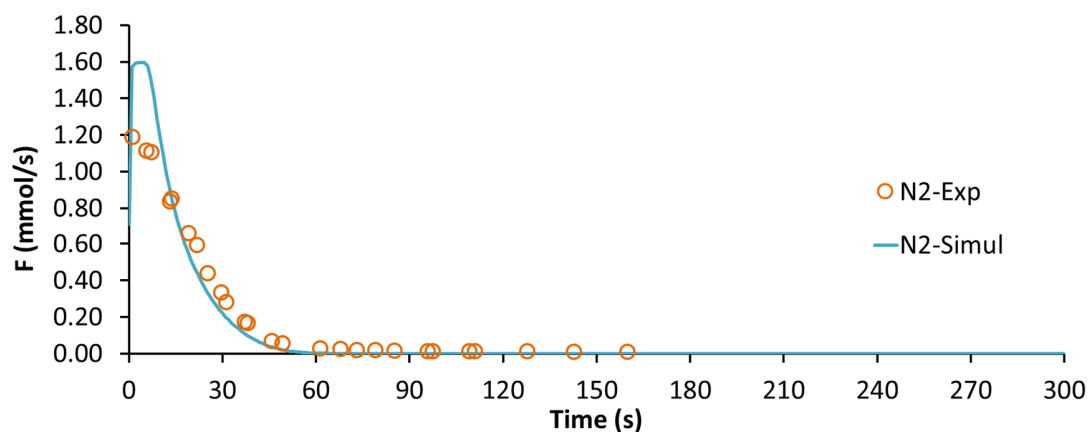


Figure 6.16: Breakthrough Curve for the desorption of the previous N_2 by flowing He at 323 K and 2 bar

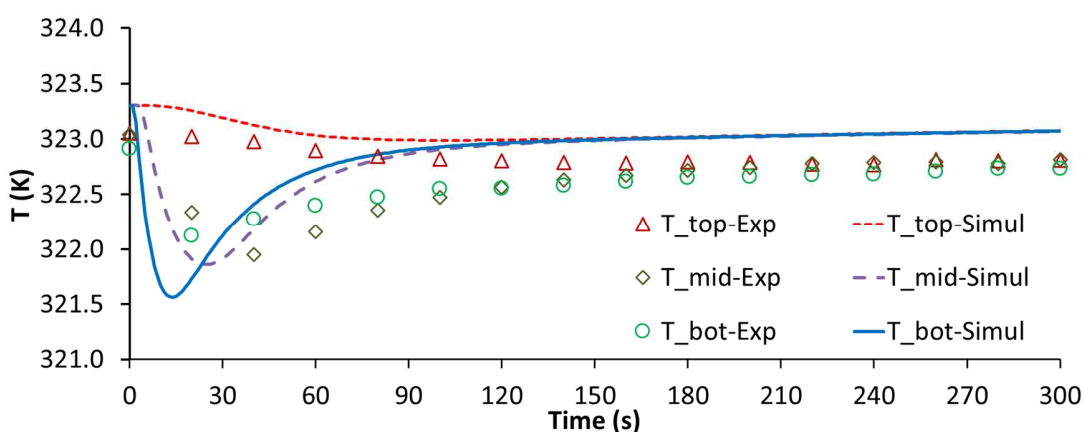


Figure 6.17: Temperature Histories at 0.07, 0.32 and 0.57 m from the outlet for the desorption of the previous N_2 by flowing He at 323 K and 2 bar

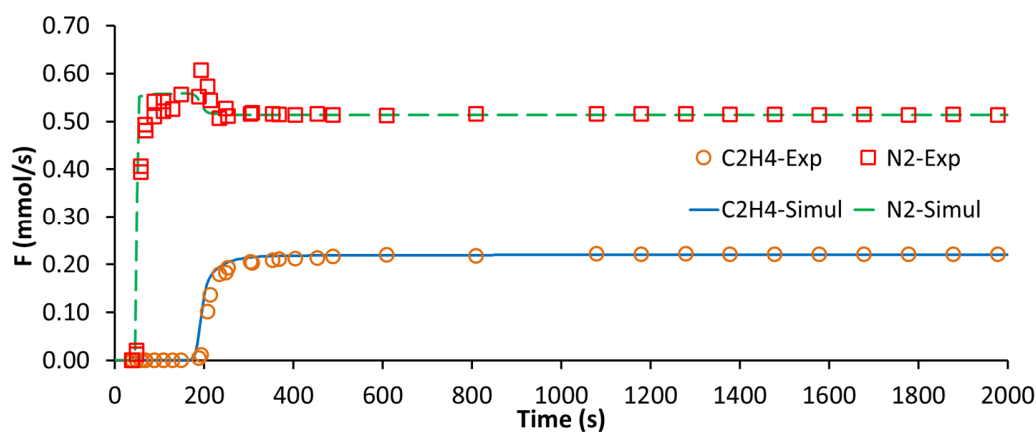


Figure 6.18: Breakthrough Curve for the adsorption of a 30/70 C_2H_4/N_2 mixture in a bed initially filled with He at 323 K and 2 bar

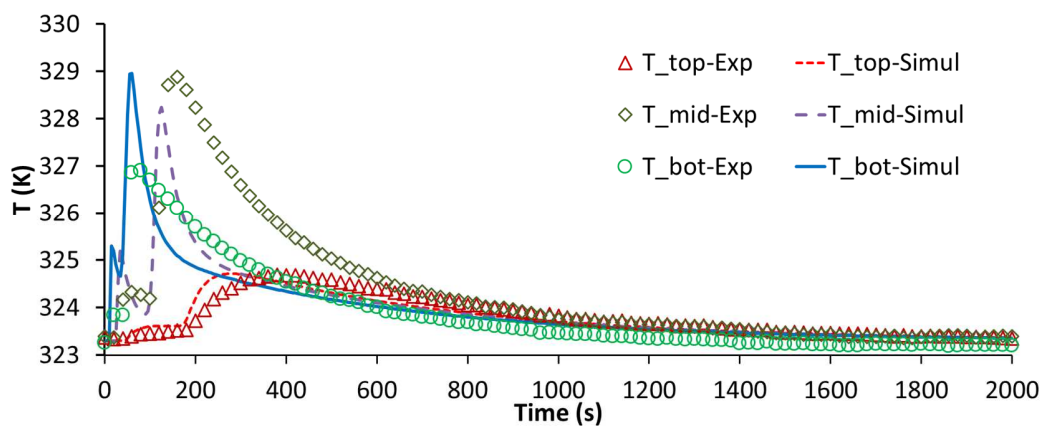


Figure 6.19: Temperature Histories at 0.07, 0.32 and 0.57 m from the outlet for the adsorption of a 30/70 C₂H₄/N₂ mixture in a bed initially filled with He at 323 K and 2 bar

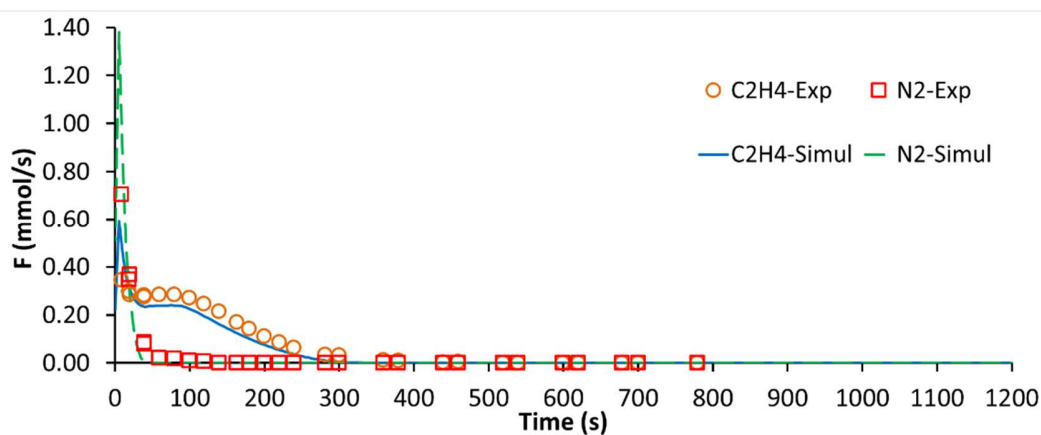


Figure 6.20: Breakthrough Curve for the desorption of the previously adsorbed 30/70 C₂H₄/N₂ mixture by flowing He at 323 K and 2 bar

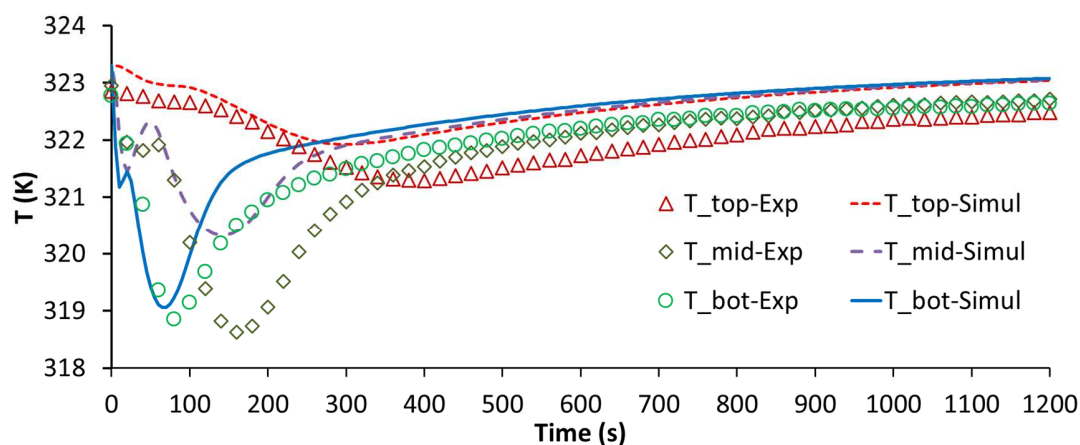


Figure 6.21: Temperature Histories at 0.07, 0.32 and 0.57 m from the outlet for the desorption of the previous 30/70 C₂H₄/N₂ mixture by flowing He at 323 K and 2 bar

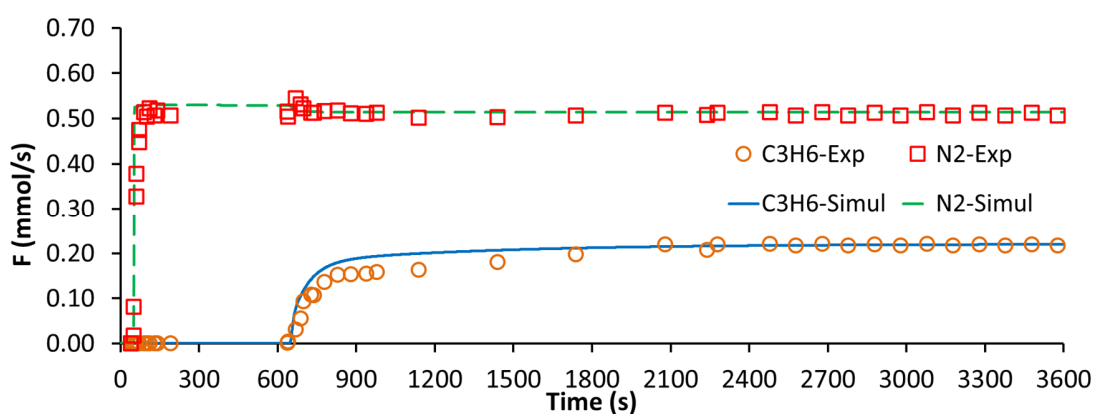


Figure 6.22: Breakthrough Curve for the adsorption of a 30/70 C_3H_6/N_2 mixture in a bed initially filled with He at 323 K and 2 bar

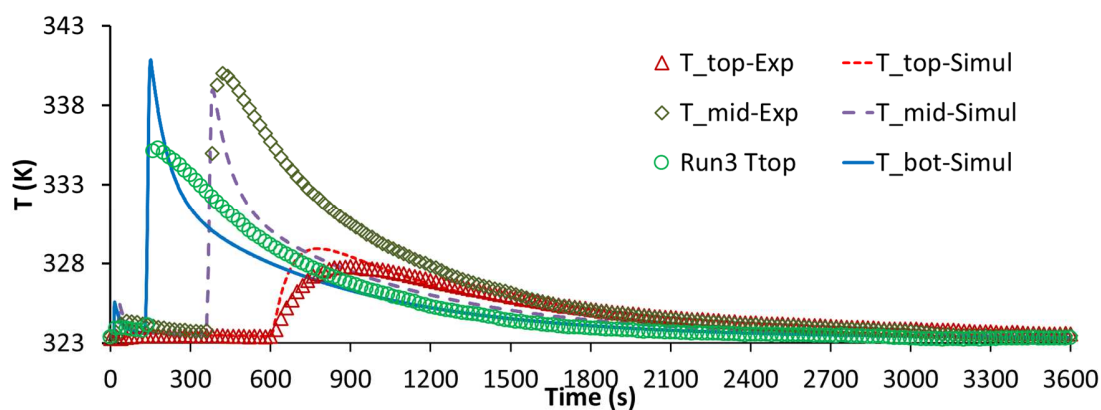


Figure 6.23: Temperature Histories at 0.07, 0.32 and 0.57 m from the outlet for the adsorption of a 30/70 C_3H_6/N_2 mixture in a bed initially filled with He at 323 K and 2 bar

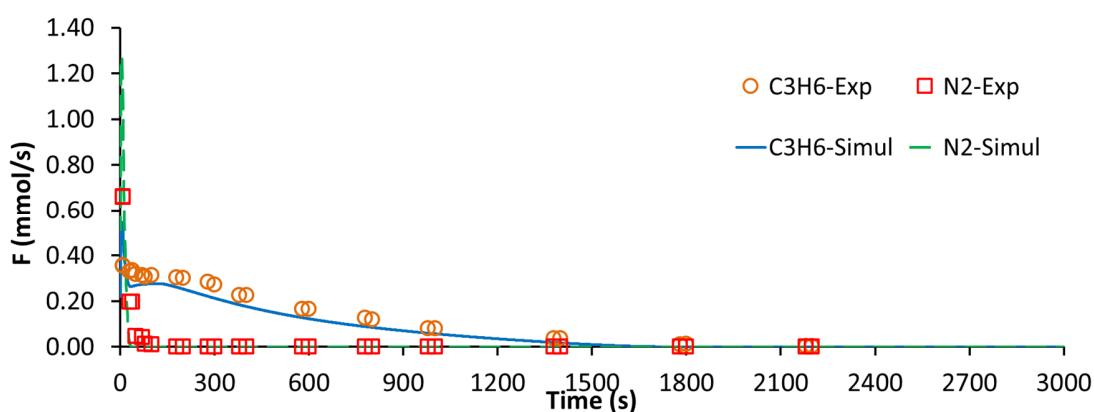


Figure 6.24: Breakthrough Curve for the desorption of the previous 30/70 C_3H_6/N_2 mixture by flowing He at 323 K and 2 bar

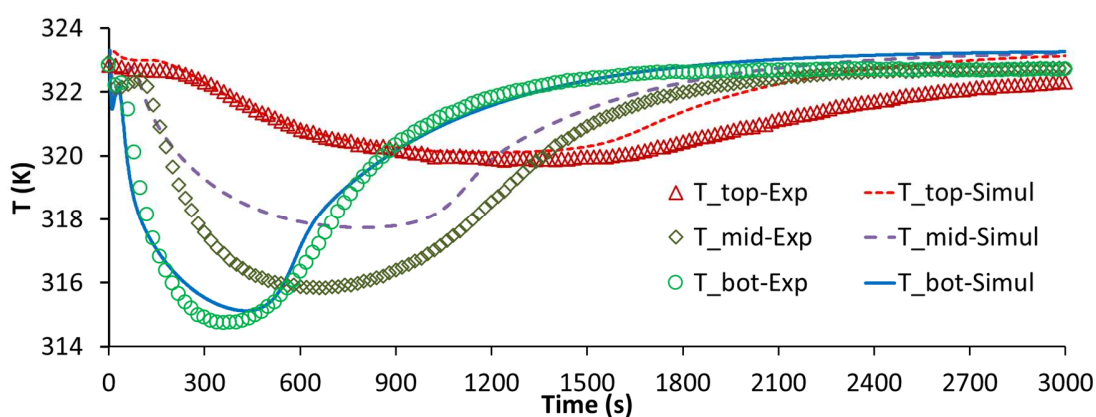


Figure 6.25: Temperature Histories at 0.07, 0.32 and 0.57 m from the outlet for the desorption of the previous 30/70 $\text{C}_3\text{H}_6/\text{N}_2$ mixture by flowing He at 323 K and 2 bar

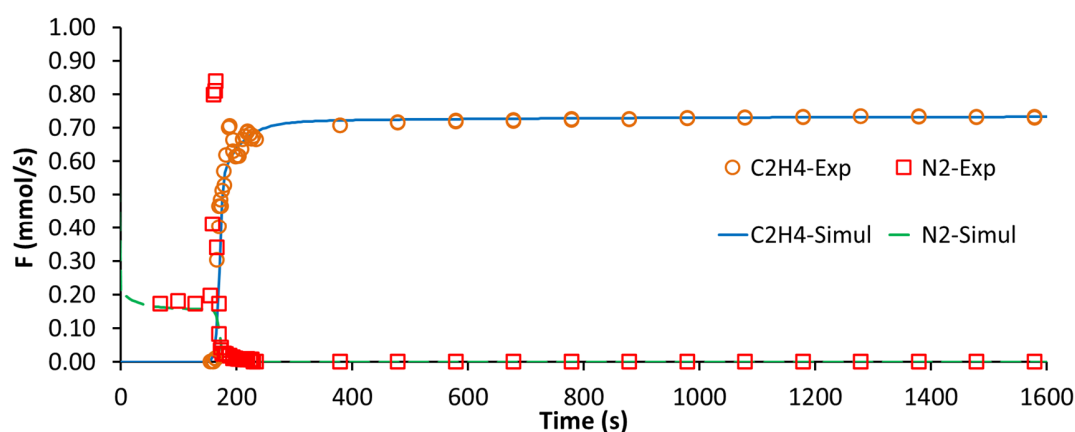


Figure 6.26: Breakthrough Curve for the adsorption of C_2H_4 in a bed initially filled with N_2 at 323 K and 2 bar

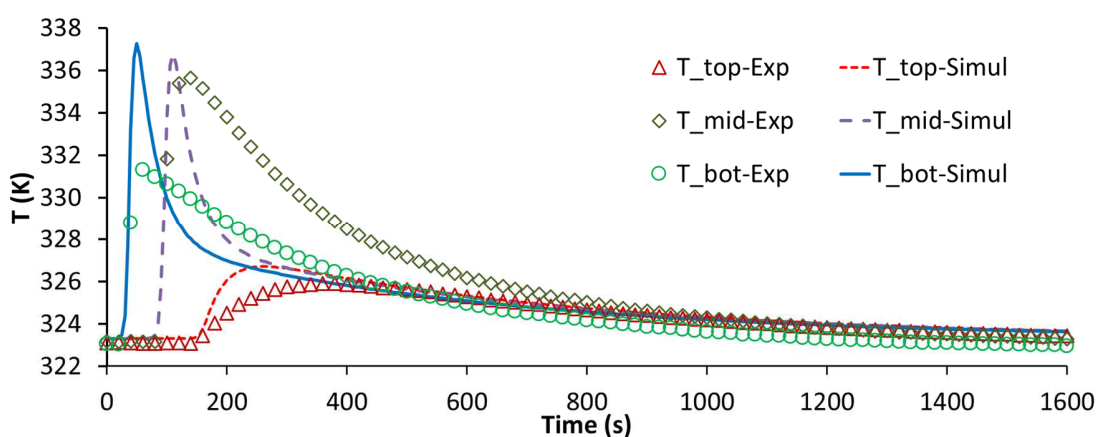


Figure 6.27: Temperature Histories at 0.07, 0.32 and 0.57 m from the outlet for the adsorption of C_2H_4 in a bed initially filled with N_2 at 323 K and 2 bar

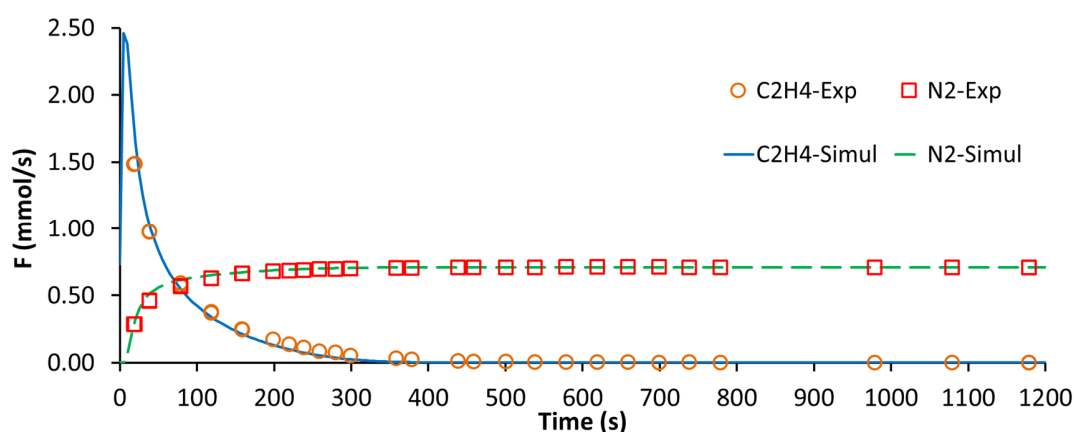


Figure 6.28: Breakthrough Curve for the desorption of the previously adsorbed C_2H_4 by flowing N_2 at 323 K and 2 bar

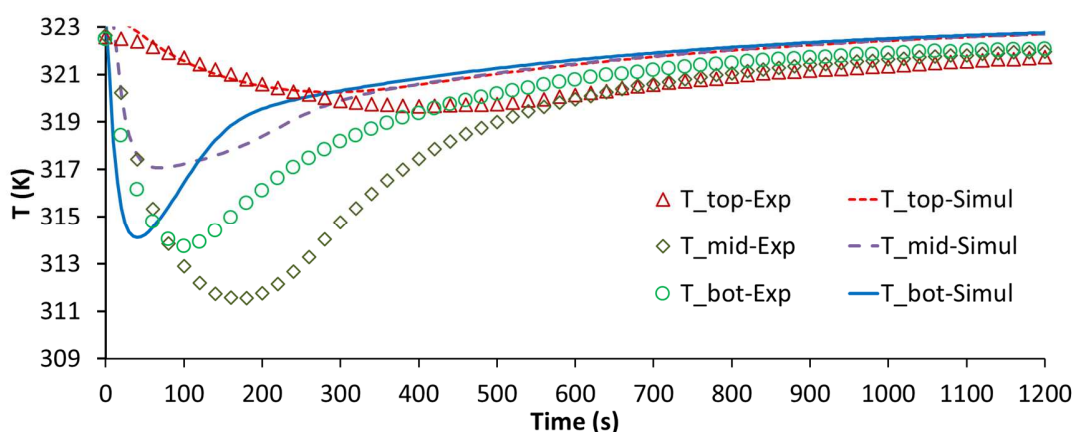


Figure 6.29: Temperature Histories at 0.07, 0.32 and 0.57 m from the outlet for the desorption of the previous C_2H_4 by flowing N_2 at 323 K and 2 bar

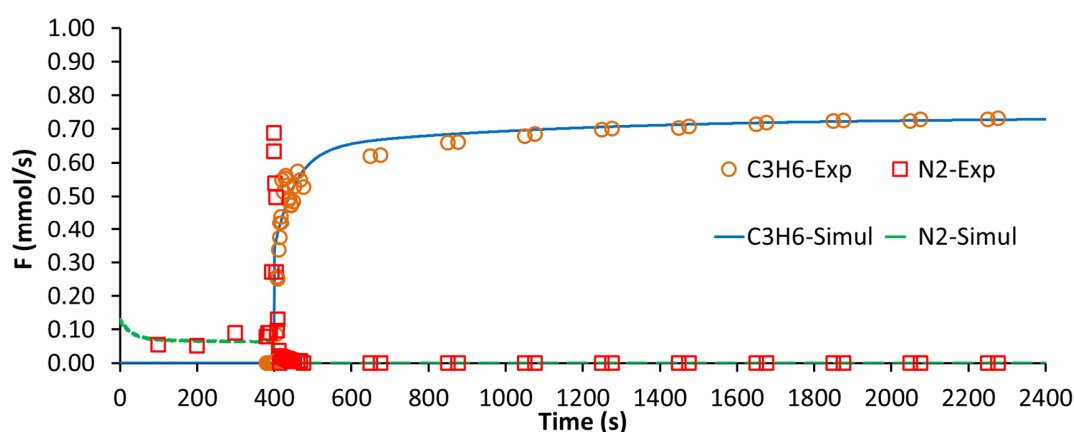


Figure 6.30: Breakthrough Curve for the adsorption of C_3H_6 in a bed initially filled with N_2 at 323 K and 2 bar

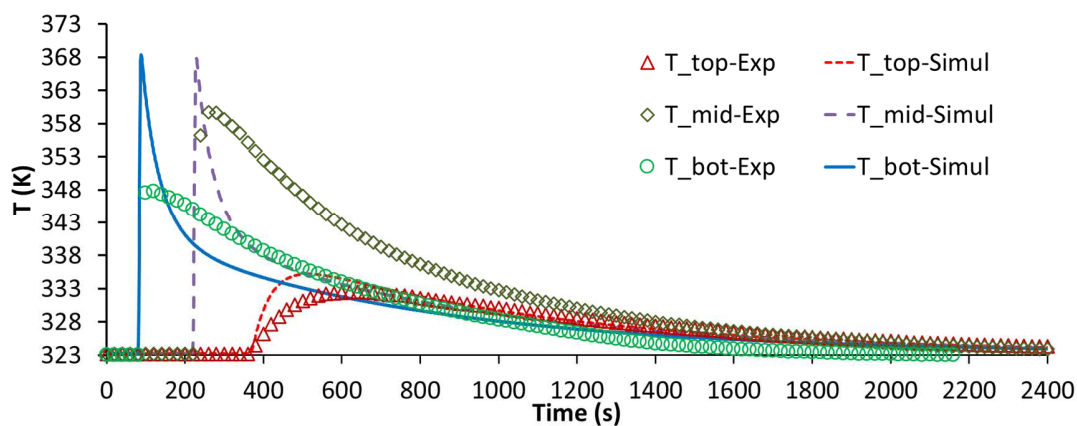


Figure 6.31: Temperature Histories at 0.07, 0.32 and 0.57 m from the outlet for the adsorption of C_3H_6 in a bed initially filled with N_2 at 323 K and 2 bar

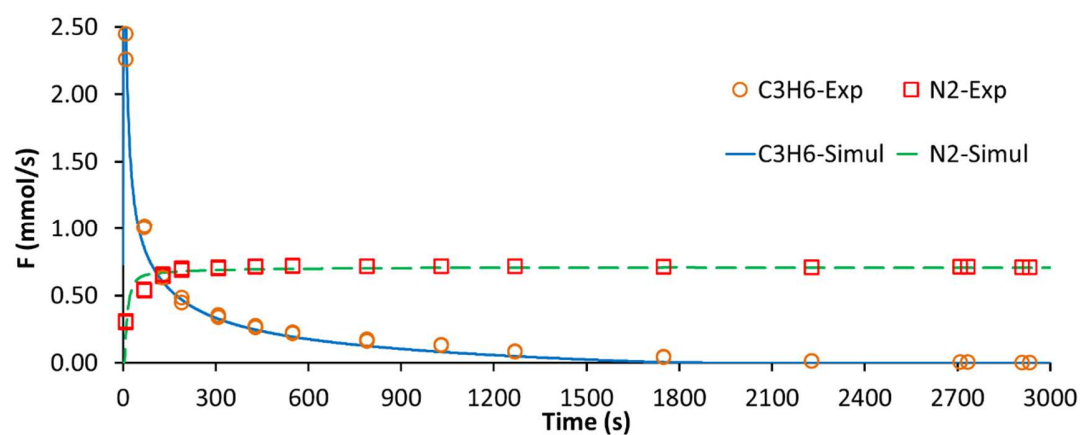


Figure 6.32: Breakthrough Curve for the desorption of the previous C_3H_6 by flowing N_2 at 323 K and 2 bar

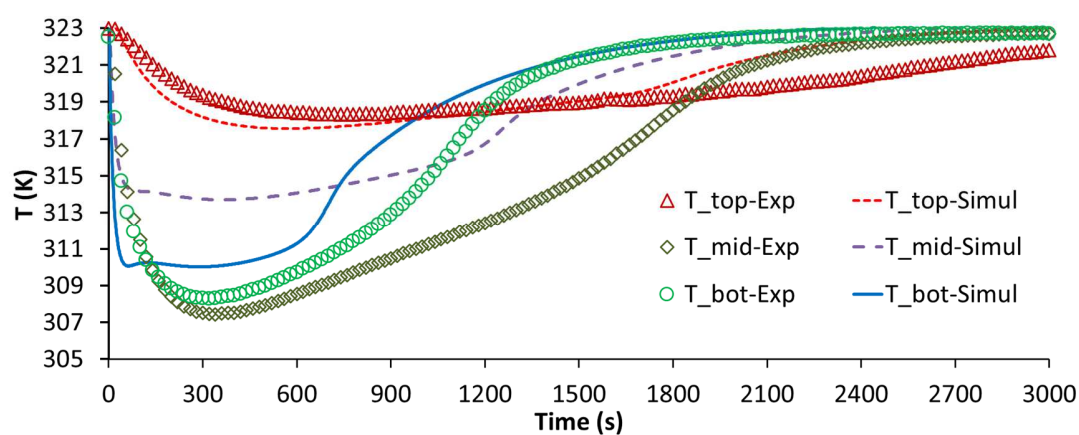


Figure 6.33: Temperature Histories at 0.07, 0.32 and 0.57 m from the outlet for the desorption of the previous C_3H_6 by flowing N_2 at 323 K and 2 bar

6.5. Ethylene/Nitrogen Separation

6.5.1. PSA Cycle Design

Although as seen from Figure 6.3, ethylene presents a favorable isotherm shape for most of the measured temperatures, a superior separation performance was obtained for a feed temperature of 343 K. At this temperature; Figure 6.34 presents a comparison of the predicted Langmuir isotherms for ethylene and nitrogen. The nitrogen Langmuir isotherm parameters used are listed in Table 5.2. From this comparison, ethylene/nitrogen selectivity is calculated at feed conditions for the value of 7.73. Although this selectivity is not high, the Rinse step's correct application should help to compensate for the expected lower purity of ethylene product. As such, the proposed PSA system will be operated in a pressure range of 0.3 to 9 bar and under an inlet and external temperature of 343 K, which will require that the feed mixture proposed in Chapter 6.1 be heated up and pressurized to the updated operating conditions.

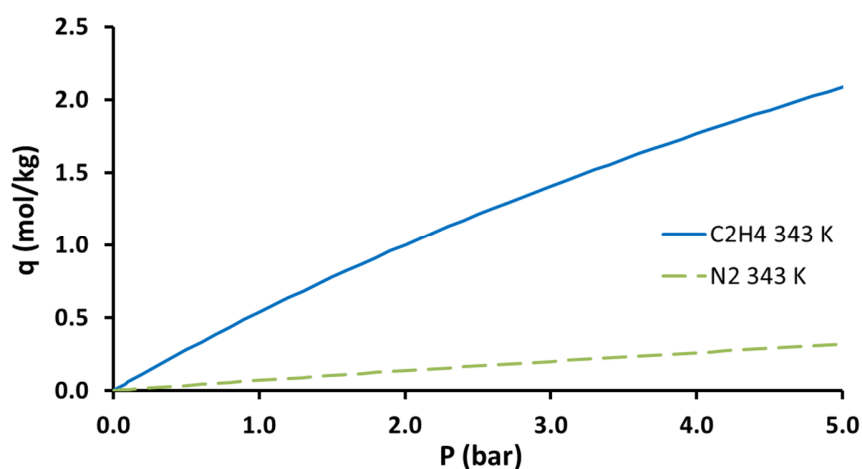


Figure 6.34: DSL isotherm model predictions for ethylene and N₂ at 343 K on the MIL-100(Fe)

The simulation of the present PSA system will follow the 1D fixed bed mathematical model and the initial and boundary conditions reported in chapter 4.7.1 for PSA cycles. The mass and thermal transport parameters were estimated using the correlations described in Chapter 4.8, at the new feed conditions and are presented in Table 6.4. Also, the blowdown

process will be controlled by a valve system following an exponential depressurization function. As similarly described in Chapter 5.4.1, the sizing of the PSA unit was estimated taking into consideration the feed flow rate conditions and the cross-section area of the column necessary to achieve an inlet velocity equal to a fraction of the minimum fluidization velocity. The length of the adsorption column was estimated considering a minimum column length to diameter ratio of 4. Following these considerations, a PSA unit with the physical properties listed in Table 6.5 was designed.

Table 6.4: Transport Parameter values used in the C₂H₄/N₂ PSA Simulation calculated at feed conditions

Axial Mass Dispersion	4.73 X 10 ⁻⁴	<i>m²/s</i>
Axial Heat Dispersion	1.06	<i>W/(m.K)</i>
Mixture Viscosity	1.65 X 10 ⁻⁵	<i>Pa.s</i>
Particle Heat Transfer Coefficient	161	<i>W/(m².K)</i>
Wall Heat Transfer Coefficient	718	<i>W/(m².K)</i>
External Heat Transfer Coefficient	44.7	<i>W/(m².K)</i>

Table 6.5: Physical and Sizing properties parameters used for the C₂H₄/N₂ PSA simulations

Column Length	10	<i>m</i>
Bed Diameter	2	<i>m</i>
Column Diameter	2.01	<i>m</i>
Bed Porosity	0.37	-
Total Adsorbent Mass	10681	<i>kg</i>

6.5.2. PSA Cycle Simulation Results

For the separation of the proposed 30/70 % ethylene/nitrogen mixture, a MIL-100(Fe) PSA system with the sizing properties listed in Table 6.5 and following the cycle step schedule and operating conditions listed in Table 6.6 is suggested. Following the cycle step schedule listed in Table 6.6, the proposed PSA cycle can be extended into a triple bed PSA system to guarantee a continuous feed consumption and product outlet, as illustrated in Figure 6.35.

As listed in Table 6.7, the reported MIL-100(Fe) PSA system is capable of producing a nitrogen stream with ethylene contamination of 1.90 ppm, and an ethylene stream with purity of 95.00 %. An ethylene productivity and recovery capacity of 2.23 mol/(kg_{ads}·h) and 21.03 kg_{C₂H₄}/(m³_{unit}·h), respectively, were obtained with a total equivalent thermal energy consumption of 10.13 MJ/kg_{C₂H₄}.

Table 6.6: Proposed C₂H₄/N₂ PSA Simulation Cycle step conditions

Steps	Step time (s)	Pressure (bar)	Flow Rate (Nm ³ /h)
Feed	380	9.0	5400
Rinse	300	9.0	5400
Blowdown	130	9.0 → 0.3	-
Purge	200	0.3	420
Pressurization	130	0.3 → 9.0	6900

Feed			Rinse		Blow	Purge	P	
B	Purge	P	Feed			Rinse		B
Rinse		Blow	Purge	P	Feed			

Figure 6.35: Extension of the proposed C₂H₄/N₂ PSA schedule to a 3 column system

Table 6.7: Detailed C₂H₄/N₂ PSA Cycle Performance Results

C ₂ H ₄ Purity	95.00	% (<i>v/v</i>)
C ₂ H ₄ in N ₂ Stream	1.90	<i>ppm</i> (<i>v/v</i>)
C ₂ H ₄ Recovery	99.99+	% (<i>v/v</i>)
N ₂ Recovery	97.74	% (<i>v/v</i>)
C ₂ H ₄ Productivity	2.23	<i>mol/(kg_{ads} · h)</i>
N ₂ Productivity	5.08	<i>mol/(kg_{ads} · h)</i>
Energy Consumption	10.13	<i>MJ/kg_{C2H4}</i>
C ₂ H ₄ Recovery Capacity	21.03	<i>kg_{C2H4}/(m³_{unit} · h)</i>

To better understand and analyze the behavior of the designed MIL-100(Fe) C₂H₄/N₂ PSA system, the proposed cycle was simulated until CSS was achieved. Figures 6.36 and 6.37 represent the temperature and pressure histories at the start, halfway, and end of the adsorption column. Figure 6.38 displays the outlet volumetric flow rate for each component at CSS. Figures 6.39 to 6.42 show the gas and solid phase concentration profiles for C₂H₄ and N₂ at the end of each PSA step.

Due to the larger size of the PSA unit, even though the adsorption column was not operated under an adiabatic regime, a high internal temperature range of 315 to 380 K was still registered throughout the cycle, as shown in Figure 6.36. The increased operating pressure range, seen in Figure 6.37, was used to achieve the 95% C₂H₄ purity requirement without increasing the already high adsorbent load (10681 kg). Indeed, the resulting increased adsorption/desorption amounts of C₂H₄ was also the main cause behind the high temperature variations along the cycle. Mostly pure N₂ is produced during the Feed and Rinse steps, while C₂H₄ is produced during the Blowdown step. During the Purge step, smaller quantities of C₂H₄ are also produced together with a higher concentration of N₂. As seen from Figure 6.41, due to the linearity of the C₂H₄ isotherm, a high quantity of C₂H₄ is required for the Rinse step. Also, as predicted by the results of the pseudo-binary breakthrough experiments, the purge step shows a significant effect in regenerating the adsorbed C₂H₄, during which the C₂H₄ front has significantly receded.

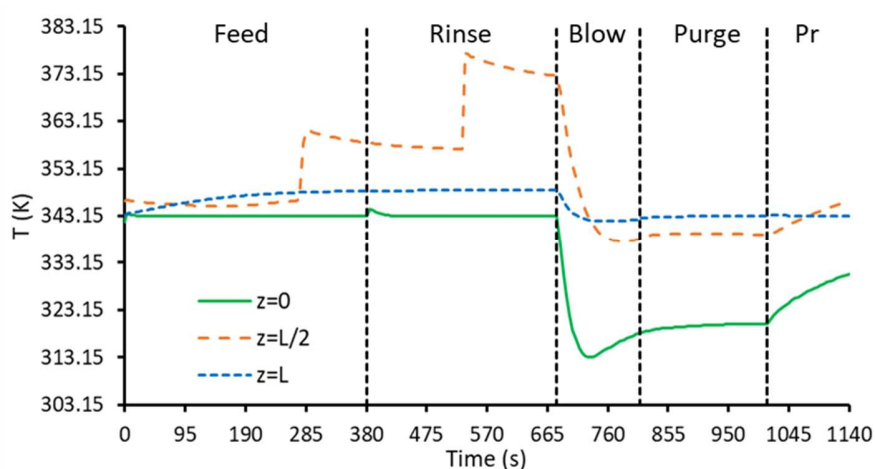


Figure 6.36: Temperature History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF for the ethylene/nitrogen PSA cycle

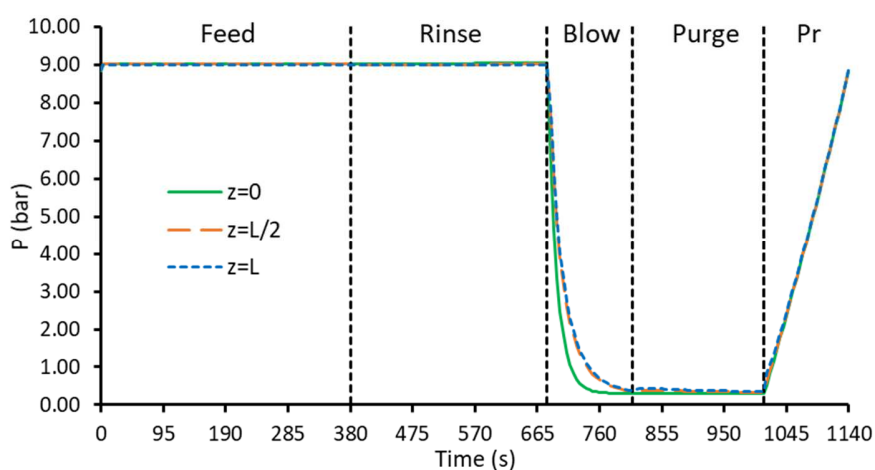


Figure 6.37: Pressure History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF for the ethylene/nitrogen PSA cycle

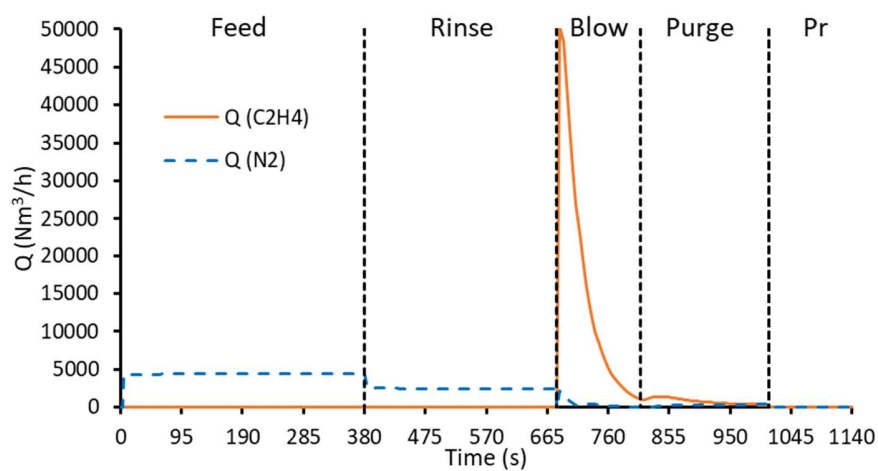


Figure 6.38: Outlet Flowrate History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF for the ethylene/nitrogen PSA cycle

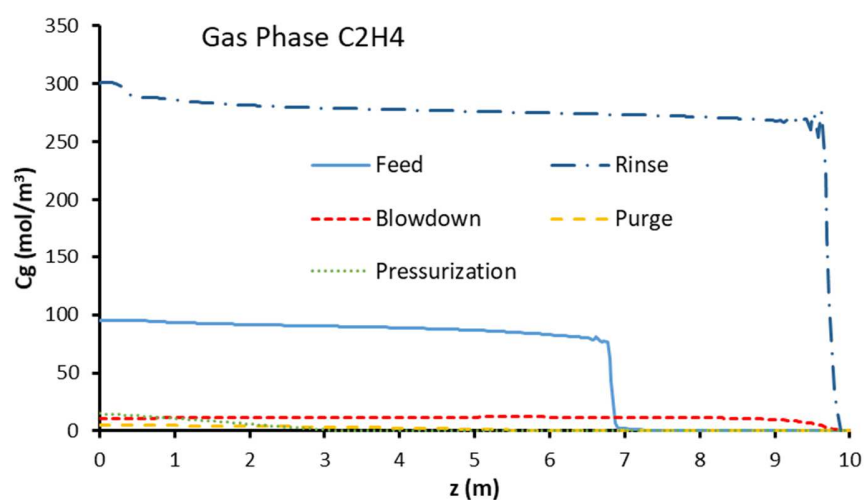


Figure 6.39: Ethylene Gas-Phase Concentration Profile, during CSS, at the end of each step of the ethylene/nitrogen PSA cycle

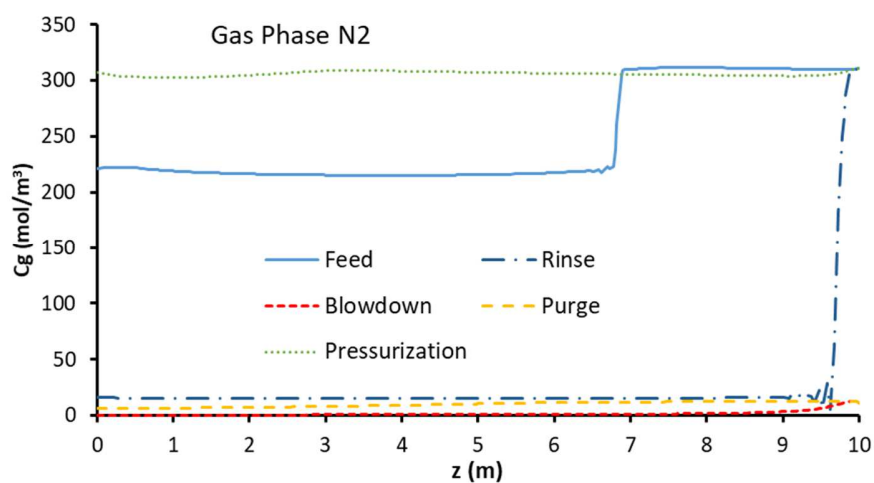


Figure 6.40: Nitrogen Gas-Phase Concentration Profile, during CSS, at the end of each step of the ethylene/nitrogen PSA cycle

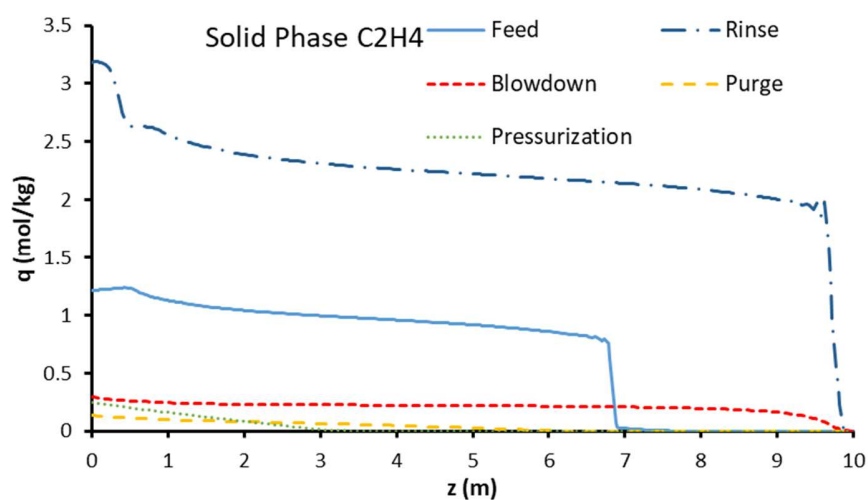


Figure 6.41: Ethylene Solid-Phase Concentration Profile, during CSS, at the end of each step of the ethylene/nitrogen PSA cycle

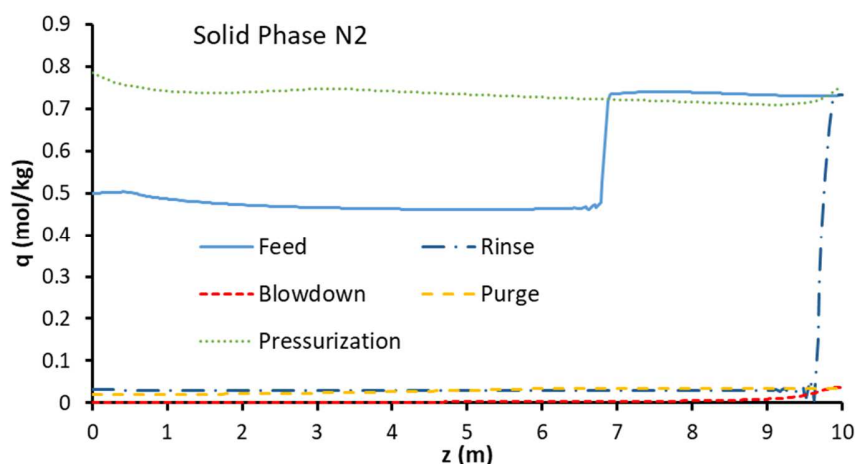


Figure 6.42: Nitrogen Solid-Phase Concentration Profile, during CSS, at the end of each step of the ethylene/nitrogen PSA cycle

6.5.3. MT-TPSA Cycle Design

For the development of the MT-TPSA cycle, a temperature range of 303 to 393 K was chosen to maximize the useful adsorption capacity of ethylene and the ethylene/nitrogen selectivity during the Feed step. By comparing the predicted Langmuir isotherms for ethylene and nitrogen on Figure 6.43, an ethylene/nitrogen selectivity of 8.62 and 5.51 can be calculated for the temperatures of 303 and 393 K. As such, taking into account the results of the breakthrough experiments, the MT-TPSA cycle will operate between a pressure and temperature range of 1 to 3 bar, and 303 to 393 K.

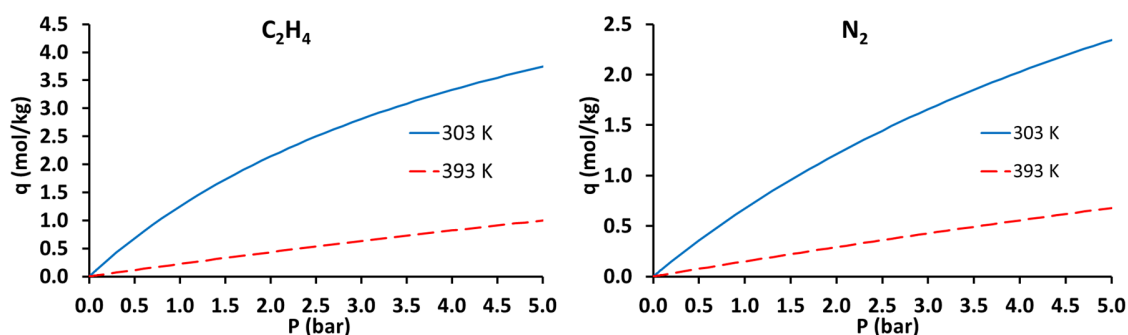


Figure 6.43: Comparison of the Langmuir isotherm model predictions for ethylene and N_2 at 303 and 393 K on the MIL-100(Fe) MOF

Since the performance validation of the equivalent 1D MT-TPSA cycle model, successfully proven in Chapter 5, should not be significantly affected by the composition of the feed mixture, then the MT-TPSA cycle designs developed in this Chapter will also follow the same model. Likewise, the tube sizing and shell design will be kept identical to the properties detailed in Chapter 5. At the same time, the Blowdown step will also be controlled by a valve system following an exponential depressurization function. The mass and thermal transport parameters were calculated for the feed conditions, using the correlations shown in Chapter 4.8, and are shown in Table 6.8. As such, following these considerations, an MT-TPSA unit with the physical properties listed in Table 6.9 was designed.

Table 6.8: Transport Parameter values used in the C₂H₄/N₂ MT-TPSA Simulation calculated at feed conditions

Axial Mass Dispersion	7.30 X 10 ⁻⁴	<i>m</i> ² / <i>s</i>
Axial Heat Dispersion	2.08	<i>W</i> /(<i>m</i> . <i>K</i>)
Mixture Viscosity	1.50 X 10 ⁻⁵	<i>Pa.s</i>
Shell Side Heat Transfer Coefficient	1633	<i>W</i> /(<i>m</i> ² . <i>K</i>)
Particle Heat Transfer Coefficient	233	<i>W</i> /(<i>m</i> ² . <i>K</i>)
Tube Side Overall Heat Transfer Coefficient	51.04	<i>W</i> /(<i>m</i> ² . <i>K</i>)

Table 6.9: Physical and Sizing properties parameters used for the C₂H₄/N₂ MT-TPSA simulations

Tube Length	8.00	<i>m</i>
Tube Inner Diameter	29.35 x 10 ⁻³	<i>m</i>
Tube Outer Diameter	31.75 x 10 ⁻³	<i>m</i>
Tube Pitch	39.69 x 10 ⁻³	<i>m</i>
Tube Clearance	7.94 x 10 ⁻³	<i>m</i>
Bed Porosity	0.37	-
Tube Thickness	1.20 x 10 ⁻³	<i>m</i>

Number of Tubes	2051	-
Total Adsorbent Mass	3777	kg
Transfer Surface Area	1637	m ²
Tube Bundle Diameter	2.02	m
Shell Diameter	2.07	m
Baffle Spacing	0.53	m
Baffle Cut	25	%
Shell Inlet velocity	0.5	m/s

6.5.4. MT-TPSA Cycle Simulation Results

The proposed C₂H₄/N₂ MT-TPSA cycle is composed of six steps: Feed, Rinse, Blowdown, Purge, Cooldown, and a Counter-Current Pressurization, which if following the cycle schedule proposed in Table 6.10 will extend the cycle to a triple MTA unit system that guarantees both a continuous feed consumption and a continuous production of purified C₂H₄ and N₂ streams, as illustrated in Figure 6.44. Therefore, as shown in Tables 6.11 and 6.12, an MT-TPSA cycle guided by the proposed cycle step configuration and operating conditions will be capable of achieving the intended purity requirements. The present MT-TPSA system can reach a C₂H₄ productivity and recovery capacity of 6.30 mol/(kg_{ads}.h) and 24.48 kg_{C₂H₄}/(m³_{unit}.h) with a total power consumption of 20.83 MJ/kg_{C₂H₄}. Of the total thermal energy requirements, 75.0 % are being dedicated to account for the operation of the heat exchanger, 24.3 % are being used for the use of the gas-phase pressurization and vacuum pumps, and 0.7 % is being used for the shell-side liquid pumps. Of the thermal work required from the heat exchanger, only a low 8.6 % of the thermal energy is used to regenerate the adsorbed ethylene.

When compared to the performance of the respective PSA system, the only advantage of the MT-TPSA system lies in its higher productivity and lower adsorbent cost. As discussed in Section 5.8, if one considers that the thermal duties of the cooling stages are more cheaply accounted for due to the use of a water cooling tower, then the necessary thermal energy consumptions can be reduced to the energy required to operate the heating stages

and the electrical energy costs. However, even then, the MT-TPSA necessary heating and electrical energy costs (13.05 MJ/kg_{C₂H₄}) still outweigh the electrical energy costs of the PSA cycle (10.13 MJ/kg_{C₂H₄}). As stated previously, with only 8.6 % of the thermal energy being used in the regeneration of the adsorbate, much of the thermal energy supplied to the system is being wasted, which resulted in much higher energy costs. Due to the quasi-linear adsorption equilibrium and low adsorption enthalpy for ethylene adsorption, an ethylene/nitrogen mixture can be achieved more economically by pressure swing processes.

Feed			Rinse	Blow	Purge	Cool	P
Purge	Cool	P	Feed			Rinse	Blow
Rinse	Blow	Purge	Cool	P	Feed		

Figure 6.44: Extension of the proposed C₂H₄/N₂ MT-TPSA schedule to a 3-MTA unit system

Table 6.10: Proposed C₂H₄/N₂ MT-TPSA Simulation Cycle step conditions

Steps	Step time (s)	Pressure (bar)	External Temperature (K)	Flow Rate (Nm ³ /h)
Feed	290	8.0	303	5400
Rinse	110	8.0	303	7361
Blowdown	160	8.0 → 1.0	303 → 393	-
Purge	120	1.0	393	480
Cooldown	140	1.0 (→ 0.49)	393 → 303	-
Pressurization	50	0.49 → 8.0	303	7200

Table 6.11: Detailed C_2H_4/N_2 MT-TPSA Cycle Performance Results

C_2H_4 Purity	95.15	% (v/v)
C_2H_4 in N_2 Stream	16.67	ppm (v/v)
C_2H_4 Recovery	99.99+	% (v/v)
N_2 Recovery	97.82	% (v/v)
C_2H_4 Productivity	6.30	$mol/(kg_{ads} \cdot h)$
N_2 Productivity	14.37	$mol/(kg_{ads} \cdot h)$
Total Energy Consumption	20.81	$MJ/kg_{C_2H_4}$
Adsorption Cooling Duty	1.35	$MJ/kg_{C_2H_4}$
Heating Duty	7.82	$MJ/kg_{C_2H_4}$
Cooling Duty	6.44	$MJ/kg_{C_2H_4}$
Gas Pump Operation	5.06	$MJ/kg_{C_2H_4}$
Liquid Pump Operation	0.15	$MJ/kg_{C_2H_4}$

Table 6.12: C_2H_4 Productivity and Recovery Capacity for the C_2H_4/N_2 MT-TPSA

C_2H_4 Productivity	0.152	$kg_{C_2H_4}/(kg_{ads} \cdot h)$
Bed C_2H_4 Recovery Capacity	60.05	$kg_{C_2H_4}/(m_{bed}^3 \cdot h)$
Unit C_2H_4 Recovery Capacity	24.83	$kg_{C_2H_4}/(m_{unit}^3 \cdot h)$

At CSS, the analysis of the cycle behavior is very similar to the other MT-TPSA cycles reported in this work. Figures 6.45 and 6.46 represent the temperature and pressure histories at the start, halfway, and end of the adsorption column, while Figure 6.47 displays the outlet volumetric flow rate for each component at CSS. Figures 6.48 to 6.51 represent the gas and solid phase concentration profiles for C_2H_4 and N_2 at the end of each cyclic step listed in Table 6.10.

From Figure 6.45, it can be observed that as a response to the rapid desorption of ethylene at the beginning of the Blowdown step, a temperature drop is registered at the same time.

Likewise, during the Pressurization step, the system's internal temperature also slightly increases due to the adsorption of nitrogen and any remaining gas-phase ethylene. In Figure 6.46, the gradual pressure increase seen during the Rinse step at the entrance, and to a minor degree at halfway of the column is caused by the use of a rinse flowrate higher than the proposed feed flowrate.

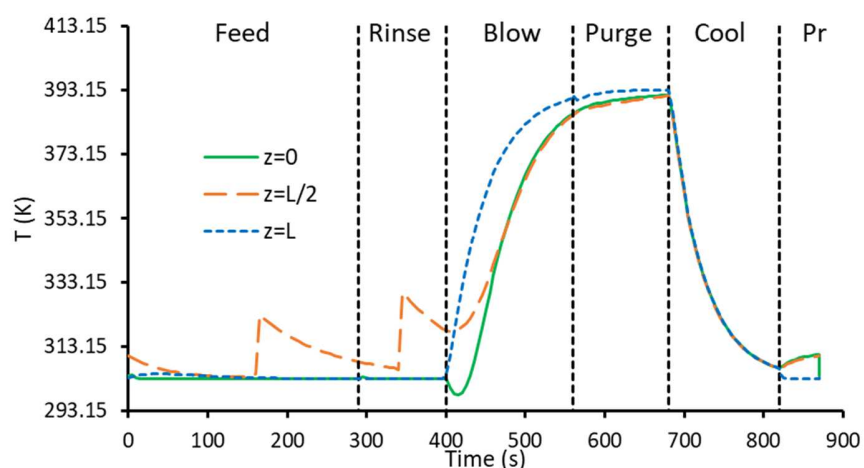


Figure 6.45: Temperature History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF for the ethylene/nitrogen MT-TPSA cycle

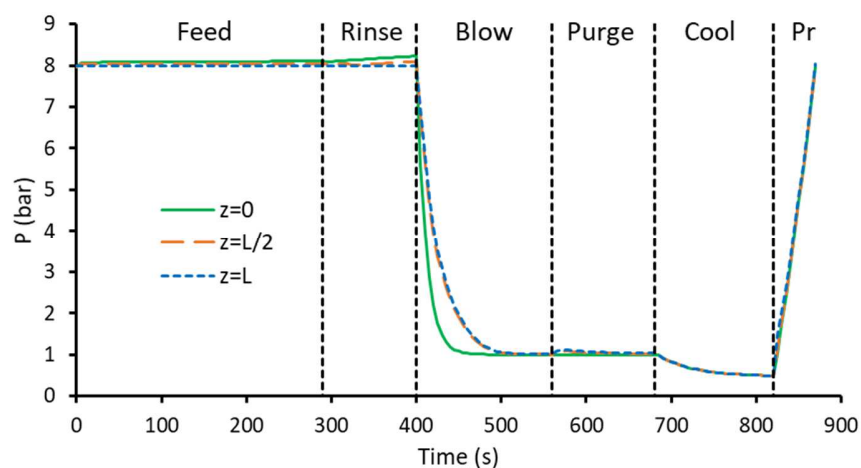


Figure 6.46: Pressure History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF for the ethylene/nitrogen MT-TPSA cycle

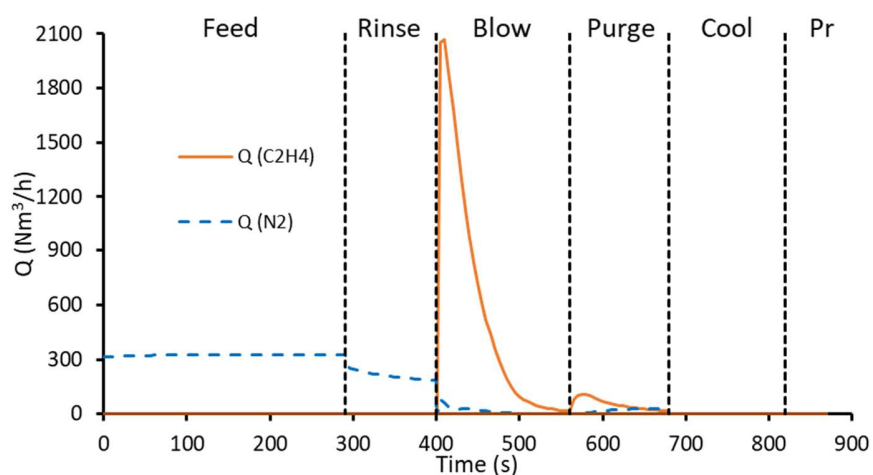


Figure 6.47: Outlet Flowrate History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF for the ethylene/nitrogen MT-TPSA cycle

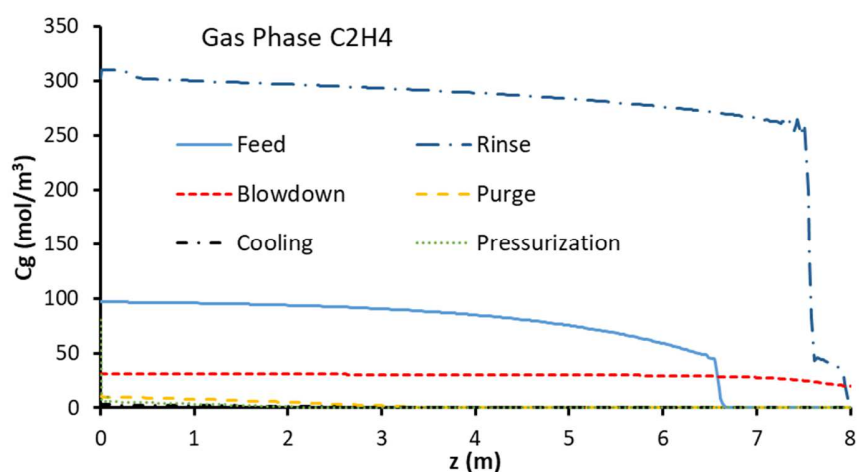


Figure 6.48: Ethylene Gas-Phase Concentration Profile, during CSS, at the end of each step of the ethylene/nitrogen MT-TPSA cycle

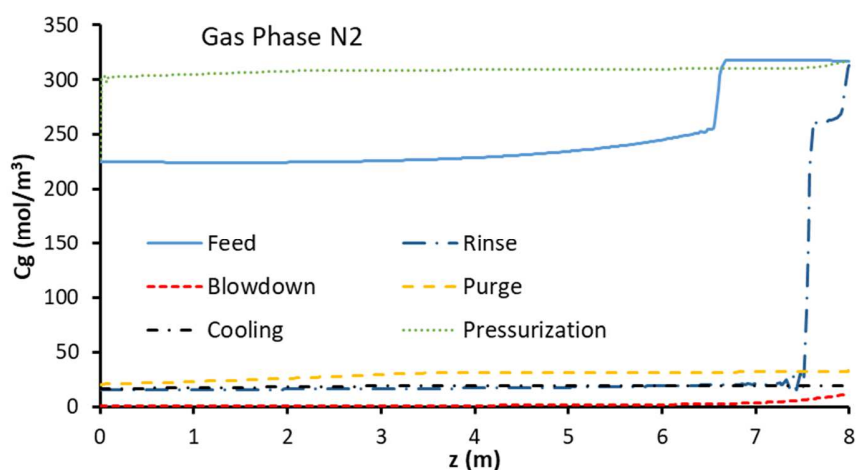


Figure 6.49: Nitrogen Gas-Phase Concentration Profile, during CSS, at the end of each step of the ethylene/nitrogen MT-TPSA cycle

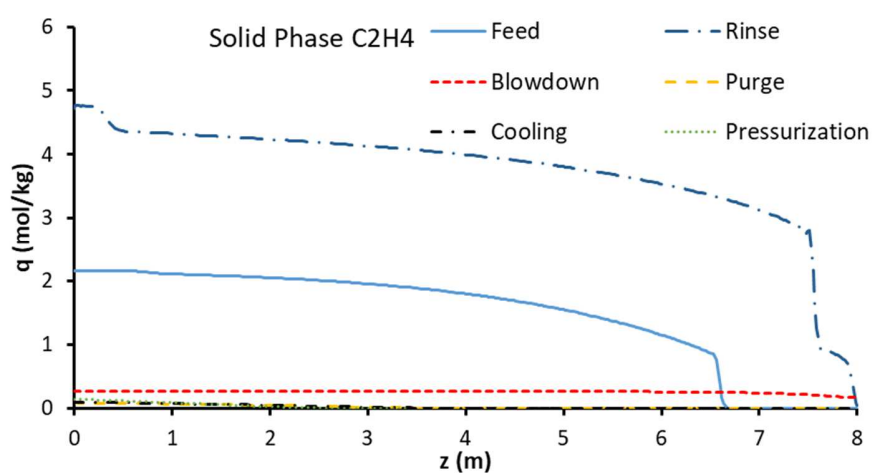


Figure 6.50: Ethylene Solid-Phase Concentration Profile, during CSS, at the end of each step of the ethylene/nitrogen MT-TPSA cycle.

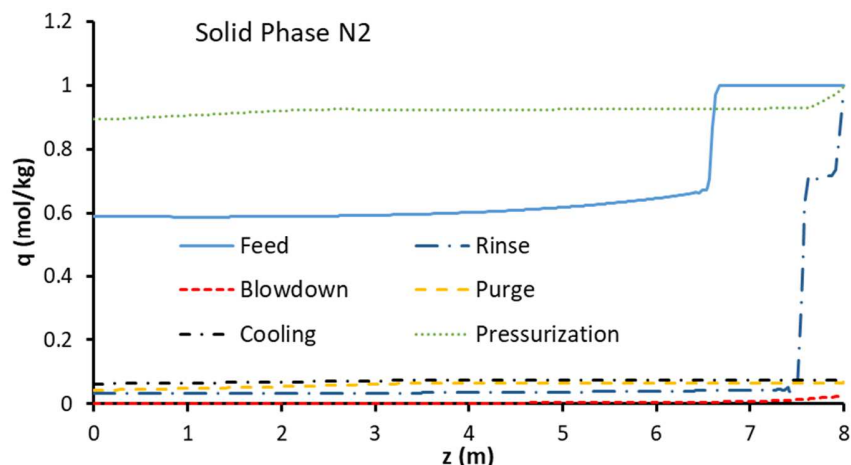


Figure 6.51: Nitrogen Solid-Phase Concentration Profile, during CSS, at the end of each step of the ethylene/nitrogen MT-TPSA cycle

6.6. Propylene/Nitrogen Separation

6.6.1. PSA Cycle Design

Unlike ethylene, the adsorption equilibrium of propylene at lower temperatures still presents a significantly sharp isotherm shape. As such, to facilitate the separation of a propylene/nitrogen mixture, the feed and external temperature were also raised to 343 K. In Figure 6.52, a comparison is made between the predicted adsorption equilibrium isotherms for propylene and nitrogen at 343 K. As seen from Figure 6.52, at 343 K the propylene isotherm presents a reasonable degree of linearity. In contrast, still, a significant level of propylene/nitrogen selectivity can be observed. For a 30/70 propylene/nitrogen mixture at 343 K and 8 bar, a propylene/nitrogen selectivity of 22.11 was calculated. Although the reported selectivity is higher than the one calculated for the ethylene/nitrogen mixture, a pressure range of 0.3 to 8 bar was still required to achieve the intended purity requirements. The proposed operating conditions required that the feed stream be separately pressurized and heated to 8 bar and 343 K before being fed into the column.

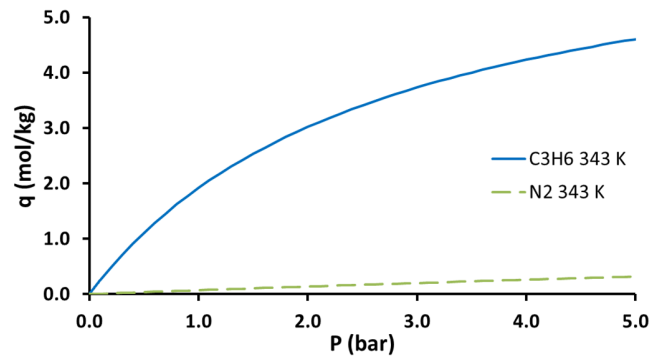


Figure 6.52: DSL isotherm model predictions for C_3H_6 and N_2 at 343 K on the MIL-100(Fe)

The 1D fixed bed mathematical model and the boundary and initial conditions specified in Chapter 4 were used to simulate the mass, thermal and momentum behavior of a PSA system, while the required mass and thermal parameters used in the simulations are presented in Table 6.13. The depressurization process of the Blowdown process is controlled by a valve system following an exponential function. As described in Chapter 5, the physical properties of the propylene/nitrogen PSA unit are reported in Table 6.14.

Table 6.13: Transport Parameter values used in the C_3H_6/N_2 PSA Simulation calculated at feed conditions

Axial Mass Dispersion	3.57×10^{-4}	m^2/s
Axial Heat Dispersion	8.48×10^{-1}	$W/(m \cdot K)$
Mixture Viscosity	1.44×10^{-5}	$Pa \cdot s$
Particle Heat Transfer Coefficient	131	$W/(m^2 \cdot K)$
Wall Heat Transfer Coefficient	660	$W/(m^2 \cdot K)$
External Heat Transfer Coefficient	44.4	$W/(m^2 \cdot K)$

Table 6.14: Physical and Sizing properties parameters used for the C_3H_6/N_2 PSA simulations

Column Length	10	m
Bed Diameter	2	m

Column Diameter	2.01	m
Bed Porosity	0.37	-
Total Adsorbent Mass	10681	kg

6.6.2. PSA Cycle Simulation Results

As seen from the information detailed in Table 6.15, the duration a five-step PSA cycle, composed of a Feed, Rinse, Blowdown, Purge, and Counter-Current Pressurization steps, will be expanded to form a triple column PSA unit, which guarantees a constant feed consumption and a constant production of both product streams, as illustrated in Figure 6.53. As shown by the performance results in Table 6.16, the proposed PSA unit following the operating condition listed in Table 6.15 is capable of producing a nitrogen stream with a propylene contamination of 19.58 ppm(v/v) and a propylene stream with a 95.06 %(v/v) purity, which are within the target purity requirements. The process can accomplish the separation with propylene productivity and recovery capacity of 1.48 mol/(kg_{ads}.h) and 21.03 kg_{C₃H₆}/m³_{unit}.h, with an equivalent thermal energy consumption of 4.37 MJ/kg_{C₃H₆}.

Table 6.15: Proposed C₃H₆/N₂ PSA Simulation Cycle step conditions

Steps	Step time (s)	Pressure (bar)	Flow Rate (Nm ³ /h)
Feed	1100	8.0	3600
Rinse	620	8.0	2640
Blowdown	240	8.0 → 0.3	-
Purge	1140	0.3	99
Pressurization	200	0.3 → 8.0	3600

Feed	Rinse	B	Purge	P
Purge	P	Feed	Rinse	B
Rinse	B	Purge	P	Feed

Figure 6.53: Extension of the proposed C₃H₆/N₂ PSA schedule to a 3 column system

Table 6.16: Detailed C₃H₆/N₂ PSA Cycle Performance Results

C ₃ H ₆ Purity	95.06	% (v/v)
C ₃ H ₆ in N ₂ Stream	19.58	ppm (v/v)
C ₃ H ₆ Recovery	99.99+	% (v/v)
N ₂ Recovery	97.77	% (v/v)
C ₃ H ₆ Productivity	1.48	mol/(kg _{ads} · h)
N ₂ Productivity	3.38	mol/(kg _{ads} · h)
Energy Consumption	4.37	MJ/kg _{C₃H₆}
C ₃ H ₆ Recovery Capacity	21.03	kg _{C₃H₆} /(m ³ _{unit} · h)

The behavior of the proposed PSA system can be further analyzed by plotting the outputs and internal profiles of the adsorption bed at CSS. The results of this analysis are very similar to those obtained in Chapter 6.4.2, with only some exceptions to be pointed out. Figures 6.54 and 6.55 represent the temperature and pressure histories at the start, halfway, and at the end of the adsorption column, while Figure 6.56 displays the outlet volumetric flowrate for each component at CSS. Figures 6.57 to 6.60 represent the gas and solid phase concentration profiles for propylene and nitrogen at the end of each cyclic step detailed in Table 6.15. From Figure 6.54, a temperature range of 301 to 397 K was registered during the entire cycle. The most elevated temperatures were recorded during the Rinse step and the lowest during the beginning of the Blowdown step. Compared to the temperature range obtained for the ethylene/nitrogen separation, the wider range obtained for the propylene separation is directly connected to the higher adsorption heat.

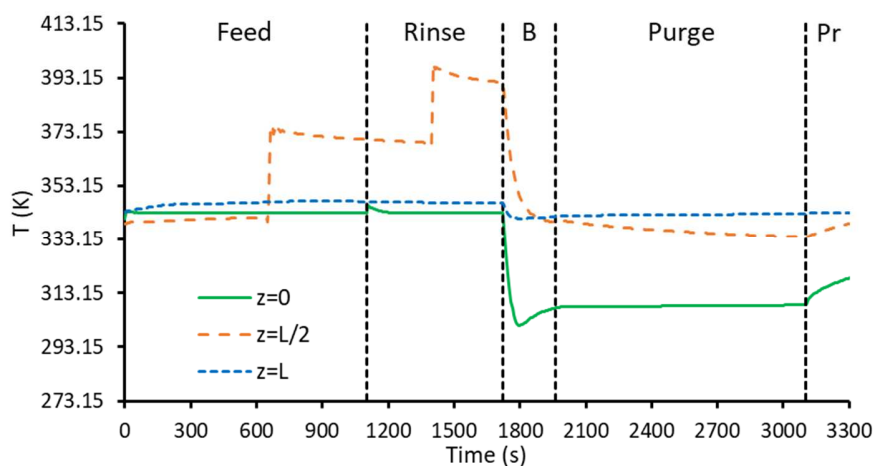


Figure 6.54: Temperature History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF for the propylene/nitrogen PSA cycle

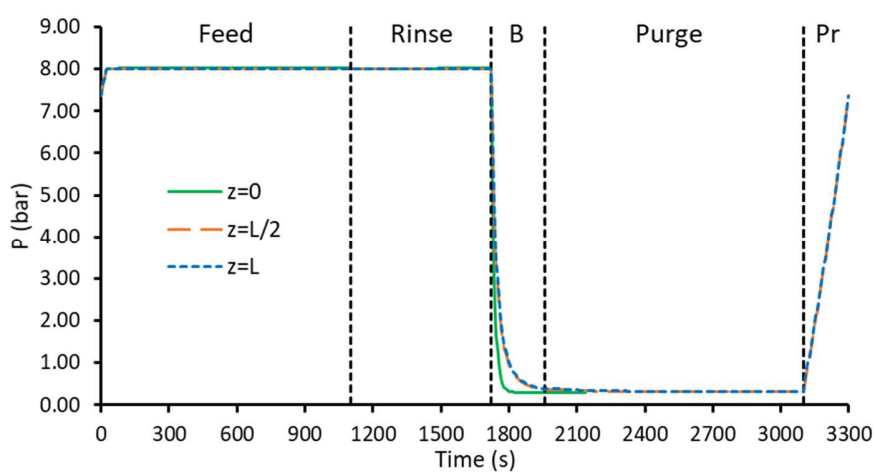


Figure 6.55: Pressure History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF for the propylene/nitrogen PSA cycle

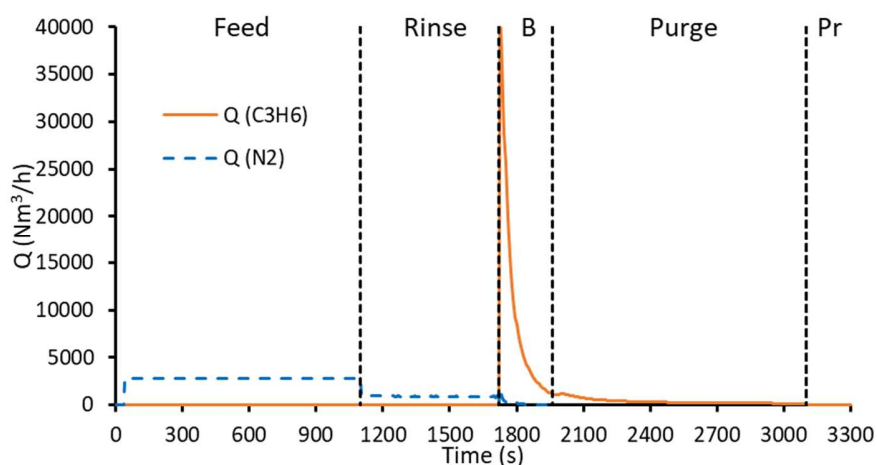


Figure 6.56: Outlet Flowrate History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF for the propylene/nitrogen PSA cycle

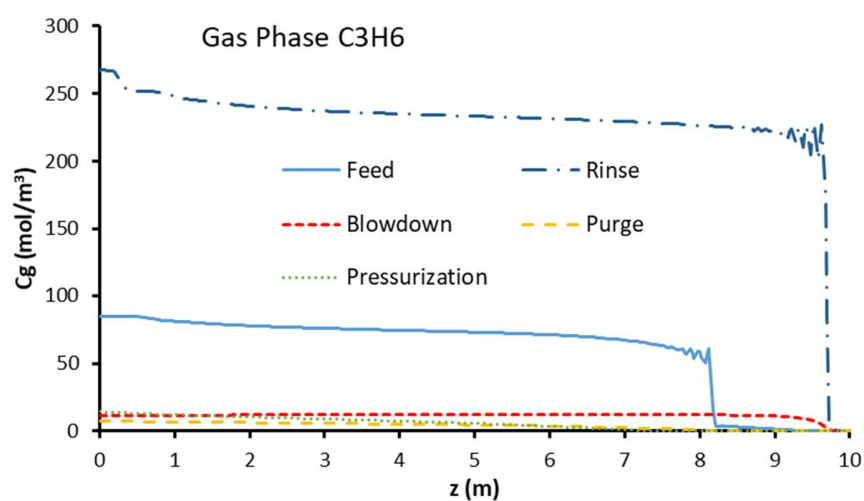


Figure 6.57: Propylene Gas-Phase Concentration Profile, during CSS, at the end of each step of the propylene/nitrogen PSA cycle

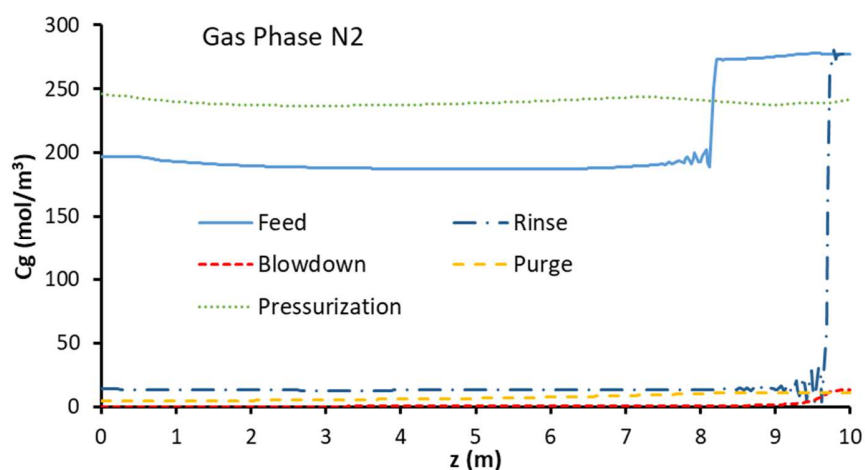


Figure 6.58: Nitrogen Gas-Phase Concentration Profile, during CSS, at the end of each step of the propylene/nitrogen PSA cycle

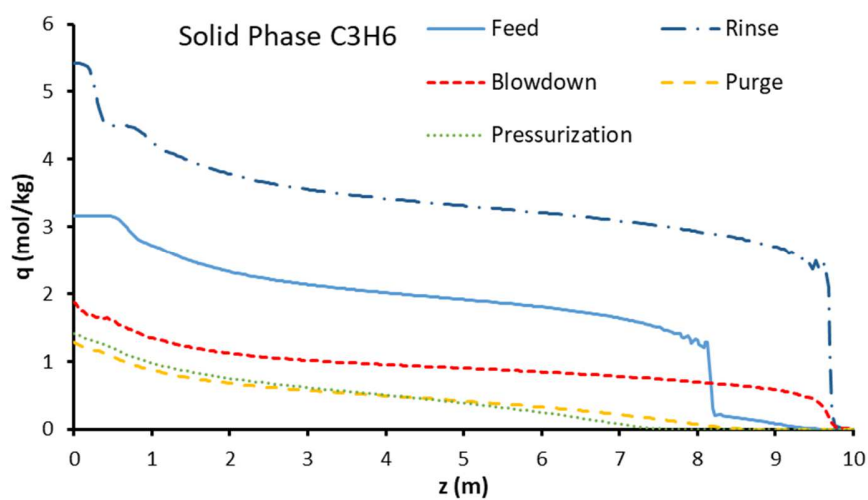


Figure 6.59: Propylene Solid-Phase Concentration Profile, during CSS, at the end of each step of the propylene/nitrogen PSA cycle

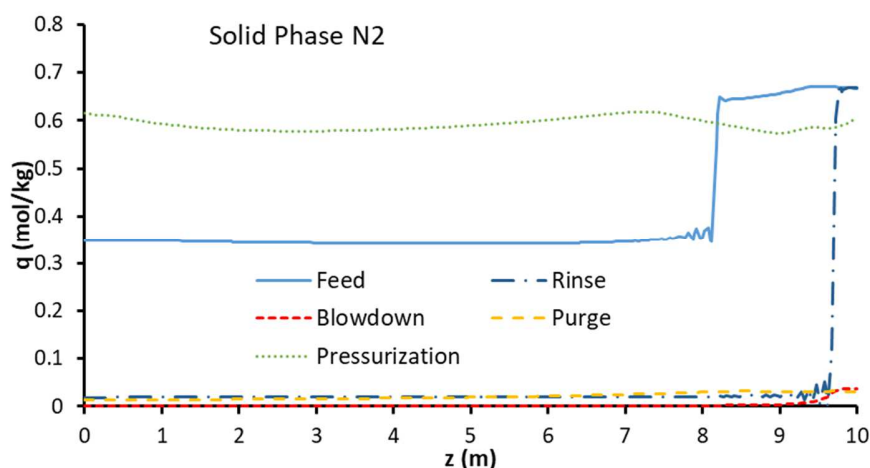


Figure 6.60: Nitrogen Solid-Phase Concentration Profile, during CSS, at the end of each step of the propylene/nitrogen PSA cycle

6.6.3. MT-TPSA Cycle Design

The MT-TPSA cycle for the separation and recovery of a propylene/nitrogen mixture was designed to operate at a pressure range of 1 to 5 bar, and a temperature range of 303 to 393 K. From Figure 6.61, a comparison is performed between the Langmuir isotherm model predictions at 303 and 393 K for propylene and nitrogen, from this comparison it can be calculated that the propylene/nitrogen selectivity for the proposed feed conditions has the value of 28.86 for 303 K, and 16.10 for 393 K.

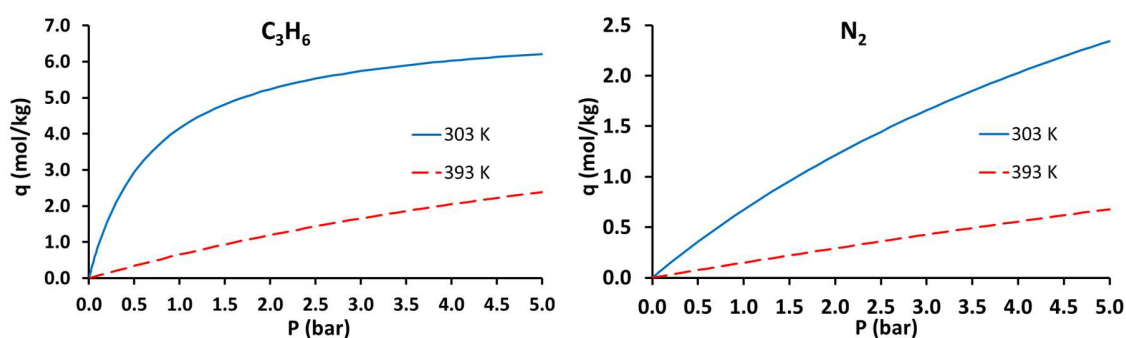


Figure 6.61: Comparison of the Langmuir isotherm model predictions for propylene and N_2 at 303 and 393 K on the MIL-100(Fe) MOF

As explained in the previous section, the equivalent 1D fixed bed mathematical model was used to simulate the MT-TPSA cycle. Likewise, the tube sizing and shell design, shown in Table 6.18 will be kept constant, and the depressurization will follow an exponential function. The mass and thermal transport parameters used in the propylene/nitrogen MT-TPSA simulation are calculated at feed conditions and are represented in Table 6.17. The sizing properties of the MT-TPSA unit are shown in Table 6.18.

Table 6.17: Transport Parameter values used in the C_3H_6/N_2 MT-TPSA Simulation calculated at feed conditions

Axial Mass Dispersion	7.69×10^{-4}	m^2/s
Axial Heat Dispersion	2.00	$W/(m \cdot K)$
Mixture Viscosity	1.36×10^{-5}	$Pa \cdot s$
Shell Side Heat Transfer Coefficient	1586	$W/(m^2 \cdot K)$
Particle Heat Transfer Coefficient	216	$W/(m^2 \cdot K)$
Tube Side Overall Heat Transfer Coefficient	48.45	$W/(m^2 \cdot K)$

Table 6.18: Physical and Sizing properties parameters used for the C_3H_6/N_2 MT-TPSA simulations

Tube Length	6.00	m
Tube Inner Diameter	29.35×10^{-3}	m
Tube Outer Diameter	31.75×10^{-3}	m
Tube Pitch	39.69×10^{-3}	m
Tube Clearance	7.94×10^{-3}	m
Bed Porosity	0.37	-
Tube Thickness	1.20×10^{-3}	m
Number of Tubes	1709	-
Total Adsorbent Mass	2359	kg
Transfer Surface Area	1023	m^2

Tube Bundle Diameter	1.86	<i>m</i>
Shell Diameter	1.91	<i>m</i>
Baffle Spacing	0.40	<i>m</i>
Baffle Cut	25	%
Shell Inlet velocity	0.5	<i>m/s</i>

6.6.4. MT-TPSA Cycle Simulation Results

By following the cycle step schedule listed in Table 6.19, the proposed C_3H_6/N_2 MT-TPSA cycle can be extended to triple MTA unit system. This system guarantees both a continuous feed consumption and a continuous production of both product streams, as illustrated by Figure 6.62. As shown by Table 6.20, an MT-TPSA system following the proposed cycle step operating conditions would be capable of producing a C_3H_6 stream with 95.32 % (v/v) purity and an N_2 stream with C_3H_6 contamination of 11.16 ppm(v/v), thus successfully accomplishing the purity requirements set out for the separation. A C_3H_6 productivity and recovery capacity of 6.72 mol/(kg_{ads}.h) and 38.91 kg_{C₃H₆}/(m³_{unit}.h) were obtained for total thermal energy consumption of 7.46 MJ/kg_{C₃H₆}. Of the total thermal energy requirements, 76.0 % are being dedicated to the operation of the heat exchanger, while 22.5 % and 1.5 % are being used to operate the gas and liquid pumps, respectively. The system reports a thermal efficiency of 14.8 %.

By comparing the performances between the present MT-TPSA and the respective PSA cycle, one can observe that even when disregarding the cooling duties, the PSA cycle demonstrates lower electrical energy cost (4.37 MJ/kg_{C₃H₆}) than the MT-TPSA system (4.65 MJ/kg_{C₃H₆}). However, the recovery capacity and adsorbent load for the MT-TPSA cycle (38.91 kg_{C₃H₆}/(m³_{unit}.h) and 2359 kg) are significantly better than those reported for the PSA system (21.03 kg_{C₃H₆}/(m³_{unit}.h) and 10681 kg).

Table 6.19: Proposed C₃H₆/N₂ MT-TPSA Simulation Cycle step conditions

Steps	Step time (s)	Pressure (bar)	External Temperature (K)	Flow Rate (Nm ³ /h)
Feed	600	5.0	303	3600
Rinse	100	5.0	303	3600
Blowdown	300	5.0 → 1.0	303 → 393	-
Purge	400	1.0	393	84
Cooldown	240	1.0 (→ 0.36)	393 → 303	-
Pressurization	160	0.36 → 5.0	303	1110

Feed			R	Blow		Purge		Cool	P
Purge	Cool	P	Feed			R	Blow		Purge
R	Blow		Purge		Cool	P	Feed		

Figure 6.62: Extension of the proposed C₃H₆/N₂ MT-TPSA schedule to a 3-MTA unit systemTable 6.20: Detailed C₃H₆/N₂ MT-TPSA Cycle Performance Results

C ₃ H ₆ Purity	95.32	% (v/v)
C ₃ H ₆ in N ₂ Stream	11.16	ppm (v/v)
C ₃ H ₆ Recovery	99.99+	% (v/v)
N ₂ Recovery	97.90	% (v/v)
C ₃ H ₆ Productivity	6.72	mol/(kg _{ads} · h)
N ₂ Productivity	15.35	mol/(kg _{ads} · h)
Total Energy Consumption	7.46	MJ/kg _{C₃H₆}
Adsorption Cooling Duty	0.84	MJ/kg _{C₃H₆}
Heating Duty	2.86	MJ/kg _{C₃H₆}
Cooling Duty	1.97	MJ/kg _{C₃H₆}
Gas Pump Operation	1.68	MJ/kg _{C₃H₆}

Liquid Pump Operation

0.11

 $MJ/kg_{C_3H_6}$

 Table 6.21: Productivity and Recovery Capacity for the C_3H_6/N_2 MT-TPSA

C_3H_6 Productivity	0.283	$kg_{C_3H_6}/(kg_{ads} \cdot h)$
Bed C_3H_6 Recovery Capacity	96.15	$kg_{C_3H_6}/(m_{bed}^3 \cdot h)$
Unit C_3H_6 Recovery Capacity	38.91	$kg_{C_3H_6}/(m_{unit}^3 \cdot h)$

Figures 6.63 and 6.64 represent the temperature and pressure histories at the start, halfway, and end of the adsorption column; while Figure 6.65 displays the outlet volumetric flow rate for each component at CSS. Figures 6.66 to 6.69 represent the gas and solid phase concentration profiles for C_2H_4 and N_2 at the end of each cyclic step listed in Table 6.19. The phenomena observed in the following Figures are similar to those discussed in Section 6.4.4 and, as such, have already been reported.

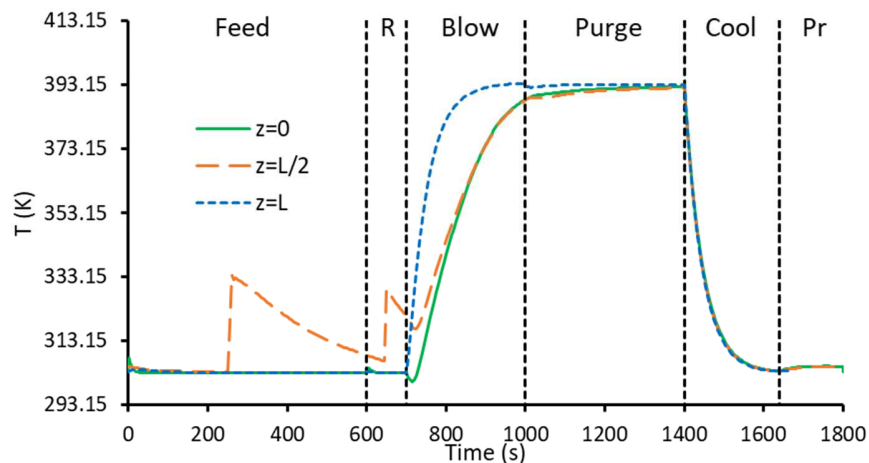


Figure 6.63: Temperature History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF for the propylene/nitrogen MT-TPSA cycle

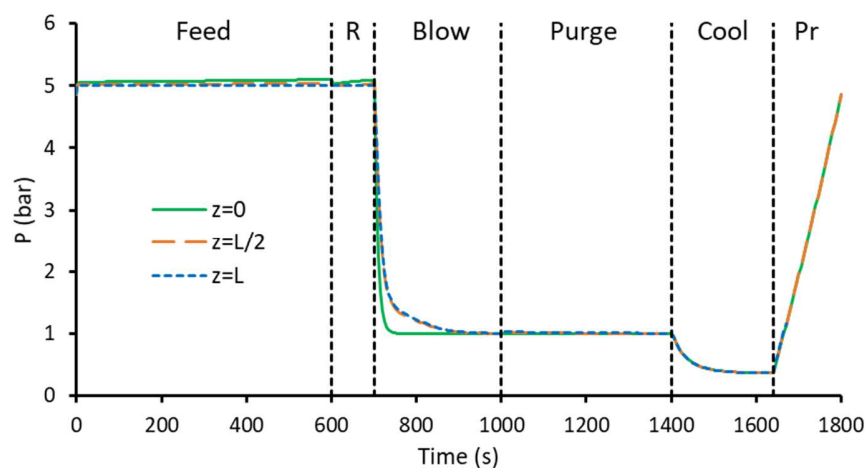


Figure 6.64: Pressure History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF for the propylene/nitrogen MT-TPSA cycle

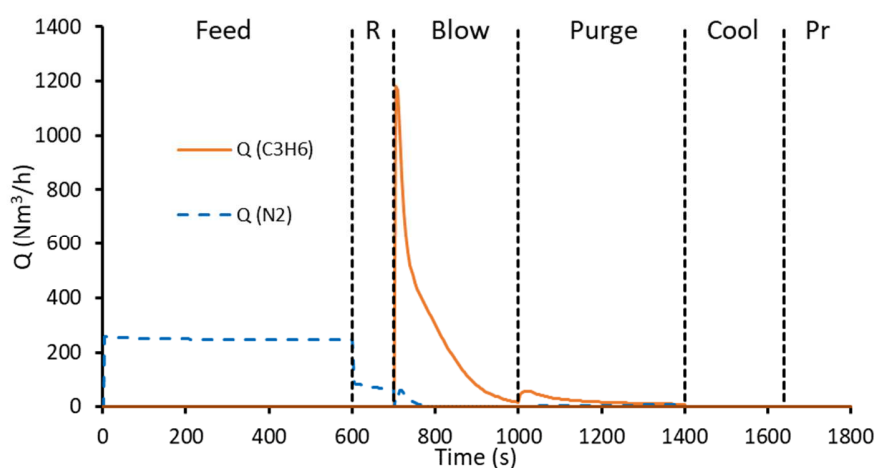


Figure 6.65: Outlet Flowrate History during CSS at the start, halfway, and end of the column of MIL-100(Fe) MOF for the propylene/nitrogen MT-TPSA cycle

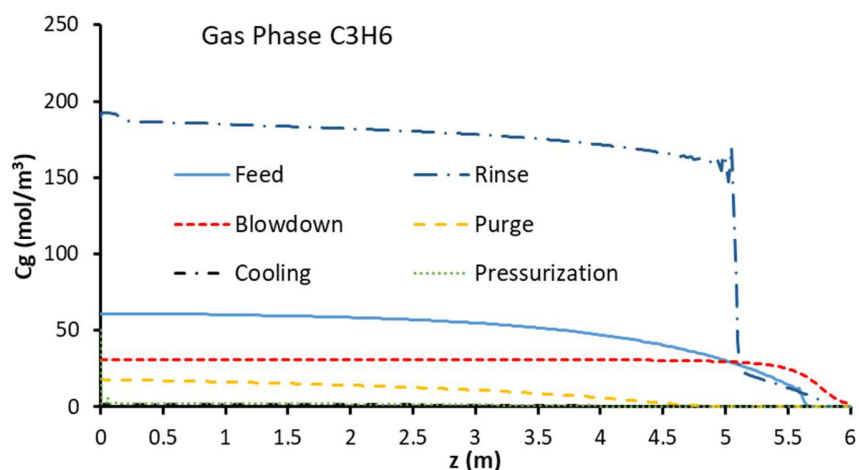


Figure 6.66: Propylene Gas-Phase Concentration Profile, during CSS, at the end of each step of the propylene/nitrogen MT-TPSA cycle

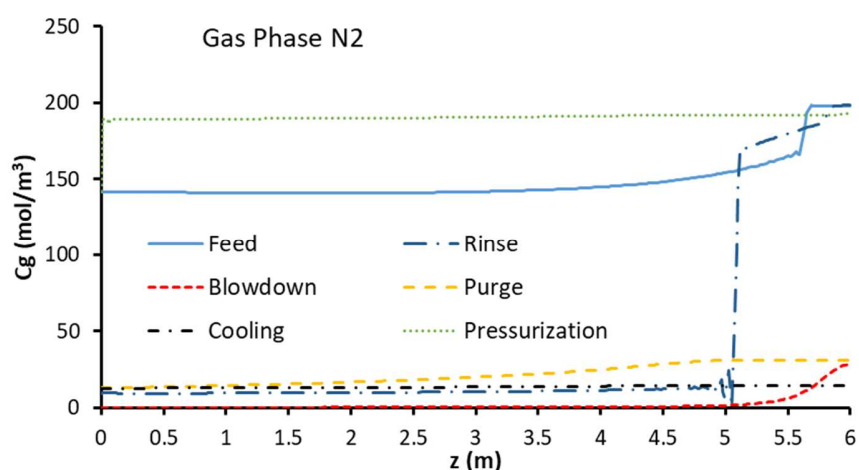


Figure 6.67: Nitrogen Gas-Phase Concentration Profile, during CSS, at the end of each step of the propylene/nitrogen MT-TPSA cycle

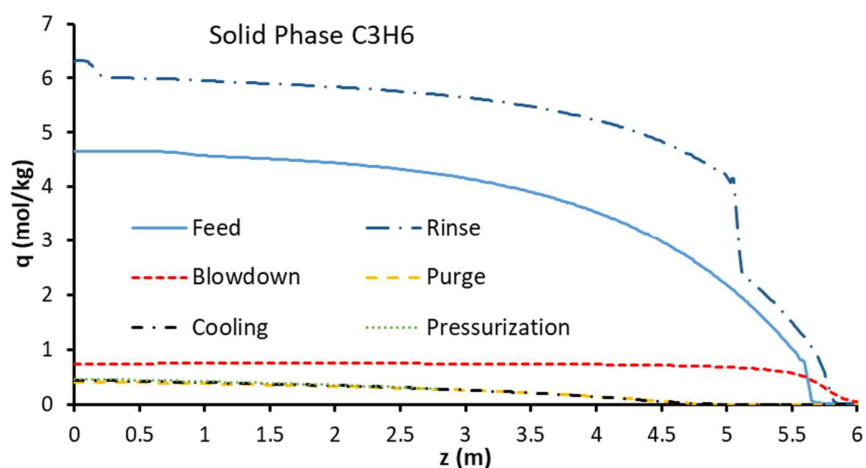


Figure 6.68: Propylene Solid-Phase Concentration Profile, during CSS, at the end of time step of the propylene/nitrogen MT-TPSA cycle

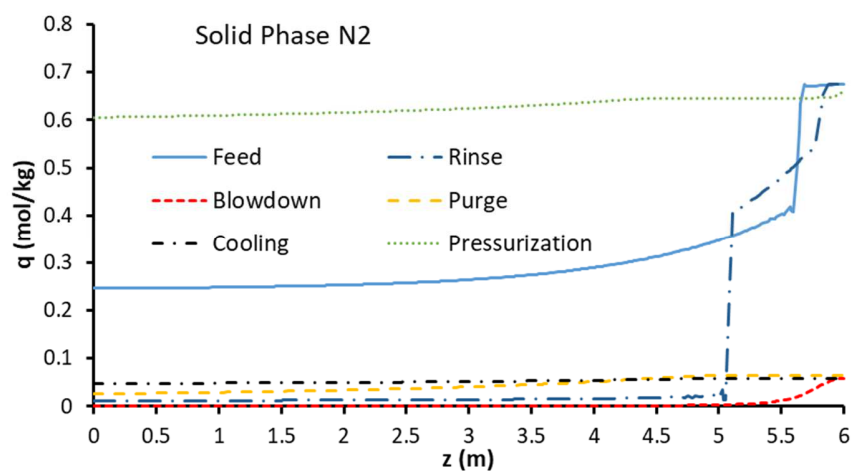


Figure 6.69: Nitrogen Solid-Phase Concentration Profile, during CSS, at the end of each step of the propylene/nitrogen MT-TPSA cycle

6.7. Conclusions

Pure component adsorption equilibrium isotherms for ethylene and propylene were measured on MIL-100(Fe) granules, using a Rubotherm magnetic suspension balance, for a range of 0 to 5 bar, and 303 to 373 K. Langmuir isotherm models were accurately fitted to the measured experimental results.

Single, binary, and pseudo-binary breakthrough curves were performed on a bench-scale single column PSA unit for ethylene/nitrogen and propylene/nitrogen mixtures. The dynamic behavior of the breakthrough experiments was successfully simulated using a 1-dimensional fixed bed mathematical model, and the pure and multicomponent extension of the Langmuir isotherm model were successfully validated using experimental data.

For the MIL-100(Fe) MOF material, a five-step PSA, and a six-step MT-TPSA cycle were designed and simulated for the separation of both an ethylene/nitrogen and a propylene/nitrogen mixture.

For the ethylene/nitrogen PSA cycle, a three-column PSA system, designed for an operating range of 0.3 to 9 bar, was capable of producing an ethylene stream with 95.00 %(v/v) purity and a nitrogen stream with ethylene contamination of 1.90 ppm(v/v), using a total adsorbent mass of 10681 kg. An ethylene productivity and recovery capacity of 2.23 mol/(kg_{ads}.h) and 21.03 kg_{C₂H₄}/(m³_{unit}.h) was achieved for total thermal energy consumption of 10.13 MJ/kg_{C₂H₄}.

For the ethylene/nitrogen MT-TPSA cycle, a three multitubular adsorber system, designed for an operating range of 1 to 8 bar and 303 to 393 K, was capable of producing an ethylene stream with 95.15 %(v/v) purity and a nitrogen stream with ethylene contamination of 16.67 ppm(v/v), using a total adsorbent mass of 3777 kg. An ethylene productivity and recovery capacity of 6.30 mol/(kg_{ads}.h) and 24.83 kg_{C₂H₄}/(m³_{unit}.h) was achieved for total thermal energy consumption of 20.81 MJ/kg_{C₂H₄}, of which a thermal energy consumption of 13.02 MJ/kg_{C₂H₄} is required to supply the heating stages and the electrical energy consumption.

For the propylene/nitrogen PSA cycle, a three-column PSA system, designed for an operating range of 0.3 to 8 bar, was capable of producing a propylene stream with 95.06 %(v/v) purity and a nitrogen stream with propylene contamination of 19.58 ppm(v/v), using a total adsorbent mass of 10681 kg. A propylene productivity and recovery capacity of 1.48 mol/(kg_{ads}.h) and 21.03 kg_{C₃H₆}/(m³_{unit}.h) was achieved for total thermal energy consumption of 4.37 MJ/kg_{C₃H₆}.

For the propylene/nitrogen MT-TPSA cycle, a three multitubular adsorber system, designed for an operating range of 1 to 5 bar and 303 to 393 K, was capable of producing a propylene stream with 95.32 %(v/v) purity and a nitrogen stream with propylene contamination of 11.16 ppm(v/v), using a total adsorbent mass of 2359 kg. A propylene productivity and recovery capacity of 6.72 mol/(kg_{ads}.h) and 38.91 kg_{C₃H₆}/(m³_{unit}.h) was achieved for total thermal energy consumption of 7.46 MJ/kg_{C₃H₆}, of which a thermal energy consumption of 4.65 MJ/kg_{C₃H₆} is required to supply the heating stages and the electrical energy consumption.

According to the results obtained, the separation and recovery of the ethylene/nitrogen mixture is better performed by the proposed PSA system. Although the respective MT-TPSA cycle succeeded in increasing the process productivity and lowering the adsorbent load, the highly increased energy costs caused by the process's low thermal regeneration efficiency lowers its economic viability.

On the other hand, for the separation and recovery of the propylene/nitrogen mixture both processes can be potential solutions. While the PSA system does display a lower energy consumption, this comes at more than four times costs in adsorbent load, which may be impractical depending on the availability of the material and space.

A performance comparison summary between all the adsorption-based separation units, developed for the separation and recovery of an ethylene/nitrogen and a propylene/nitrogen mixture, is shown in Table 6.22.

Table 6.22: Performance Comparison between the PSA and MT-TPSA separation systems proposed for ethylene and propylene recovery

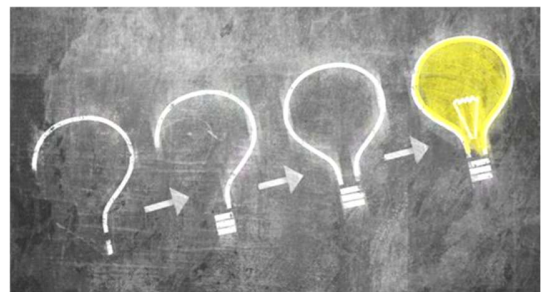
Ethylene Recovery		Propylene Recovery		
PSA	MT-TPSA	PSA	MT-TPSA	
Temperature and Pressure				
343	303 – 393	343	303 – 393	K
0.3 – 9	1 – 8	0.3 – 8	1 – 5	bar
Productivity				
6.3×10^{-2}	1.5×10^{-1}	6.2×10^{-2}	2.8×10^{-1}	$kg_{LO}/(kg_{ads} \cdot h)$
21	25	21	39	$kg_{LO}/(m_{unit}^3 \cdot h)$
	60		96	$kg_{LO}/(m_{bed}^3 \cdot h)$
Energy Requirements				
10.13	20.81	4.37	7.46	MJ/kg_{LO}

6.8. References

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Chapter 7

Conclusions and Future Work



7.1. Summary

In this work, adsorption-based processes have successfully been proposed to control and recover unreacted monomers in nitrogen-rich gas vent streams in poly(vinyl chloride), polyethylene, and polypropylene industries. More specifically, the developed separation units must have the ability to control the monomer concentration on process units vent streams, to below the OSHA standards of gaseous exhaust streams (8 ppm(w/w) for vinyl chloride, and 20 ppm (v/v) for light olefins). They must be capable of producing a 95 %(v/v) monomer purity stream to be recycled into the polymerization process.

Adsorption equilibrium data for vinyl chloride, ethylene, propylene, and nitrogen was successfully measured using gravimetric methods on MIL-100(Fe), activated at 433 K. Equilibrium data for vinyl chloride and nitrogen were also obtained on samples of Maxsorb and Carbotech DGK carbons. All gravimetric measurements were performed at 303, 323, and 373 K for a pressure range of 0 to 5 bar, except vinyl chloride which was obtained at a range of 0 to 2.5 bar, due to safety reasons.

Single, binary, and pseudo-binary breakthrough experiments were performed on a bench-scale single column PSA unit and were successfully simulated using the developed fixed bed mathematical model for the ethylene/nitrogen and propylene/nitrogen mixtures.

For the recovery of vinyl chloride, preliminary testing was performed to ascertain the viability of standard cyclic adsorption separation systems using equilibrium data found in the literature. From this research, the Multi-tubular Temperature and Pressure Swing Adsorption cycle was successfully modeled and validated using a two-dimensional fixed bed model. In turn, an equivalent one-dimensional model was proposed to simulate the radial thermal behavior of temperature-intensive adsorption processes and save on computational time and resources. From the experimental equilibrium results obtained, two final adsorption-based separation systems are suggested.

A three-column, five-step PSA cycle, operated at a temperature of 343 K and between a pressure range of 0.1 to 7 bar, was capable of producing a vinyl chloride stream with 95.40 %(v/v) purity and a nitrogen stream with propylene contamination of 6.14 ppm(w/w), using a total MIL-100(Fe) mass of 900 kg. A vinyl chloride productivity and recovery capacity of

3.52 mol/(kg_{ads}.h) and 71.89 kg_{VCM}/(m³_{unit}.h) were achieved for total thermal energy consumption of 2.48 MJ/kg_{VCM}.

A two MTA , six-step Maxsorb MT-TPSA unit, designed for an operating range of 1 to 2.5 bar, and 303 to 393 K, was capable of producing a vinyl chloride stream with 95.11 %(v/v) purity and a nitrogen stream with an propylene contamination of 4.78 ppm(w/w), using a total adsorbent mass of 376 kg. A vinyl chloride productivity and recovery capacity of 8.41 mol/(kg_{ads}.h) and 69 kg_{VCM}/(m³_{unit}.h) was achieved for a total thermal energy consumption of 3.05 MJ/kg_{VCM}, of which 1.82 MJ/kg_{VCM} are necessary to supply thermal energy during the heating stages and electrical energy for the operation of the gas and liquid pumps.

As such, depending on the level of integration of the separation unit into the plants' design, either the MIL-100(Fe) PSA or the Maxsorb MT-TPSA systems can be a potential solution.

For the recovery of ethylene, a three-column, five-step PSA system was suggested. The proposed cycle is operated at a temperature of 343 K and between a pressure range of 0.3 to 9 bar, using a total of 10681 kg of MIL-100(Fe). An ethylene purity of 95.00 %(v/v) was achieved together with an ethylene contamination of 1.90 %(v/v) and a nitrogen recovery of 97.74 %(v/v). An ethylene productivity and recovery capacity of 2.23 mol/(kg_{ads}.h) and 21.03 kg_{C₂H₄}/(m³_{unit}.h) were achieved for equivalent thermal energy consumption of 10.13 MJ/kg_{C₂H₄}, which accounts for the electrical energy consumption of operating the gas pressurization and vacuum pumps.

A potential PSA and an MT-TPSA system are suggested for propylene recovery, depending on the integrating process. A three-column, five-step PSA cycle, operated at a temperature of 343 K and between a pressure range of 0.3 to 8 bar, was capable of producing a propylene stream with 95.06 %(v/v) purity and a nitrogen stream with propylene contamination of 19.58 ppm(v/v), using a total MIL-100(Fe) mass of 10681 kg. A propylene productivity and recovery capacity of 1.48 mol/(kg_{ads}.h) and 21.03 kg_{C₃H₆}/(m³_{unit}.h) was achieved for a total equivalent thermal energy consumption of 4.37 MJ/kg_{C₃H₆}.

A three-MTA , six-step MT-TPSA unit, designed for an operating range of 1 to 5 bar and 303 to 393 K, was capable of producing a propylene stream with 95.32 %(v/v) purity and a nitrogen stream with propylene contamination of 11.16 ppm(v/v), using a total mass of MIL-

100(Fe) of 2359 kg. A propylene productivity and recovery capacity of $6.72 \text{ mol}/(\text{kg}_{\text{ads}}\cdot\text{h})$ and $38.91 \text{ kg}_{\text{C}_3\text{H}_6}/(\text{m}^3_{\text{unit}}\cdot\text{h})$ was achieved for total thermal energy consumption of $7.46 \text{ MJ}/\text{kg}_{\text{C}_3\text{H}_6}$, of which $4.65 \text{ MJ}/\text{kg}_{\text{C}_3\text{H}_6}$ are necessary to supply thermal energy during the heating stages and electrical power for the operation of the gas and liquid pumps.

While the MT-TPSA cycle displays higher energy consumption, this analysis does not account for any heat integration available at the industrial plant. Nonetheless the higher reported productivity and recovery capacity could outweigh the long-term economic costs.

7.2. Suggestions for Future Work

At the end of this research work, while most of the initial objectives have been successfully accomplished, many new lines of research are open for future work.

As shown by the adsorption equilibrium measurements for vinyl chloride, the Maxsorb activated carbon showed a similarly favorable isotherm behavior to MIL-100(Fe). As such, considering the higher adsorption capacity of the Maxsorb material, the development of a PSA cycle for the separation of vinyl chloride/nitrogen mixtures has the potential for increased performance. Similarly, for the same reasons, the study of the adsorption performance of the Maxsorb adsorbent should also be expanded for the ethylene/nitrogen and propylene/nitrogen separations.

In the present work, the low selectivity of the ethylene/nitrogen mixture in MIL-100(Fe) severely hampered the performance of both the PSA and MT-TPSA cycles; however, this lower selectivity together with the linear isotherms observed for ethylene at medium to high temperatures would be ideal for the development of a Dual Reflux Pressure Swing Adsorption system. These systems, with a configuration similar to a distillation column, aim to create two high purity products by the formation of concentration shock fronts during both the adsorption and purge of the monomer, which requires both high linearity and low selectivity between the adsorbent/adsorbate system.¹⁻³

One of the major difficulties encountered during the development of this work was the reconciliation of the high nitrogen purity control threshold with the high monomer

concentration of the feed. This combination of requirements is too steep to be effectively accomplished by one system without the use of high adsorbent loads or more energy-intensive regeneration processes. For future work, a two-unit system should be considered to accomplish this separation. The first unit should operate under the conditions of a bulk separation, where a mostly equivalent binary mixture is used to produce two high purity product streams, of which one should ensure the 95 % (v/v) monomer purity requirement. Due to the higher monomer concentration, this separation should be performed using an adsorbent material with lower adsorption heat, and more favorable isotherms, such as MIL-100(Fe) or the Maxsorb carbon would facilitate regeneration for a PSA system. The second unit should operate under the conditions of a “capture”/“polishing” separation, where an adsorbent material with a sharp isotherm shape, such as the Carbotech DGK and the Pittsburgh PCB, would be used to effectively capture a small concentration of monomer and ensure the production of pure nitrogen. The regeneration of the second unit, likely performed by thermal swing, would then be recycled into the first unit's feed.

Alternatively, as seen from the literature, the operation of the first unit could also be performed using a membrane system, which would leave the nitrogen purity control to the second adsorption-based polishing unit.

7.3. References

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