

Gas-phase simulated moving bed for methane upgrade

Thesis presented to the Faculty of Engineering of the University of Porto for the

Ph.D. degree in Chemical and Biological Engineering

By

Rafael Osório Marques Dias

Supervisor:

Professor Ana Mafalda Ribeiro

Co-supervisors:

Professor Alexandre Filipe Porfírio Ferreira

Professor Alírio Egídio Rodrigues



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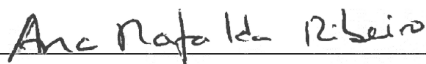
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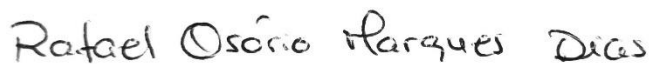
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STATEMENT

In order to fulfil the Rules of Ethics of the Doctoral Program of Chemical and Biological Engineering (PDEQB), we hereby declare that all contents of the thesis presented by Rafael Osório Marques Dias, entitled “Gas-phase simulated moving bed for methane upgrade,” are exclusively from the author. The contents of subchapter 6.4 present an exception since they were obtained in collaboration with Ana Jorge Meireles Pereira and, as such, are also part of the thesis “Additive manufacturing of structured adsorbents for adsorption-based processes”. Accordingly, all the results here shown, excluding the exception mentioned above, were obtained by the author of the thesis and resulted in the original publications presented further ahead.



(Ana Mafalda Almeida Peixoto Ribeiro)



(Rafael Osório Marques Dias)

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ABSTRACT

The separation of methane and nitrogen mixtures is an important step when upgrading low-quality natural gas. This thesis focuses on developing a novel adsorption-based separation process using the gas-phase Simulated Moving Bed (SMB) technology as an alternative method to the state-of-the-art technologies.

In this study, an SMB Performance Indicator (SPI) was introduced, a new metric that enables rapid screening of adsorbent/desorbent pairs without the need for extensive experimentation or simulation. For the screening process, pure component isotherms must be obtained, and preliminary values for pressure, temperature, and feed composition should be defined in advance. The performance indicator can then be calculated using the competitive adsorption selectivity of CH₄ over N₂ and the methane uptake under the specified conditions, along with the heats of adsorption for both components of the gas mixture. The SPI was validated for the CH₄/N₂ separation using CO₂ as the desorbent gas, and its broader applicability was demonstrated for alternative desorbents, such as Ar, and for different applications, such as olefins/paraffins separation.

Three materials were tested for the separation of CH₄/N₂ mixtures by gas-phase SMB: commercial BPL activated carbon, extruded Maxsorb pellets, and 3D-printed Maxsorb monoliths. Adsorption equilibria, dynamic breakthrough experiments, and SMB cyclic operations were conducted for each material. The isotherms show a preferential adsorption of CO₂ for all materials, at the measured temperature and pressure range, followed by CH₄, N₂ and Ar. Dynamic tests validated the mathematical model and confirmed CO₂ and Ar as effective desorbents for this separation, as both could displace the mixture and be displaced in return. The SMB cycles showed that complete separation was achievable with both Ar and CO₂ as desorbents, with Ar performing better in terms of purity, recovery, and productivity across all tested adsorbents. The best performance was obtained using the pelletised Maxsorb, yielding a methane-rich stream with 99.3% purity and 97.2% recovery at a productivity of 17.8 kg·m⁻³_{ads}·h⁻¹ in the cycle using CO₂, and 100.0% purity and 98.9% recovery, with a productivity of 35.1 kg·m⁻³_{ads}·h⁻¹ when Ar was used as the desorbent. Among the three adsorbents, the Maxsorb extrudates offer higher maximum productivity per adsorbent mass, as predicted by the SPI, whereas BPL provides higher maximum productivity per column volume.

A hybrid SMB/PSA process was conceptualized and modelled, where adsorbent regeneration is accomplished through a sequence of PSA sub-steps in combination with displacement chromatography with the methane product, effectively removing the desorbent species from the process. Simulation results showed that the hybrid process could achieve a methane purity of 97% and nitrogen purity of 99%, while recovering part of the purge outlet stream and optimizing the

purge flow rate improved overall recoveries and productivities. Maintaining very low desorption pressures (0.1 bar) was found necessary to achieve a good process performance, leading to higher power consumption ($503.0 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}_{\text{CH}_4}$).

Keywords: adsorption, methane upgrade, activated carbon, simulated moving bed

RESUMO

A separação de misturas de metano e azoto é uma etapa crucial no processo de valorização de gás natural de baixa qualidade. Esta tese centra-se no desenvolvimento de um processo inovador de separação por adsorção, utilizando a tecnologia de leito móvel simulado (Simulated Moving Bed - SMB) em fase gasosa, como alternativa às tecnologias de referência atualmente existentes.

Neste estudo, foi introduzido um *SMB Performance Indicator*, SPI, uma nova métrica que permite a triagem rápida de pares de adsorvente/desorvente sem necessidade de trabalho experimental ou simulação extensiva. Para o processo de triagem, é necessário obter isotérmicas de adsorção dos componentes puros e definir previamente valores preliminares de pressão, temperatura e composição da alimentação. O indicador de desempenho pode então ser calculado com base na seletividade competitiva de adsorção entre o CH₄ e o N₂ e a capacidade de adsorção de metano nas condições especificadas, juntamente com os calores de adsorção de ambos os componentes da mistura gasosa. O SPI foi validado para a separação CH₄/N₂ utilizando CO₂ como gás desorvente, tendo sido demonstrada a aplicabilidade mais ampla desta métrica com desorventes alternativos, como o Ar, e para diferentes aplicações, como a separação de olefinas/parafinas.

Foram testados três materiais para a separação de misturas de CH₄/N₂ por SMB em fase gasosa: carvão ativado comercial BPL, *pellets* extrudidos de Maxsorb e monólitos Maxsorb produzidos por impressão 3D. Foi medido o equilíbrio de adsorção e realizadas experiências dinâmicas de ruptura e ciclos de SMB para cada material. As isotérmicas mostram uma adsorção preferencial de CO₂ em todos os materiais, na gama de temperaturas e pressões estudadas, seguida de CH₄, N₂ e Ar. Os testes dinâmicos validaram o modelo matemático e confirmaram o CO₂ e o Ar como desorventes eficazes para esta separação, uma vez que ambos foram capazes de deslocar a mistura e de ser deslocados por ela. Os ciclos de SMB demonstraram que é possível alcançar uma separação completa com ambos os desorventes (CO₂ e Ar), sendo que o Ar apresentou melhor desempenho em termos de pureza, recuperação e produtividade em todos os adsorventes testados. O melhor desempenho foi alcançado com os *pellets* de Maxsorb, obtendo-se uma corrente rica em metano com 99,3% de pureza e 97,2% de recuperação, e uma produtividade de 17,8 kg·m⁻³_{ads}·h⁻¹ no ciclo com CO₂; e 100,0% de pureza e 98,9% de recuperação, com uma produtividade de 35,1 kg·m⁻³_{ads}·h⁻¹ quando se utilizou Ar como desorvente.

Entre os três adsorventes, os extrudados de Maxsorb apresentam maior produtividade máxima por massa de adsorvente, como previsto pelo SPI, enquanto o BPL proporciona maior produtividade máxima por volume de coluna.

Foi ainda conceptualizado e modelado um processo híbrido SMB/PSA, onde a regeneração do adsorvente é realizada através de uma sequência de sub-etapas de PSA, em combinação com cromatografia por deslocamento utilizando parte da corrente de produto de metano, permitindo remover de forma eficaz o desorvente do processo. Os resultados da simulação mostraram que o processo híbrido é capaz de atingir uma pureza de metano de 97% e de azoto de 99%, sendo que a recuperação parcial da corrente de saída da sub-etapa de purga e a otimização do caudal de purga melhoraram as recuperações e produtividades de forma geral. Verificou-se que manter a pressão das sub-etapas de dessorção muito baixas (0.1 bar) é essencial para alcançar um bom desempenho do processo, o que conduz a um maior consumo energético ($503,0 \text{ W} \cdot \text{h} \cdot \text{kg}^{-1}_{\text{CH}_4}$).

Palavras-chave: adsorção, valorização de metano, carvão ativado, leito móvel simulado

OUTPUTS AND AUTHOR CONTRIBUTIONS

During the doctoral program, I have contributed to the seven research articles listed below. Of these articles, I was the first author in three of them and shared co-authorship in one. This thesis is based on the first four articles, with a fifth article being prepared for submission. Other contributions and outputs, such as oral presentations, are also listed below.

Articles in international journals

1. *A performance indicator for the screening of adsorbent/desorbent pairs for gas-phase simulated moving bed applications*

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Rafael O. M. Dias, Idelfonso B. R. Nogueira, Alexandre F. P. Ferreira, Alírio E. Rodrigues, Ana M. Ribeiro

In this article, my contributions were the following: (i) developing a *gPROMS/MATLAB* algorithm to expedite the simulation of the separation regions, (ii) performing all numerical simulations of fluid flow and mass transport and contributed to (iii) discussing the results, (iv) writing the paper, and (v) performing revisions following reviews.

2. *Gas-Phase Simulated Moving Bed for Methane/Nitrogen Separation Using a Commercial Activated Carbon*

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In this article, my contributions were the following: (i) performing all experimental work, (ii) performing all numerical simulations of fluid flow and mass transport and contributed to (iii) discussing the results, (iv) writing the paper, and (v) performing revisions following reviews.

3. *Methane upgrading on pelletised Maxsorb activated carbon by gas-phase simulated moving bed*

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- 2. *Gas-phase simulated moving bed for methane/nitrogen separation using a commercial activated carbon***

2022 AIChE Annual Meeting, 13-18 November 2022, Phoenix, Arizona, USA

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- 3. *Methane upgrading on pelletized Maxsorb by gas-phase simulated moving bed***

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- 4. *Gas-phase simulated moving bed for methane and nitrogen separation using Maxsorb extrudates***

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R. O. M. Dias, M. J. Regufe, A. A. Pereira, A. F. P. Ferreira, A. E. Rodrigues, A. M. Ribeiro

5. Methane and nitrogen separation by gas-SMB in activated carbon monoliths manufactured via 3D-printing

2024 AIChE Annual Meeting, 27 - 31 October 2024, San Diego, California, USA

<https://www.aiche.org/conferences/aiche-annual-meeting/2024>

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A. Pereira, R. O. M. Dias, D. Lourenço, M. J. Regufe, A. E. Rodrigues, A. M. Ribeiro, A. F. P. Ferreira

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NOTATION

List of Symbols

$\mathcal{A}$	adsorption surface area	$\text{m}^2 \cdot \text{kg}^{-1}$
A	cross-section area of the column	m^2
a_0 to a_4	parameters of the polynomial equation for heat capacity calculation	
A_1 to A_8	empiric constants	
a_p	particle/monolith channel specific area	m^{-1}
$b_{0,i}$	adsorption affinity constant at infinite temperature	bar^{-1}
b_i	temperature-dependent adsorption affinity constant of component i	bar^{-1}
C_i^F	feed concentration of component i	$\text{mol} \cdot \text{m}^{-3}$
$C_{g,i}$	fluid phase concentration of component i	$\text{mol} \cdot \text{m}^{-3}$
$C_{g,T}$	total concentration in the fluid phase	$\text{mol} \cdot \text{m}^{-3}$
$C_{\text{inlet},i}$	total inlet gas phase concentration of component i	$\text{mol} \cdot \text{m}^{-3}$
$C_{\text{inlet},T}$	total inlet gas phase concentration	$\text{mol} \cdot \text{m}^{-3}$
c_P	gas mixture molar heat capacity at constant pressure	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
$c_{P,i}$	molar heat capacity at constant pressure of component i	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
$\overline{C_{p,i}}$	averaged mole concentration of component i inside the particle	$\text{mol} \cdot \text{m}^{-3}$
$\hat{c}_{P,i}$	specific heat at constant pressure of component i	$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
$\hat{c}_{PS}$	solid specific heat	$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
$\hat{c}_{PW}$	column wall specific heat	$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
$C_{s,i}$	concentration at the solid interface of component i	$\text{mol} \cdot \text{m}^{-3}$
c_V	gas mixture molar heat capacity at constant volume	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
$c_{V,i}$	molar heat capacity of component i at constant volume	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
D_{ax}	axial dispersion coefficient	$\text{m}^2 \cdot \text{s}^{-1}$
DC	desorbent consumption	$\text{m}_{\text{STP, desorbent}}^3 \cdot \text{kg}_{\text{CH}_4}^{-1}$
d_{eq}	internal diameter of the column considering approximation to a cylindrical column	m
$D_{i,j}$	binary molecular diffusivity of component i and j	$\text{m}^2 \cdot \text{s}^{-1}$
$D_{k,i}$	Knudsen diffusivity of component i	$\text{m}^2 \cdot \text{s}^{-1}$
D_m	molecular diffusivity of the gas mixture	$\text{m}^2 \cdot \text{s}^{-1}$
$D_{m,i}$	molecular diffusivity of component i	$\text{m}^2 \cdot \text{s}^{-1}$
$D_{\text{micro},i}$	micropore diffusivity of component i	$\text{m}^2 \cdot \text{s}^{-1}$
d_p	particle diameter	m
$D_{p,i}$	macropore diffusivity of component i	$\text{m}^2 \cdot \text{s}^{-1}$

$\bar{d}_{\text{pore}}$	average pore size	nm
d_w	internal column diameter	m
e	width of the column wall	m
F	molar flow rate	mol·s ⁻¹
F_{disp}	displacement gas molar flow rate	mol·s ⁻¹
F_j	molar flow rate in each zone j	mol·s ⁻¹
h_f	film heat transfer coefficient between the gas phase and the solid / monolith wall	W·m ⁻² ·K ⁻¹
h_w	film heat transfer coefficient between the gas phase / monolith wall and the column wall	W·m ⁻² ·K ⁻¹
k_f	film mass transfer coefficient	m·s ⁻¹
k_g	thermal conductivity for the gas mixture	W·m ⁻² ·K ⁻¹
$k_{g,i}$	thermal conductivity of component i	W·m ⁻² ·K ⁻¹
k_{macro}	mass transfer resistance coefficient at the macropore level	s ⁻¹
k_{micro}	mass transfer resistance coefficient at the micropore level	s ⁻¹
k_{SM}	particle geometry factor	
L	column length	m
l_w	monolith wall thickness	m
m	adsorbent mass	kg
M	molecular weight	kg·mol ⁻¹
M_i	molecular weight of the component i	kg·mol ⁻¹
M_{ij}	molecular weight of the mixture between component i and j	kg·mol ⁻¹
n	heterogeneity factor for Sips and Toth models	
$n_{\text{pg,out},i}$	amount of i exiting the column during the purge sub-step	mol
NC	number of components	
N_{sites}	number of sites	
Nu	Nusselt number	
P	total pressure of the system	Pa or bar
P_i	partial pressure of component i	bar
P_i^0	hypothetical pressure of the pure component i	bar
P_{high}	pressure at the end of Section III	Pa
P_{inlet}	inlet pressure	Pa
P_{low}	low pressure during the desorption sub-steps	Pa
Pr	Prandtl number	
$Prod$	productivity	kg _{A,B} · m _{ads} ⁻³ · h ⁻¹
P_{outlet}	outlet pressure	Pa

P_u	desorbent-free basis purity	%
Q	flow rate	$\text{m}^3 \cdot \text{s}^{-1}$
Q_{disp}	displacement gas flow rate	SLPM
$Q_{\text{F,max}}$	maximum feed flow rate in the hybrid process	SLPM
q_i	adsorbed concentration of component i	$\text{mol} \cdot \text{kg}^{-1}$
q_i^*	adsorbed concentration of component i in equilibrium with $\overline{C_{p,i}}$	$\text{mol} \cdot \text{kg}^{-1}$
$\overline{q}_i$	particle averaged adsorbed concentration of component i	$\text{mol} \cdot \text{kg}^{-1}$
q_i^0	uptake of the pure component i at P_i^0	$\text{mol} \cdot \text{kg}^{-1}$
$q_{\text{m},i}$	saturation capacity of component i	$\text{mol} \cdot \text{kg}^{-1}$
Q_{pg}	purge flow rate	SLPM
$Q_{\text{pg,min}}$	minimum purge flow rate	SLPM
q_t	total adsorbed amount	$\text{mol} \cdot \text{kg}^{-1}$
Re	Reynolds number	
Rec	Recovery	%
R_g	ideal gas constant (=8.314)	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
r_p	pore radius	cm
R_p	particle radius	m
R_{micro}	characteristic length of the micropore	m
S_{BET}	BET surface area	$\text{m}^2 \cdot \text{g}^{-1}$
Sc	Schmidt number	
Sh	Sherwood number	
S_{LANGMUIR}	Langmuir surface area	$\text{m}^2 \cdot \text{g}^{-1}$
t	time	s
T	temperature of the system	K
t_{blow}	blowdown sub-step duration	s
T_{inlet}	inlet temperature	K
t^*	switching time	s
T_g	temperature of the gas phase	K
t_{pg}	purge sub-step duration	s
t_{press}	pressurization sub-step duration	s
T_s	temperature of the solid phase	K
T_w	temperature of the wall of the column	K
T_{∞}	the temperature of the surroundings	K
U	overall heat transfer coefficient	$\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$

u_0	superficial gas velocity	$\text{m}\cdot\text{s}^{-1}$
$u_{0,\text{inlet}}$	inlet superficial gas velocity	$\text{m}\cdot\text{s}^{-1}$
u_s	interstitial solid velocity	$\text{m}\cdot\text{s}^{-1}$
v_j	interstitial fluid velocity in section j	$\text{m}\cdot\text{s}^{-1}$
V_{micro}	micropore volume	$\text{cm}^3\cdot\text{g}^{-1}$
W_{blow}	power consumption resultant from the vacuum pump during the blowdown sub-step in the hybrid process	W
W_{disp}	power consumption resultant from the compression of the displacement gas in the hybrid process	W
W_{pg}	power consumption resultant from the vacuum pump during the purge sub-step in the hybrid process	W
W_T	total power consumption	W
x_i	molar fraction in the adsorbed phase of pure component i	
y_i	molar fraction in the gas phase of pure component i	
$\bar{y}$	average molar fraction	
Z	reduced spreading pressure	$\text{mol}\cdot\text{kg}^{-1}$
z	axial direction	m

Greek letters

α_{AB}	ideal selectivity of component A over component B	
α_w	ratio of the internal surface area to the volume of the column wall	m^{-1}
α_{wl}	ratio of the logarithmic mean surface area of the column shell to the volume of the column wall	m^{-1}
γ	ratio between the heat capacity of the gas mixture at constant pressure and the heat capacity of the gas mixture at constant volume	
γ_j	dimensionless ratio of the interstitial fluid and solid velocities in section j	
$\Delta H_{i,k}$	enthalpic parameter of component i for site k	$\text{J}\cdot\text{mol}^{-1}$
$\Delta H_{\text{iso},i}$	isosteric heat of adsorption	$\text{J}\cdot\text{mol}^{-1}$
$\Delta n_{\text{blow},\text{CH}_4}$	amount of methane produced during the blowdown sub-step	mol
ΔP_{blow}	pressure difference between the start and end of the blowdown sub-step	Pa
$\Delta q_{\text{blow},\text{CH}_4}$	adsorbed concentration change observed during the blowdown sub-step	$\text{mol}\cdot\text{kg}^{-1}$
ε	bed porosity	
ε_i	minimum pair-potential energy	K
ε_p	Particle/monolith wall porosity	
ε_t	total porosity	
η	compressor/vacuum pump efficiency	

k	Boltzmann constant	
λ	heat axial dispersion coefficient	$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
λ_i	adsorptivity, $\lambda_i = q_{\text{m},i}b_i$	
μ	gas mixture viscosity	$\text{Pa}\cdot\text{s}$
μ_i	pure gas viscosity	$\text{Pa}\cdot\text{s}$
ρ	gas mixture density	$\text{kg}\cdot\text{m}^{-3}$
ρ_b	bulk density	$\text{kg}\cdot\text{m}^{-3}$
ρ_p	particle/monolith wall apparent density	$\text{kg}\cdot\text{m}^{-3}$
ρ_s	solid density	$\text{kg}\cdot\text{m}^{-3}$
ρ_w	column wall density	$\text{kg}\cdot\text{m}^{-3}$
π	spreading pressure	$\text{J}\cdot\text{m}^{-2}$
σ	Lennard-Jones parameter	$\text{\AA}$
σ_{ij}	interaction value between component i and component j	$\text{\AA}$
τ_p	particle tortuosity	
Φ_{ij}	Wilke's coefficients	
ω	acentric factor	
ω_F, ω_G	equilibrium theory parameter defined as solution of Equation (7.5)	
Ω_D	collision integral for the calculation of the binary molecular diffusivity	
Ω_{μ_i}	collision integral for the calculation of the viscosity of component i	
Ω_M	LDF factor for macropores	
Ω_m	LDF factor for micropores	

Subscripts and superscripts

i	component of the mixture
j	Section number
k	Number of columns
I, II, III, IV	Section I, II, III and IV, respectively
D, F, R, X, IV	Desorbent, Feed, Raffinate, Extract, and recycle streams
A, B	Heavy and light component

Abbreviations

AC	activated carbon
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API	adsorption performance indicator
bcm	billion cubic meters
BPR	back-pressure regulator
BT	breakthrough
CBM	coalbed methane
CMC	carboxymethylcellulose
CMM	coal mine methane
DAEBDF	differential-algebraic equation - backward differentiation formulae
Disp	displacement gas
FID	flame ionization detector
G	gravimetric
GC	gas chromatography
IAST	ideal adsorption solution theory
LDF	linear driving force
LFG	landfill gas
LNG	liquified natural gas
MFC	mass flow controller
MOF	metal organic framework
MTZ	mass transfer zone
NG	natural gas
OCFEM	orthogonal collocation on finite elements method
Pg	purge
PLC	programmable logic controller
Press	pressurization
PSA	pressure swing adsorption
SMB	simulated moving bed
SPI	SMB performance indicator
TCD	thermal conductivity detector
TMB	true moving bed
UMA	University of Malaga
V	volumetric
VAM	ventilation air methane
VPSA	vacuum pressure swing adsorption
ZP	zero-point

CHAPTER 1 – INTRODUCTION

1.1. Relevance and Motivation

With global warming being one of the main concerns in our society, many actions are being taken, especially to address the problem of greenhouse gases such as CO₂. In the Paris Climate Conference (COP21), in 2015, a global consensus was reached to reduce greenhouse gas emissions in order to hold the increase in the global average temperature below 2 °C [1]. One way to diminish the CO₂ emissions is to substitute energy sources such as coal with less polluting ones, such as natural gas (NG). Because methane has the highest H-to-C ratio of any fossil fuel and its combustion results in less carbon monoxide (CO) and carbon dioxide (CO₂) released per unit of energy generated [2], it is considered a cleaner fuel. In 2022, the demand for natural gas reached 3985 billion cubic meters (bcm), with its global primary energy consumption share reaching 24.0% [3].

Due to the rise in demand, the exploration of unconventional methane sources, such as coalbeds, landfill gas (LFG), and shale gas, has been gradually increasing over the years because of the depletion of conventional wells. In these sources, methane content can be as low as 60%, with contaminants such as nitrogen and carbon dioxide [4]. Recovering the methane gas present in these sources can be difficult, especially when considering the pipeline specifications. For pipeline gas, the nitrogen content is required to be lower than 3-4% [5-8], depending on the governing body, since it not only dilutes the heating value of the natural gas and increases the compression volume of the stream but also can cause transportation problems due to stratification inside the pipes, namely flow instability and increased pressure drop [9]. However, the similarity in physiochemical properties between methane and nitrogen poses a challenge in the separation process.

On a large scale, the conventional method for methane-nitrogen separation is cryogenic distillation, taking advantage of the difference in methane and nitrogen volatility. The process involves multistage distillation columns, operating at cryogenic temperatures to liquefy the methane gas, allowing the nitrogen to be rejected from the stream, leading to very high energy consumption [10]. This way, it becomes inefficient from an economic standpoint for small-scale applications, creating a gap in the industry for more energy-efficient and scalable solutions.

When compared to cryogenic distillation, adsorption-based processes are very appealing thanks to their easy scalability, and low equipment and operating costs. However, the performance of the solid materials for CH₄/N₂ separation becomes an issue due to their low selectivity. The use of a gas-phase separation process based on the simulated moving bed (SMB) technology is promising since it is known to be able to separate compounds even with a low adsorption selectivity. Although traditionally used in liquid-phase separations, it can offer significant potential for gas-phase applications due to its ability to operate at almost isobaric and isothermal conditions, leading to low energy usage [11-14]. Despite this, the implementation of SMB for methane-nitrogen separation remains underexplored, representing a novel and impactful direction for research.

As such, this thesis focuses on the application of the gas-phase SMB technology for the separation of methane and nitrogen. The successful implementation of this process will allow the separation of CH_4 and N_2 more efficiently, especially for small/medium scale production of purified methane, with beneficial impacts in both environmental and energy sectors.

1.2. Outline and objectives

This work aims to develop a new and advanced adsorption process for the separation of nitrogen from methane based on the gas-phase SMB technology. To do so, selecting the appropriate adsorbent and desorbent to be used in the process and studying its adsorption equilibrium and multi-component adsorption dynamics is vital to implement a mathematical model that can describe the system and effectively design the process. For this matter, a literature review on adsorbents and their performance for the herein studied separation was performed. Then, an SMB performance indicator was developed to easily select the most efficient adsorbent/desorbent pair for a specific SMB application. Adsorption equilibrium isotherms and fixed bed experiments were conducted for the chosen materials, and gas-phase SMB processes were designed for each pair. Then, an *in-silico* study was performed to design an SMB/PSA hybrid unit, removing the need for the desorbent gas in the process.

Chapter 1 is the introduction, where the relevance and motivation of this work are described, highlighting the main objectives of the work.

Chapter 2 presents the state-of-the-art on methane and nitrogen separation. It starts with a brief explanation of why exploring new methods for this separation is necessary and a description of the conventional methods. The main research topics on the simulation moving bed technology are also addressed. Then, a literature review was conducted on the recent developments in adsorptive processes for methane upgrade.

Chapter 3 presents the model equations used for characterising the single and multicomponent adsorption equilibrium and the system's dynamic behaviour. A summary of the mass and energy balances and momentum equations, as well as the initial and boundary conditions used in the fixed bed, SMB, and SMB/PSA hybrid process modelling, are presented in this chapter. The procedure for the determination of the separation region is also described.

Chapter 4 consists of the development of a new performance indicator specifically designed for SMB applications, the SMB Performance Indicator (SPI). This new indicator allows for an expedite selection of the adsorbent material and desorbent gas used in an SMB process.

In **Chapter 5**, the materials utilised in this work are depicted, i.e., the selected adsorbents and the respective characterization and shaping process are described. Also, the experimental methods implemented and the respective set-ups used for acquiring the adsorption equilibrium isotherms and performing the fixed-bed and SMB experiments are described.

Chapter 6 focuses on the conventional gas-phase SMB cycles designed to separate an equimolar mixture of methane and nitrogen over the selected materials, using carbon dioxide and argon as potential desorbent gases. Three materials were tested, and their performance was compared: a commercial activated carbon, BPL, in the form of granules, and in-house extruded pellets and 3D-printed monoliths produced with Maxsorb activated carbon. For each case, the single component adsorption equilibrium was measured, dynamic tests were conducted, and two SMB cycles were proposed and performed. For the monolith material, a third SMB cycle was operated in closed-loop mode. All experimental data was validated with the proposed phenomenological model, which was implemented in the *gPROMS* software. The results were then crossed to identify which adsorbent/desorbent pair presents the best performance for this separation.

Chapter 7 focuses on the design and simulation of an SMB/PSA hybrid process, where the adsorption regeneration is achieved through pressure swing and displacement chromatography using the heavy product, eliminating the need for the desorbent gas in the process. In this computational study, the *gPROMS* software was used to develop the simulation code for modelling the SMB/PSA system. The chapter presents the obtained simulation results, highlighting the performance of the process under various operating conditions. A parametric study was conducted to investigate the influence of the key process parameters on the hybrid system's performance, providing insights into its potential for methane/nitrogen separation.

Chapter 8 summarizes the main conclusions and limitations observed and presents some suggestions for future work.

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CHAPTER 2 – STATE OF THE ART

2.1. Natural gas

Natural gas is a product of the decomposition of plant-based and organic matter that accumulated beneath several layers of sediment and rock, millions of years ago. Due to being exposed to enormous heat and pressure, the remains are converted into oil and natural gas. Comprised predominantly by methane, natural gas can occur in crude oil wells, denominated conventional associated natural gas. In this case, it is recovered as a byproduct of the crude oil distillation, being obtained at the top of the distillation unit. When the gas is not connected to an oil source – conventional non-associated natural gas – the natural gas can be extracted directly from the well. Natural gas can also be obtained from unconventional sources, such as shale gas, coalbed methane (CBM), tight gas from low-permeability rocks, gas hydrates, biogas generated from the decomposition of organic matter in landfills or wastewater treatment plants, and gas in geopressurized zones [1].

Because of the way in which it is formed, natural gas contains many compounds other than methane and its composition varies depending on the reserve. Besides methane, natural gas is often comprised of hydrocarbon derivatives, low-boiling aromatic hydrocarbon derivatives (derivatives of benzene), non-hydrocarbon constituents such as nitrogen, carbon dioxide (CO₂), water (H₂O), hydrogen sulphide (H₂S), and mercaptan derivatives, as well as trace quantities of other inerts such helium and argon [1].

Natural gas is a very versatile resource, being utilised in several applications, such as domestic use, industrial use for climatization, cooling and heating processes, cogeneration (production of heat and electricity) and as a raw material for the production of synthesis gas (syngas, which is composed mainly of hydrogen and carbon monoxide) by steam-reforming in the petrochemical industry. It is also utilised in other industrial sectors, such as ceramics, glass, textile, food, metallurgic, pharmaceutical and in the production of fertilizers, among others [1]. Besides its utility in the industry, natural gas can also be used as a fuel for transportation, as a less pollutant and more economical alternative to diesel and gasoline.

Regarding the transportation of natural gas, it occurs mainly through gas pipelines. However, when it is necessary to traverse long-distances, cooling of the gas can occur until it liquifies, which reduces the volume occupied and allows for a much easier storage and shipping of the liquified natural gas (LNG) [1].

With global warming and CO₂ emissions remaining a pressing issue, natural gas continues to be favoured when in contrast to other hydrocarbon fuels due to its combustion resulting in a lower carbon intensity per unit of energy generated [2]. In 2023, natural gas accounted for 23.2% of the total primary energy consumption (Figure 2.1) [3].

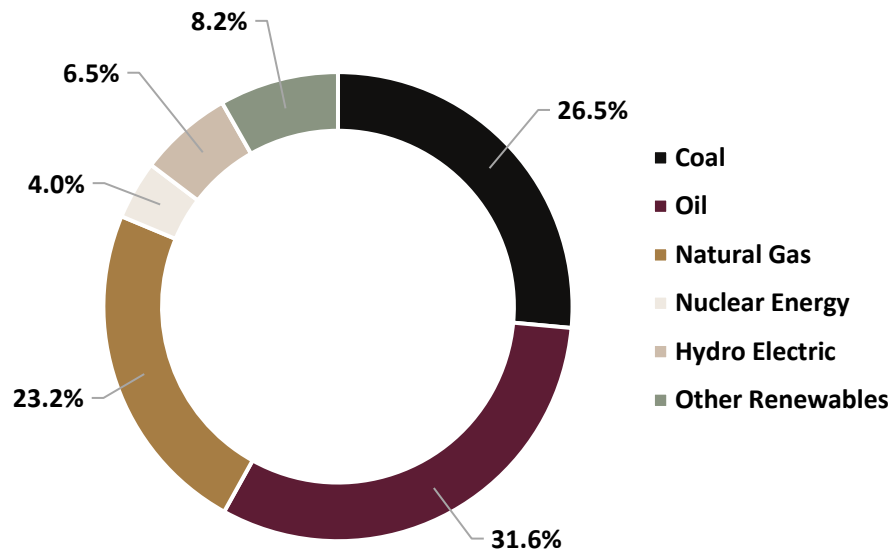


Figure 2.1 – Shares of global primary energy consumption by fuel in 2023. Data from Energy Institute [3].

In recent years, the global natural gas demand and consumption have been heavily influenced by major world events, like the COVID-19 pandemic and the ongoing conflict between Russia and Ukraine. The pandemic in 2020 resulted in a decline in the natural gas markets due to global lockdowns and reduced industrial activity, marking one of the biggest demand shocks in recent times [4]. This was followed by the Russian invasion of Ukraine in 2022, which led to the disruption of the Russian gas supply pipelines to Europe by approximately 80 billion cubic meters (bcm), resulting in an energy crisis [5]. In response, the European Union implemented policies to reduce natural gas consumption, which resulted in a more than 15% reduction in gas consumption in both 2023 and 2024 when compared to the previous five year average [5]. Nevertheless, the global natural gas demand rebounded in 2024, increasing by 2.7%, equivalent to 115 billion cubic meters (bcm), reaching a new all-time high of 4174 bcm [6]. This increase was driven by emerging and developing economies in Asia, mainly China and India [6].

With increasing world population and productivity, it is expected that the global natural gas markets will continue to rise. In fact, according to BP's *Energy Outlook 2024*, the global natural gas demand is expected to reach approximately 4700 bcm by 2050, if the current trajectory is maintained [7]. LNG traded volume is expected to increase by approximately 70% as Europe and Asia will heavily rely on it to meet the rising NG demand [7].

Data from 2023 show that a share of 11.6 % of the world consumption of natural gas corresponds to Europe, expending *circa* 463.4 bcm [3]. In 2023, the European gas trade of pipeline natural gas amounts to 340.8 bcm, with 111.6 bcm being imported mainly from Russia, Algeria, and Azerbaijan. LNG imports amount to 169.1 bcm, being sourced primarily from the United States, Qatar, Russia, Algeria, Nigeria [3]. Despite the efforts, Russia continues to be one of the main suppliers of natural gas to Europe, accounting for 15% of the total imports in 2023 [3].

In Portugal, natural gas consumption fell by 28.2% between August 2022 and April 2024, aligning with energy-saving directives implemented by the European Union [8]. Nevertheless, the country became increasingly reliant on LNG, with 98% of its natural gas in 2024 imported through the Sines LNG Terminal [9]. The LNG imports are primarily sourced from Nigeria and the USA, while a small fraction of natural gas arrives by pipeline from Spain [10]. In 2023, the consumption of natural gas reached 4.5 bcm, which is equivalent to 0.1% of the world consumption [3].

2.2. Methane and nitrogen separation

Depending on the unconventional gas source, the nitrogen content in the methane gas streams varies. For coalbed methane, CH₄ content can go as low as 60% [1]. In landfill gas, which is produced from the anaerobic decay of waste, N₂ content can range from 5 to 25%, especially when air infiltrates during active gas extraction at subatmospheric pressures, which is necessary to ensure higher CH₄ recovery and to avoid its release in the atmosphere [11]. Additional methane-containing streams requiring treatment include coal mine methane (CMM) and ventilation air methane (VAM), which are diluted streams resultant from coal mining activity. Due to their low methane concentration (as low as 30% for CMM and below 1% for VAM), they are very difficult to be separated with conventional methods. As such, these streams are either energetically valorised through combustion or released to the atmosphere, contributing to the greenhouse effect, meaning that both resources are not properly exploited [12, 13].

Being an inert gas, nitrogen removal is challenging and done only when its content exceeds 3-4% for pipeline natural gas, depending on the governing body, to maximize the calorific value of the fuel, or 1% for liquefied natural gas (LNG), to prevent stratification and roll-over of the product during shipping, which is the spontaneous mixing of two cryogenic liquid layers in a tank and can lead to rupture of the tank [14, 15]. In Table 2.1, the typical composition range of pipeline NG and LNG is presented.

Table 2.1 - Typical composition (molar basis) range of pipeline natural gas and liquified natural gas.

Component	NG composition	LNG composition
<i>Hydrocarbons</i>		
Methane	> 0.75	0.84 - 0.99
Ethane	< 0.10	< 0.05
Propane	< 0.05	< 0.03
<i>n</i> -Butane	< 0.02	< 0.01
Isobutane	< 0.01	< 0.01
Pentane and heavier hydrocarbons	< 0.05	-
<i>Non-hydrocarbons</i>		
Nitrogen and other inerts	< 0.03	< 0.01

To produce pipeline gas, one can blend a nitrogen contaminated outflow with a methane-rich natural gas [14]. However, this is not a long-term solution and necessitates a high purity stream in

the first place. As such, alternative methods must be considered in order to meet the target specifications.

To separate two components from a mixture, the difference in their physical properties must be exploited. In Table 2.2, some important properties of methane and nitrogen are presented.

Table 2.2 - Physical properties of methane and nitrogen [16].

Component	Normal boiling point (K)	Kinetic diameter (Å)	Polarizability ($\times 10^{-25}$ cm ³)	Dipole moment ($\times 10^{18}$ esu·cm)	Quadrupole moment ($\times 10^{-26}$ esu·cm ²)
Nitrogen	77.4	3.64	17.6	0	1.52
Methane	111.7	3.82	26.0	0	0

Due to the similarity in physical properties, nitrogen removal is very challenging. As can be observed, both compounds have a comparable kinetic diameter, limiting the feasibility of kinetic-based separation processes. In these cases, the adsorbent materials must possess an intermediate pore size for an effective molecular sieving. This can be accomplished by finding materials with such characteristics or finely tuning the pore diameter to obtain a material that is able to exploit the kinetic diameter difference between the two molecules.

The difference in polarizability and electrostatic properties between both compounds indicates that a process based on adsorption equilibrium is possible, if a material with a good performance is utilised. CH₄ has a higher polarizability when compared to N₂, allowing it to interact more strongly with adsorbents through induced dipole-induced dipole (London dispersion) forces [17]. This makes materials with high surface polarizability exhibit higher affinity toward CH₄, which is the case of activated carbons. On the other hand, N₂ possesses a quadrupole moment, enabling electrostatic interactions between the adsorbent surface and the permanent electric moment of the molecule [17]. This leads to a low selectivity between CH₄ and N₂ in most adsorbents. Therefore, selecting or designing adsorbents that can exploit the electrostatic properties of both molecules is crucial to effectively separate this mixture through equilibrium-based adsorption processes.

The main difference between methane and nitrogen is their normal boiling points, which makes distillation a viable separation method. However, because of their low boiling points, the process needs to be operated in cryogenic conditions, resulting in high energy consumption.

As such, when blending is not an option, other methods can be utilised for the removal of N₂, among them cryogenic distillation, absorption, membrane permeation, and adsorption [14]. These methods are described in more detail below.

The conventional method of purification of a nitrogen contaminated methane stream is **cryogenic distillation**. For this technology, the driving force is the volatility difference between the two gas molecules. At the intermediate stages of this process, at a pressure of 3150 kPa, their boiling points

increase to 178.5 K and 124.5 K [18], which means that a distillation separation process can be effectively achieved by lowering the temperature to about 133 K. This system, called a nitrogen rejection unit (NRU), is usually implemented at the end of a natural gas purification process, and can reduce the percentage of nitrogen present in a stream to values under 1% [14, 18]. Different process designs are implemented according to the N_2 content in the feed gas, inlet flow rate, presence of contaminants, product specifications. The most common cryogenic technology units are the single-column heat-pumped process, the dual-column process and the dual-column process with a pre-fractionation step [18]. Prior to the NRU, the inlet gas is compressed, and a pre-treatment of the feed stream is necessary to remove any contaminants that could freeze downstream in the cryogenic unit, such as water, CO_2 and heavy hydrocarbons. Excess H_2S and mercury are also removed upstream of the NRU. In the single-column process, the nitrogen is removed as an overhead product in the distillate with 99% purity and pure methane (99%) is produced at the base of the column. To provide the reboiler and condenser necessary duties, a closed-loop heat pump cycle is utilised [18]. For higher N_2 content in the feed gas (above 20%), the single-column process is no longer efficient, due to condensation problems in the upper trays of the distillation column. As such, a dual-column NRU can be utilized, allowing partial removal of the N_2 in a high-pressure column, with the bottom product being fed to a low-pressure column for further nitrogen rejection. The dual-column system can be coupled to a prefractionation column, recovering a portion of the hydrocarbons present in the inlet stream at a higher temperature. Consequently, the stream is enriched in nitrogen, which is then processed in the main distillation columns [18].

The main drawbacks of nitrogen removal from methane streams by cryogenic distillation are the necessity of a pre-treatment to remove water and carbon dioxide, as well as other impurities, from the stream, to avoid blockage of the equipment, and the high equipment and operating costs, since the process is very energy intensive. This means that, for this process to be economically viable, the distillation columns must process a high volume of gas (above $4.90 \text{ m}^3 \cdot \text{s}^{-1}$), therefore, making it impracticable for medium/small scale production of purified methane [19]. Notwithstanding these disadvantages, the degree of maturity of this process makes it the most used method for the separation of this gas mixture for large scale installations.

Absorption processes are also utilised for methane purification, in which a liquid solvent is fed through the top of a tower and the gas stream is bubbled in countercurrent. This way, the compound with greater solubility in the chosen solvent is absorbed in the liquid phase, while the purified gas is collected at the top of the column. Afterward, the absorbed gas can be recovered by *stripping*. While this process is mostly used for the purification of carbon dioxide contaminated natural gas, using amine-based solutions, it can be adapted to effectively remove N_2 if the solvent used has a high absorption capacity and if it is easily regenerated, while using an appropriate liquid circulation rate to minimize costs. Research on liquid ammonia as an N_2 -selective solvent

was done, however, it is unsuitable for this separation due to its hazardous nature and because the process is economically unfeasible (utilising large volumes of solvent) [14]. Lean oil absorption technology is also used for methane purification, by absorbing the CH_4 from the gas stream with a hydrocarbon oil and then regenerating it through sequential flash vessels, yielding a methane stream with a purity higher than 96 %. However, this technique is a less competitive alternative with respect to cryogenic process because of the low absorption capacity of the solvent for CH_4 , requiring high solvent circulation rates, and the need of recompression of the gas stream, making it energy intensive [14]. Kim *et al.* evaluated the performance of 73 commonly used liquid solvents in a computational study, with a focus on enriching diluted coal mine gas streams [20]. Among the solvents studied, 1-octanamine demonstrated relatively high CH_4/N_2 selectivity (above 10). Despite this, all solvents displayed very low Henry's constants for CH_4 , indicating limited gas solubility [20].

Another conventional method is the use of **membranes** to purify natural gas. In contrast to cryogenic distillation, the use of membrane technology for separation has low energy requirement, which makes it very appealing, although these materials are very expensive, and their maintenance cost is high. The membrane types that have been studied for the separation of nitrogen and methane include polymer membranes [21, 22], inorganic molecular sieve membranes [23-26] and mixed matrix membranes [27], with the molecular sieving membranes being exclusively nitrogen-selective, a consequence of the kinetic diameter of the molecules. The performance of a membrane is generally evaluated based on two indicators: the permeability and the selectivity. Polymeric membranes, such as PDMS, can achieve high N_2 permeance, but are usually CH_4 -selective [22]. Several molecular sieve membrane materials have demonstrated performance above the polymer membranes for this separation. Among these, SSZ-13 membranes exhibit the highest reported N_2/CH_4 selectivities, although their N_2 permeances remain relatively moderate [24]. In contrast, AlPO-18 membranes offer very high nitrogen permeances, however, with only mild selectivity [25]. SAPO-34 membranes stand out by exhibiting the best overall performance, achieving high N_2 permeances and N_2/CH_4 selectivities as high as 11.3 [26].

Membrane techniques have been applied at industrial scale for the purification of CH_4 streams with low N_2 content, by using multi-stage processes capable of reducing the N_2 feed concentration by more than half [14]. The *NitroSepTM* system, produced by *MTR Industrial Separations*, utilises proprietary membranes that are CH_4 -selective. In this process, a methane stream containing 8% to 12% nitrogen is compressed and passed through a series of membrane modules. The first stage produces a permeate stream with high methane purity, meeting the specifications required for pipeline gas, while the nitrogen-rich residue is further processed in a second membrane stage. This stage yields a nitrogen-depleted permeate, which is recycled back into the feed stream to improve methane recovery, and a nitrogen-rich residue gas that is used as fuel. This system is able to yield a methane recovery above 90% [28].

Adsorption-based processes are very appealing for gas separation thanks to the easy scalability and low equipment and operating costs when compared to other traditional processes such as cryogenic distillation. Regarding the separation of CH₄/N₂ mixtures, a N₂-selective adsorbent would be preferable since it removes the need for recompression of the methane stream. However, for the majority of the available adsorbents, methane is the most adsorbed gas. Among the adsorption-based processes, pressure swing adsorption (PSA) is a viable option from an economic standpoint. Yet, it is necessary to find materials with high capacity, high selectivity, and that are easy to regenerate, to effectively implement this technology. But, as a consequence of the similarity in the molecules physical properties, the selectivity of the majority of the materials used as adsorbents is low [19].

This said, two types of PSA processes can be employed for this separation, depending on the underlying separation mechanism: kinetic-based and equilibrium-based. The kinetic-based PSA processes use adsorbent materials in which N₂ diffuses faster than CH₄, taking advantage of the slight difference in their kinetic diameters. On the other hand, equilibrium-based PSA relies on differences in adsorption affinities, with CH₄ exhibiting a stronger interaction with the adsorbent surface than N₂ (for the majority of the materials). As a result, the CH₄-rich product must be recompressed before being injected into the pipeline, adding to operational costs. This way, the choice between kinetic and equilibrium PSA depends on the specific application, with both approaches being found at an industrial scale [29, 30].

Several materials have been studied for the separation of this gaseous mixture through adsorption techniques. For kinetic-based separation processes, titanosilicates and cation-exchanged derivatives [31-35], carbon molecular sieves [36-39], and zeolites, such as clinoptilolites [40-42], can be utilised. For equilibrium-based separations, adsorbents such as activated carbons (AC) [43-52], zeolites [49, 53-59], and MOFs [49, 50, 60-67] have proven to effectively separate nitrogen-contaminated methane streams.

Titanosilicates, particularly ETS-4 and its derivatives, have been extensively studied due to their tuneable pore structures, allowing the pore size to be finely adjusted to a pore size intermediate to the kinetic diameter of both molecules (3.7 Å) [31]. This allows CH₄ to pass through the adsorbent bed while N₂ is retained, delivering a high purity methane stream (above 99%) at a high pressure. Regarding the modified forms of ETS-4, Sr-ETS-4 and Ba-ETS-4 have demonstrated enhanced performance and thermal stability [31, 35]. These materials are utilised in the *Molecular Gate*TM process, developed by *Guild Associates* [29]. Recently, Weh *et al.* studied the separation of an 85% CH₄ and 15% N₂ feed mixture by dual-reflux PSA (DR-PSA) using an ETS-4 adsorbent, showing it can upgrade the CH₄ stream to pipeline specifications, however, producing a N₂-rich stream that does not meet the environmental regulations (<1% CH₄) [34]. Wilkins *et al.* have evaluated the adsorption equilibrium and diffusion of CH₄ and N₂ over a barium-exchanged reduced pore zorite

(Ba-RPZ). This material exhibited kinetic selectivities that can be orders of magnitude greater than other titanosilicate-type adsorbents, like the Sr-ETS-4 [68].

Carbon molecular sieves (CMS) can also take advantage of the diffusion rate difference of the molecules. Cavenati *et al.* assessed the performance of a CMS-3K in terms of adsorption equilibrium and kinetics [36]. Fatehi *et al.* have shown the potential of CMS to separate CH₄/N₂ mixtures, obtaining methane streams with 75% and 96% purity from a feed stream containing 60% and 92% CH₄, respectively [37]. A CMS-3K was implemented in a layered bed to separate a 60% CH₄/20% CO₂/20% N₂ feed stream, obtaining a methane product stream with 88.8% purity and 66.2% recovery [38]. Bhadra and Farooq compared the performance of CMS and ETS-type materials to achieve above 96% methane streams [32]. Recently, an optimization study of a 6-step PSA process using a Takeda CMS achieved a high purity and high recovery (above 90%) methane stream [39].

Activated carbons show significant promise for CH₄/N₂ separation, primarily due to their high surface area and rapid adsorption kinetics, which favour equilibrium-driven adsorption. Their relatively low cost, combined with high ideal adsorption selectivity when compared to materials of different nature, make them very effective for this application. Several studies in the literature have confirmed their performance. Erden *et al.* simulated three different VPSA cycles with a four-step configuration using a BPL activated carbon to separate an 88% CH₄/12% N₂ feed stream. The best-performing cycle exhibited a 99.4% CH₄ purity and a 99.2% recovery [43]. This VPSA cycle was later revisited by Brandani *et al.*, where the process was redesigned to use close to atmospheric pressure at the end of the desorption step and optimise the step configuration without hindering the performance significantly (>96% purity, >90% recovery), using a Norit RB2 activated carbon [44]. A patent was also published which used both CMS and AC to effectively upgrade biogas streams with a multi-stage VPSA, able to separate a feed stream comprised of 48% CH₄, 35% CO₂, 12% N₂ and 5% O₂ and produce a methane stream with above 97% purity [30].

For the activated carbons tested, the equilibrium selectivities can go up to 5.5 and adsorption capacities of 1.10 mmol/g, which is the case of the pitch-based activated carbon beads studied by Wu *et al.* [51]. Other commercial ACs studied include the Norit R1 Extra [45], Maxsorb [46], Norit RB3 [48], and BPL [47].

Regarding zeolites, naturally occurring clinoptilolites and their ion-exchanged forms have been investigated as potential adsorbents for CH₄ and N₂ separation [40]. Recently, Kennedy *et al.* evaluated the performance of clinoptilolite modified through Fe³⁺ and Cs⁺ cation exchange, reporting separation factors up to 7.3 for the Fe³⁺-exchanged form, outperforming activated carbons [41]. Silva *et al.* investigated the adsorption equilibrium and kinetics of binderless zeolite 5A, observing no mass transfer resistance for CH₄ and N₂ and an adsorption selectivity of approximately 2.0 [53]. Among chabazite-type molecular sieves, chabazite-K demonstrated a

higher IAST selectivity (~ 5.2) when compared to SAPO-34 and SSZ-13, although SSZ-13 exhibited the highest methane uptake ($1.38 \text{ mmol}\cdot\text{g}^{-1}$ vs 0.7 and $0.73 \text{ mmol}\cdot\text{g}^{-1}$ for CHA-K and SAPO-34, respectively) [54]. Additionally, ZSM-5 with a Si/Al ratio of 30 showed an adsorption capacity of 0.71 mmol/g at 313 K and 1 bar , with a CH_4/N_2 selectivity of 3.3 for an equimolar mixture [55]. Silicalite-1 has been evaluated for the separation of a $50/50 \text{ CH}_4/\text{N}_2$ mixture by PSA, where a three-bed cycle achieved a methane product with 96.3% purity and 96.7% recovery, with a productivity of $0.078 \text{ kg}_{\text{CH}_4}\cdot\text{kg}^{-1}\cdot\text{h}^{-1}$ [56].

Due to the highly tuneable and functional pore surface, MOFs are very appealing since their adsorption performance can be improved for specific separations. Combining the best properties of the traditional adsorbents, their interest is emerging from a research standpoint, with several materials being studied and synthesized for the CH_4/N_2 separation. For instance, the ATC-Cu MOF, synthesized by Niu *et al.*, exhibited a record-high CH_4 uptake ($2.9 \text{ mmol}\cdot\text{g}^{-1}$), along with a high selectivity of 9.7 at 298 K and 1 bar [69]. More recently, Zhao *et al.* reported a scalable MOF achieving an outstanding IAST selectivity of 19.1 for an equimolar mixture, with an uptake of $1.08 \text{ mmol}\cdot\text{g}^{-1}$, under the same conditions [70]. MIL-120(Al) has shown the highest adsorption capacity for CH_4 among other aluminium-based MOFs ($1.50 \text{ mmol}\cdot\text{g}^{-1}$), while also exhibiting a higher diffusion rate for CH_4 than for N_2 [71]. Several other materials also demonstrated excellent performance for this separation, such as the Al-CDC MOF [72], $[\text{Ni}_3(\text{HCOO})_6]$ MOF [60], Cu-MOF [73], ZIF-94 [63] and SBMOF-1 [66], with notable methane uptakes of 1.43 , 0.82 , 0.63 , 1.51 and $0.92 \text{ mmol}\cdot\text{g}^{-1}$ and high adsorption selectivities of 13.1 , 6.18 , 11.5 , 7.0 and 11.5 , respectively, at 298 K and 1 bar .

Some computational studies in the literature have explored the use of MOFs as the stationary phase. Maté *et al.* modelled a dual PSA process for the herein studied separation using the $[\text{Ni}_3(\text{HCOO})_6]$ MOF. The designed process was able to separate an equimolar CH_4/N_2 mixture, obtaining a methane stream with a purity of 96% and a nitrogen effluent with a purity of 99.97% , producing $1.7\times 10^{-4} \text{ mol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$ of CH_4 [74]. Jaramillo and coworkers reported a N_2 -selective material, later used in an optimization study by Wilkins *et al.*, for the separation of CH_4/N_2 mixtures by PSA [75, 76]. At optimal conditions, the simulations yielded a methane stream with 96% purity and 88.3% recovery.

As an alternate adsorption-based process, SMB is an alluring option since it is able to separate compounds even with low adsorption selectivities. In this case, equilibrium-based adsorbents are preferred because of the co-occurrence of adsorption/desorption during each cycle. However, its primary disadvantage is the attainment of the products mixed with the desorbent, which have to be separated *a posteriori*.

2.3. Simulated Moving Bed

The SMB technology was first patented in 1961 by Broughton and Gerhold (Universal Oil Products) for liquid phase separations and was later developed at an industrial scale by the same company for liquid separation in the refinery industry, marketed with the name Sorbex [77]. In the 70s, this system was adapted for the separation of *p*-xylene from its isomers (PAREX system) and was later applied for the separation of sugars, namely sucrose/fructose for the production of high fructose corn syrup (SAREX system) [78, 79]. The SMB technology also found new applications in the pharmaceutical industry, for example, in enantiomer separation resorting to chromatography. This way, new SMB systems emerged, such as the Licosep (from Novasep) and the homemade FlexSMB system, both available at the Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE - LCM) (see Figure 2.2).



Figure 2.2– Liquid phase SMB systems at LSRE-LCM: in the left, Licosep 12-26 unit; in the right, homemade FlexSMB unit.

Even though this process is mainly used for liquid separations, it is possible to adapt it for gas separations, even when the compounds present in the mixture to separate have very low adsorption selectivities, *i.e.*, the separation factor is close to unity [80]. Some research work has proven this, with early efforts dating back to the 1990s.

The first attempt on a gas-phase SMB was designed in 1992 by Storti *et al.*, to separate a *m*-xylene and *p*-xylene mixture using isopropylbenzene as a desorbent and a zeolite material as an adsorbent [81]. Later in the decade, Mazzotti and co-workers studied the separation of linear/non-linear paraffins, carried out in a six-port vapor-phase SMB [82], while Juza *et al.* applied this gas-SMB technology in the pharmaceutical industry, for chiral separations, more specifically, for the separation of highly volatile enantiomers of enflurane, at 323 K, using cyclodextrin derivatives packed columns [83]. LaCava and McKeigue demonstrated that gas mixtures can be separated in

an SMB without the use of an eluent, in a patented process described as continuous pressure difference driven adsorption process [84]. In 1997, Rothchild patented a process for the selective adsorption of nitrogen from air by coupling simulated moving bed chromatography with pressure swing adsorption (which was patented as pressure swing chromatography). In this process, pressure swing is utilized to induce desorption and gas flow through the columns. It was claimed that the method provides both high product purity and high efficiency, with approximately 100 % product yield [85]. Cheng and Wilson published two patents for separating propylene from a C3 hydrocarbon mixture of propylene and propane by SMB with vacuum swing adsorption, achieving high-purity propylene at a high recovery rate [86, 87]. From 2000 to 2002, Biressi *et al.* continued the research on chiral separations, publishing works regarding the separation of volatile inhalation anaesthetic enantiomers, such as enflurane and isoflurane, using gas-phase SMB chromatography [88-90]. Later, in 2008, Kostroski and Wankat further expanded on this research by coupling the gas-phase SMB technology with pressure swing adsorption (PSA) [91]. In 2009, the authors applied this system for the separation of concentrated binary gases, more specifically, the separation of a H₂/CH₄ mixture [92].

Gas-SMB processes for other separations available in the literature include CH₄/CO₂ [93, 94] and patented processes for the separation of H₂/He and D₂/He [95]. Regarding the separation of a CH₄/CO₂ mixture, Mota *et al.* resorted to a novel single-column setup, asynchronously shifting the inlet/outlet ports, packed with activated carbon using nitrogen as the eluent. Also, their group mimicked a 4-column SMB process experimentally, where they were able to obtain both extract and raffinate streams with a purity of 98 % [93, 94]. More recently, Ribeiro *et al.* designed and implemented experimentally a two column, relay, SMB for CH₄/CO₂ separation using N₂ as the carrier gas, producing high desorbent-free purity products (above 99%) [96].

In the past few years, research on the separation of light olefin/paraffin mixtures [80, 97-108] have emerged, bringing some major scientific developments regarding this technology. Firstly, Rao *et al.* designed a hybrid SMB/PSA process to separate propane/propylene mixtures, where the adsorbent is regenerated by pressure swing. In this computational work, the authors show that it is possible to achieve a pure separation of the C₃ mixture with high productivity (100-300 mol·kg⁻¹·h⁻¹). However, to accomplish this, the regeneration step must be performed at a high vacuum of 0.01 kPa [107]. Lamia *et al.* published two articles on the propane/propylene separation using the SMB technology, testing the performance of isobutene and 1-butene, as the desorbent over 13X zeolite and promising results were obtained [101, 102]. In 2008, Rodrigues *et al.* patented a method for the separation of the referred mixture by gas-phase SMB with high purity and productivity, where 13X zeolite and 1-butene or isobutene were the selected adsorbent/desorbent pair [108, 109]. Granato *et al.* published a paper, entirely *in silico*, where potential desorbents were studied for the propane/propylene separation, also on a zeolite 13X [100]. Campo *et al.* further studied the propane/propylene gas separation on an improved zeolite 13X, using isobutane as a

desorbent, presenting a computational study for the attainment of polymer-grade propylene (99.9 % purity) from propane/propylene feed ratio of 1:4. Simulations have shown that a recovery of 99.9 % and productivity of $17.6 \text{ mol}\cdot\text{kg}^{-1}\cdot\text{h}^{-1}$ was accomplished [97]. In 2015, Martins and co-workers from our research group tested a novel installation with eight columns for this gas separation, with a 4-2-2 column configuration, suppressing the Zone IV and operating in open loop, with fresh eluent fed to the system during the entirety of the experiment. To do so, the columns were filled with zeolite 13X with a 20 % binder, being able to recover 99.5 % of polymer grade propylene with a purity of 99.9 % and a productivity of $114.1 \text{ kg}_{\text{C}_3\text{H}_6}\cdot\text{h}^{-1}\cdot\text{m}_{\text{ads}}^{-3}$ and propane with a recovery of 99.7 %, purity of 98.1 % and productivity of $30.4 \text{ kg}_{\text{C}_3\text{H}_6}\cdot\text{h}^{-1}\cdot\text{m}_{\text{ads}}^{-3}$ [80]. While providing proof of concept, this achievement has opened the door to several gas-phase SMB experiments within our group. The lab-scale gas-phase SMB unit, available at LSRE-LCM, will be disclosed in detail in Section 5.6. From this point on, Martins *et al.* published a research work on the recovery of high purity ethylene from an ethane/ethylene mixture, using a binderless 13X zeolite, *via* gas-phase SMB, with a traditional configuration of four zones in a closed loop circuit, where 99.5% of ethylene was recovered with a purity of 99.8% and producing $1.99 \text{ mol}\cdot\text{kg}^{-1}\cdot\text{h}^{-1}$ [106]. More recently, Martins *et al.* also published a work on the production of high purity ethylene with CuBTC beads as the adsorbent *via* the gas phase SMB technology, showing promising results, with 90% of the ethylene being recovered, with a purity of 95% and productivity up to $0.66 \text{ mol}\cdot\text{kg}^{-1}\cdot\text{h}^{-1}$ [104].

With recent reports of paraffin selective materials in the literature, such as ZIF-8, which presents an adsorption selectivity for ethane/ethylene of 2.1, a study was performed by Martins *et al.* using propane and carbon dioxide as possible desorbents. The experiment using propane resulted in a low ethylene purity of 82.7 % and low recovery of 77.1 %. On the other hand, when carbon dioxide was utilized as the desorbent gas, remarkable results were obtained, with ethylene reaching 99.6 % purity and a 94.2 % recovery [103].

Seabra *et al.* published a paper on the ethylene/ethane separation by gas-phase SMB in binderless zeolite 13X monoliths, with a 3-2-2-1 column configuration, in open loop, obtaining ethylene with 97.7% purity and recovery above 90%, with a productivity of $16.9 \text{ kg}_{\text{C}_2\text{H}_4}\cdot\text{h}^{-1}\cdot\text{m}_{\text{ads}}^{-3}$ [110]. Later, Seabra *et al.* studied the separation by SMB of C3 hydrocarbons using CO₂ as a desorbent and binderfree zeolite 13X beads as the adsorbent material, at mild temperature (323 K). In this study, non-ideal adsorption behaviour was observed for the adsorbate-adsorbent pairs, and thus, a RAST-aNRTL model was used to describe the multicomponent adsorption equilibrium. For an equimolar feed mixture, a propylene purity of 98.8% was obtained, with a recovery above 98% and a high throughput of $40.8 \text{ kg}_{\text{C}_3\text{H}_6}\cdot\text{h}^{-1}\cdot\text{m}_{\text{ads}}^{-3}$ [111].

The application of the SMB technology for CH₄ and N₂ separation has garnered significant attention in recent years. In 2021, Qian *et al.* introduced a hybrid process combining VPSA with

SMB operation using AC beads. In this experimental work, the authors reported enhanced CH₄ purity and recovery compared to PSA processes, producing a high-purity CH₄ stream (99.99%) with a 98.6% recovery [112]. Then, commercial coconut shell AC was tested for the separation of this mixture by the improved VPSA process [113]. Building upon their previous works, the authors investigated the use of a ZSM-5 zeolite in their pilot VPSA-SMB unit. The best run achieved a 99% purity CH₄ stream with increased recovery (99.6%), however, with a power consumption 10 kJ.mol⁻¹_{CH₄} higher than what was observed with the AC materials [114].

The presented state of the art shows how promising this process is regarding difficult separations, where the mixture components present very low adsorption selectivity, which is the case of CH₄/N₂.

2.4. References

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CHAPTER 3 – THEORY AND MODELLING

3.1. Introduction

To design separation units, it is essential to develop a mathematical model that can describe the adsorption equilibrium and dynamic behaviour within the system, easily predicting the experimental results. By successfully validating the proposed model, we can simulate and optimize the process and its performance without relying solely on extensive experimental runs, allowing us to change and test different operating conditions. Also, it allows for the design of more efficient systems and helps scale up from pilot scale to industrial level.

In this chapter, firstly, the pure and multicomponent adsorption equilibrium models are depicted. Then, the fixed-bed mathematical model used to describe both breakthrough and SMB experimental results and to simulate the SMB/PSA hybrid process is depicted.

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

3.2. Adsorption equilibrium models

Adsorption equilibrium models describe how the adsorbate molecules distribute between the fluid phase and the surface of an adsorbent at equilibrium. This equilibrium is represented by the amount of adsorbate adsorbed as a function of the partial pressure, at a constant temperature (isotherms). They present one of the most important tools for characterising porous materials, *i.e.*, assessing their capacity in adsorbing certain adsorbates and designing industrial adsorption processes. To fit the experimental data, various models can be utilised. The models used in this thesis are briefly described below.

The Langmuir model is widely used to describe the adsorption behaviour of molecules on a solid surface. This model assumes that adsorption occurs on a fixed number of energetically homogeneous sites, wherein each active site adsorbs one molecule, with no interaction with neighbouring adsorbed molecules, and where the probability of adsorbing is equal for every active site [1].

The Langmuir isotherm equation, presented below, relates the equilibrium adsorption capacity, q_i , to the pressure, P_i , through the maximum adsorption capacity, $q_{m,i}$, and the affinity constant, b_i .

$$q_i = q_{m,i} \frac{b_i P_i}{1 + b_i P_i} \quad (3.1)$$

The dependence on temperature of the affinity parameter follows the Van't Hoff equation:

$$b_i = b_{0,i} \exp\left(\frac{-\Delta H_i}{R_g T}\right) \quad (3.2)$$

where $b_{0,i}$ is the affinity constant at infinite temperature, ΔH_i is the heat of adsorption, R_g is the ideal gas constant, and T is the system temperature.

Under high values of pressure, the term $b_i P_i \gg 1$, reducing the Langmuir isotherm to $q_i = q_{m,i}$, meaning that the adsorbent is completely saturated, as its equilibrium adsorption capacity is equal to its saturation capacity. At low sorbate concentrations, the term $b_i P_i \ll 1$, reducing the Langmuir model equation to the linear isotherm model.

When the surface of the material is heterogeneous, the Dual-Site Langmuir model can be utilised. In this model, the material has available not one but two different adsorption sites which follow the Langmuir considerations, a stronger site that adsorbs first and a secondary one. The total amount adsorbed onto the surface of the material is given by the sum of the contribution of each site. This way, the DSL model can be represented by Equation (3.3).

$$q_i = q_{m,1,i} \frac{b_{1,i} P_i}{1 + b_{1,i} P_i} + q_{m,2,i} \frac{b_{2,i} P_i}{1 + b_{2,i} P_i} \quad (3.3)$$

Where subscripts 1 and 2 correspond to site 1 and 2 of the DSL model. In this equation, q_i is the amount adsorbed in equilibrium with the bulk phase at the partial pressure P_i , $q_{m,i}$ is the saturation capacity of the pure component i and b_i is the affinity constant. This temperature-dependent parameter is expressed by the Van't Hoff equation, for each site (Equation(3.2)).

The Sips model is an empirical isotherm that encompasses the Langmuir hypothesis but introduces a heterogeneity factor, n , that accounts for deviations to the Langmuir model. If n is equal to 1, then the Sips model reduces to the Langmuir model, indicating a homogeneous adsorption surface. If $n < 1$, it suggests cooperative adsorption, where adsorbate-adsorbate interactions enhance adsorption. When $n > 1$, it indicates adsorbent surface heterogeneity, meaning adsorption sites have different affinities for the adsorbate. This way, it can also be used for heterogeneous surfaces, resulting in a combination of the Langmuir and Freundlich isotherms [2]. This way, as is the case of the Freundlich isotherm, the Sips equation does not reduce to Henry's law at low pressure values.

$$q_i = q_{m,i} \frac{b_i P_i^{1/n}}{1 + b_i P_i^{1/n}} \quad (3.4)$$

The Toth model is an empirical modification of the Langmuir model that is utilised to describe heterogeneous adsorption systems with sub-monolayer coverage [3].

$$q_i = q_{m,i} \frac{b_i P_i}{[1 + (b_i P_i)^n]^{1/n}} \quad (3.5)$$

For both Sips and Toth models, the affinity parameter, b_i , can also be obtained using the Van't Hoff equation.

To describe the multicomponent adsorption equilibrium, the extended form of either the Langmuir model or the DSL model was utilised:

$$q_i = q_{m,i} \frac{b_i P_i}{1 + \sum_{j=1}^{NC} b_j P_j} \quad (3.6)$$

$$q_i = q_{m,1,i} \frac{b_{1,i} P_i}{1 + \sum_{j=1}^{NC} b_{1,j} P_j} + q_{m,2,i} \frac{b_{2,i} P_i}{1 + \sum_{j=1}^{NC} b_{2,j} P_j} \quad (3.7)$$

where the subscript i corresponds to each component, P_i is the partial pressure, and NC is the number of components in the system.

The extended Langmuir isotherm / extended DSL isotherm has the advantage of being able to represent the multicomponent adsorption equilibrium with an analytical equation, which minimizes the computational effort during the simulations.

For developing the SMB performance indicator presented in Chapter 4, the multicomponent adsorption equilibrium was predicted using the Ideal Adsorbed Solution Theory (IAST). Developed in 1965 by Myers and Prausnitz, the IAST is based on solution thermodynamics and simply requires the pure-component adsorption equilibrium data for the calculation of the multicomponent equilibria. This approach stands on the assumption that the multicomponent mixture behaves as an ideal adsorbed solution at constant pressure and temperature and, therefore, no interaction occurs between the adsorbates in the adsorbed phase, with all adsorbates having the same available surface area and the adsorbent material being inert [4].

The IAST describes the equilibrium between the adsorbed phase and the ideal gas phase at a constant temperature analogously to *Raoult's* law for vapor-liquid equilibrium:

$$x_i P_i^0 = y_i P \quad (3.8)$$

where x_i and y_i are the mole fractions of component i in the adsorbed and the gas phase, respectively.

At adsorption equilibrium, the reduced spreading pressure, Z , must be the same for each component of the mixture and is calculated from the Gibbs adsorption isotherm equation:

$$Z = \frac{\pi \mathcal{A}}{R_g T} = \int_0^{P_i^0} \frac{q_i^0(P)}{P} dP \quad (3.9)$$

where π is the spreading pressure, $\mathcal{A}$ is the adsorption surface area, R_g is the universal gas constant, T is the temperature of the system, P_i^0 is the hypothetical pressure of the pure

component i that yields the same spreading pressure as the adsorbed mixture on the surface, and q_i^0 is the uptake of the pure component i , given by the isotherm.

The total adsorbed amount, q_t , is then obtained with the following expression:

$$\frac{1}{q_t} = \sum \frac{x_i}{q_i^0} \quad (3.10)$$

The system of equations is then solved numerically while obeying the following constraints:

$$\sum x_i = 1 \quad (3.11)$$

$$\sum y_i = 1 \quad (3.12)$$

As aforementioned, for the IAST calculations of the multicomponent adsorption equilibrium, the pure-component adsorption equilibrium isotherms are required. The success of the results depends on the accuracy of the fitting parameters for the pure-component equilibrium data, especially at low coverage and high pressure, to avoid substantial errors in the multicomponent data [4]. For these calculations, the Langmuir, Dual-Site Langmuir, Sips, or Toth isotherm models were used. If the reviewed data was fitted with one of these models, the parameters were used as reported in the literature. When the isotherm parameters were not disclosed, or the data was reported with a different isotherm model, the experimental points were extracted and fitted with the adsorption equilibrium model that provided the best fit.

3.3. Isosteric Heat of Adsorption

Knowing the isosteric heat of adsorption of the components present in a gas mixture is key when designing an adsorption-based process since their value is correlated with the thermal effects in the adsorber during both adsorption and desorption steps [5]. The isosteric heat of adsorption, ΔH_i , can be estimated through the adsorption equilibrium data by using the Clausius-Clapeyron equation:

$$(-\Delta H_i) = R_g T^2 \left(\frac{\partial \ln P_i}{\partial T} \right)_q \quad (3.13)$$

with the derivative being evaluated at constant adsorbed concentration, q . The isosteric heat of adsorption can be assessed from the slope of the plot of $\ln P$ as a function of $1/T$.

For the heat of adsorption calculation used in the SMB performance indicator (Chapter 4), the values are calculated through the equation presented by D. Do [4]:

$$(-\Delta H_i) = \frac{q_{m,1,i} \frac{b_{1,i}(-\Delta H)_{1,i}}{(1 + b_{1,i}P_i)^2} + q_{m,2,i} \frac{b_{2,i}(-\Delta H)_{2,i}}{(1 + b_{2,i}P_i)^2}}{q_{m,1,i} \frac{b_{1,i}}{(1 + b_{1,i}P_i)^2} + q_{m,2,i} \frac{b_{2,i}}{(1 + b_{2,i}P_i)^2}} \quad (3.14)$$

where 1 and 2 correspond to the adsorption site and P_i is the partial pressure of component i , considering the same conditions of the IAST calculations.

3.4. Selectivity

The selectivity is a key parameter for the screening of adsorbent materials, measuring the competitiveness of adsorption between two adsorbates in a gas mixture. For adsorption equilibrium-based separations, the ideal selectivity of component A over component B, α_{AB} , can be calculated as follows:

$$\alpha_{AB} = \frac{q_A y_B}{q_B y_A} \quad (3.15)$$

where q_A and q_B are the capacities for components A and B, respectively and y_A and y_B are the molar fractions of components A and B, respectively, in the fluid phase, at equilibrium.

3.5. Breakthrough curves

Fixed-bed experiments are very important when designing a cyclic process, allowing the assessment of the dynamic behaviour for single and multicomponent adsorption. In a fixed-bed experiment, a column, packed with an adsorbent material, is previously saturated (or regenerated) and is continuously fed with a stream of constant composition. This way, at the column inlet, a step perturbation on the feed composition is imposed, and the concentration front moves through the bed, changing its shape depending on the adsorption isotherm, flow rate and diffusion, with the mass transfer between fluid and solid phases occurring in a section of the bed, referred to as the mass transfer zone (MTZ). As the fluid flows through the bed, mass transfer occurs between the fluid and the adsorbent particles that come into contact with the fluid until the entire bed is in equilibrium with the influent. At the column outlet, the breakthrough occurs and the concentration of the fluid phase changes until it is equal to the feed concentration. For saturation, the time it takes for the adsorbate to reach the column outlet is known as the breakthrough time, considered when the concentration is around 5% of the feed concentration [6].

As mentioned in the previous paragraph, the adsorption equilibrium isotherm determines the shape of the breakthrough curve, with the transport phenomena in the bed and within the particles having a secondary effect on its shape.

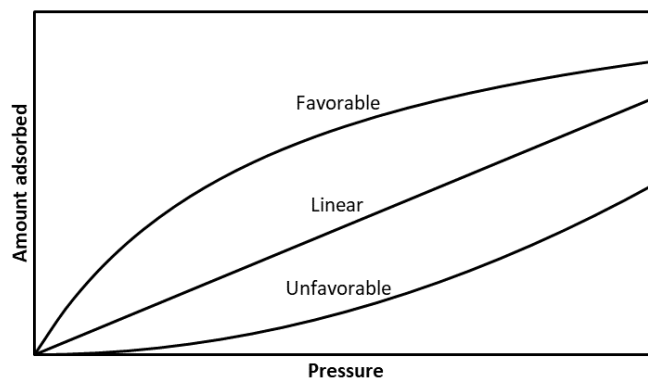


Figure 3.1 - Shapes of isotherms for determining the shape of the breakthrough curve.

Figure 3.1 shows favourable, linear, and unfavourable isotherm shapes. When the adsorption equilibrium isotherm is concave, i.e., the second derivative of its function is negative, the isotherm is favourable, leading to a steep breakthrough curve (compressive wave). Contrarily, if the adsorption isotherm is convex, i.e., the second derivative is positive, the isotherm is unfavourable, which means that the lower concentrations travel faster, leading to a dispersive breakthrough curve (dispersive wave). In a cyclic process, a sharp concentration front is essential for an efficient separation [6].

The breakthrough curve is the concentration history of the solute at the column end. When the wave front reaches the outlet, the adsorbate content (and consequently the molar flow rate) at the end stream starts to increase, until it equals the feed conditions (thermal and mass adsorption equilibrium), which marks the end of the adsorption step. Afterwards, the regeneration of the bed can be accomplished by temperature swing, pressure swing, introducing an inert species to displace the adsorbed phase or introducing a species with higher affinity to displace the adsorbed phase. In a fixed bed experiment, the desorption step is carried out by feeding either a non-adsorbing species or a desorbent that is able to displace the adsorbate. This way, at the column end, in case of an inert or less adsorbing gas, there is an increase in the flow rate caused by the displacement of the gas from the adsorbent, followed by a flow rate decrease (dispersive wave). On the other hand, if the desorbent adsorbs more than the gas mixture, the front is compressive and the flow rate decreases until the breakthrough of the heavy component [6].

Also, integrating the area above the adsorption curve can give an estimation of the uptake of the adsorptive material.

Furthermore, the shape of the curve also gives important information regarding the mass transfer properties of the studied system.

3.6. Fixed-bed Mathematical Model

Once the study of equilibrium and the adsorption dynamics is complete, a mathematical model that is able to describe the dynamic behaviour of multicomponent adsorption inside a fixed-bed column can be developed to design an SMB or SMB/PSA hybrid process, also taking into account the transport phenomena. This model was used to simulate and predict the fixed-bed experiments and to simulate the results obtained for the performed SMB cycles, hybrid process simulations and compute the separation regions. The mass, momentum, and energy balance equations that encompass the mathematical model and the initial and boundary conditions are presented below. The proposed model assumes ideal gas behaviour of the bulk phase, plug flow with axial dispersion, no radial mass, temperature, and velocity gradients, external mass and heat resistances expressed with the film model, bidispersed adsorbent particle with mass transfer resistances in both macropore and micropores expressed with the linear driving force (LDF) model, isothermal profile inside the particles and homogeneously packed columns with constant porosity [7].

Mass balance to the gas phase:

$$\frac{\partial}{\partial z} \left(\varepsilon D_{ax} C_{g,T} \frac{\partial y_i}{\partial z} \right) - \frac{\partial}{\partial z} (u_0 C_{g,i}) - \varepsilon \frac{\partial C_{g,i}}{\partial t} - (1 - \varepsilon) a_p k_f (C_{g,i} - C_{s,i}) = 0 \quad (3.16)$$

where z is the axial position along the bed, t is the time, ε is the bulk porosity, D_{ax} is the axial dispersion coefficient, $C_{g,T}$ is the total concentration in the fluid phase, y_i is the molar fraction of component i , u_0 is the superficial velocity inside the column, $C_{g,i}$ is the concentration of component i in the fluid phase, a_p is the particle specific area, k_f is the film mass transfer coefficient and $C_{s,i}$ is the concentration of component i at the solid interface.

Mass balance to the solid phase at the macropore/mesopore scale:

$$\frac{\partial \overline{C_{p,i}}}{\partial t} = k_{macro} (C_{s,i} - \overline{C_{p,i}}) - \frac{\rho_p}{\varepsilon_p} \frac{\partial \overline{q_i}}{\partial t} \quad (3.17)$$

where $\overline{C_{p,i}}$ is the averaged mole concentration of component i , k_{macro} is the macropore mass transfer resistance coefficient, ε_p is the particle porosity, ρ_p is the apparent particle density, and $\overline{q_i}$ is the average adsorbed amount of component i inside the particle per mass unit of solid.

For monoliths, some changes must be considered in Equations (3.16) and (3.17). The specific area, a_p , corresponds to the monolith channel specific area, ρ_p changes to the monolith wall apparent density and ε_p to the wall porosity.

The mass transfer resistance coefficient in the macropores, k_{macro} , is given by the following expression:

$$k_{\text{macro}} = \frac{\Omega_M D_{p,i}}{R_p^2} \quad (3.18)$$

where Ω_M is the adsorbent geometry factor, equal to 15 for spherical adsorbents (granules, beads), 8 for cylinders (pellets) and 3 for slabs [8, 9], $D_{p,i}$ is the macropore diffusivity, R_p is the particle radius. In the case of the granulates, the particles were approximated to spheres. In the case of pellets and monoliths, the particles were approximated to cylinders.

Mass balance to the solid phase at the micropore level:

$$\frac{\partial \bar{q}_i}{\partial t} = k_{\text{micro}} (q_i^* - \bar{q}_i) \quad (3.19)$$

where q_i^* is the adsorbed concentration in equilibrium with $\bar{C}_{p,i}$.

The mass transfer resistance coefficient at the micropore level, k_{micro} , can be obtained by the following expression:

$$k_{\text{micro}} = \frac{\Omega_m D_{\text{micro},i}}{R_{\text{micro}}^2} \quad (3.20)$$

where Ω_m is a factor which depends on the pore shape, with a value of 15, 8 or 3 when the pore is approximated to a sphere, cylinder or slab, respectively [8, 9], $D_{\text{micro},i}$ is the micropore diffusivity, R_{micro} is the characteristic length for diffusion of the micropores. For the studied materials, the micropores were approximated to slabs.

Ideal gas law:

$$P = \sum_{i=1}^{NC} C_{g,i} R_g T_g \quad (3.21)$$

Where P is the pressure evaluated locally at the axial position z , R_g is the ideal gas constant, T_g is the temperature of the fluid phase and NC is the number of components.

Momentum balance:

$$-\frac{\partial P}{\partial z} = \frac{150\mu(1-\varepsilon)^2}{\varepsilon^3 d_p^2} u_0 + \frac{1.75(1-\varepsilon)\rho}{\varepsilon^3 d_p} u_0 |u_0| \quad (3.22)$$

where μ is the gas mixture viscosity, ρ is the gas mixture density and d_p is the particle diameter. For the monolith materials, instead of d_p , the monolith wall thickness, l_w , is used.

Energy balance to the gas phase:

$$\begin{aligned} \frac{\partial}{\partial z} \left(\lambda \frac{\partial T_g}{\partial z} \right) - u_0 C_{g,T} c_P \frac{\partial T_g}{\partial z} + \varepsilon R_g T_g \frac{\partial C_{g,T}}{\partial t} - (1 - \varepsilon) a_p h_f (T_g - T_s) \\ - \frac{4h_w}{d_w} (T_g - T_w) - \varepsilon C_{g,T} c_V \frac{\partial T_g}{\partial t} = 0 \end{aligned} \quad (3.23)$$

where λ is the heat axial dispersion coefficient, T_g , T_s , T_w are the gas, particle, and wall temperatures, respectively, c_P and c_V are the specific heats at constant pressure and volume, respectively, h_f is the film heat transfer coefficient, h_w is the heat transfer coefficient between the fluid phase and the column wall, and d_w is internal wall diameter, equal to the bed diameter.

Energy balance to the solid phase:

$$\begin{aligned} (1 - \varepsilon) \left[\rho_p \sum_{i=1}^{NC} \bar{q}_i c_{V,i} + \rho_p \hat{c}_{P_s} + \varepsilon_p \sum_{i=1}^{NC} \bar{C}_{p,i} c_{V,i} \right] \frac{\partial T_s}{\partial t} \\ = \rho_b \sum_{i=1}^{NC} \sum_{k=1}^{N_{sites}} \left[(-\Delta H_{i,k}) \frac{\partial \bar{q}_{i,k}}{\partial t} \right] + (1 - \varepsilon) a_p h_f (T_g - T_s) + (1 - \varepsilon) \varepsilon_p R_g T_s \sum_{i=1}^{NC} \frac{\partial \bar{C}_{p,i}}{\partial t} \end{aligned} \quad (3.24)$$

with $\hat{c}_{P_s}$ being the solid specific heat per mass unit and ΔH_i being the enthalpic parameter of component i and site k .

Energy balance to the column wall:

$$\rho_w \hat{c}_{P_w} \frac{\partial T_w}{\partial t} = \alpha_w h_w (T_g - T_w) - \alpha_{wl} U (T_w - T_\infty), \quad (3.25)$$

$$\alpha_w = \frac{d_w}{e(d_w + e)}; \alpha_{wl} = \frac{2}{(d_w + e) \ln \left(\frac{d_w + 2e}{d_w} \right)} \quad (3.26)$$

where ρ_w is the wall density, $\hat{c}_{P_w}$ is the wall specific heat at constant pressure (per mass unit), α_w is the ratio of the internal surface area to the volume of the column wall, α_{wl} is the ratio of the log mean surface area to the volume of the column wall, U is the overall heat transfer coefficient, T_∞ is the column surrounding temperature, and e is the wall thickness.

The values of α_w and α_{wl} for a bed packed with monoliths is calculated with the same equations, where d_w is substituted by d_{eq} , which is the equivalent monolith diameter if it were approximated to a cylinder.

In the case of monoliths, the term $\frac{4h_w}{d_w} (T_g - T_w)$, present in the gas-phase energy balance is moved to the solid phase, with T_g changing to T_s . Also, d_w is substituted by d_{eq} .

Flux equality at the solid surface:

$$\frac{a_p k_f}{\varepsilon_p} (C_{g,i} - C_{s,i}) = k_{\text{macro}} (C_{s,i} - \overline{C_{p,i}}) \quad (3.27)$$

The initial and boundary conditions used in both fixed bed and SMB experiments are presented below.

Initial conditions

$$y_i = 0, \quad i \neq \text{desorbent} \quad (3.28)$$

$$y_{\text{desorbent}} = 1 \quad (3.29)$$

$$\frac{\partial \bar{q}_i}{\partial t} = 0 \quad (3.30)$$

$$C_{g,T} = C_{\text{inlet},T} \quad (3.31)$$

$$T_g = T_s = T_w = T_{\text{inlet}} \quad (3.32)$$

Boundary conditions for each bed

$z = 0, \text{inlet:}$

$$u_{0,\text{inlet}} C_{\text{inlet},i} = u_0 C_{g,i} - \varepsilon D_{\text{ax}} C_{g,T} \frac{\partial y_i}{\partial z} \quad (3.33)$$

$$u_{0,\text{inlet}} C_{\text{inlet},T} = u_0 C_{g,T} \quad (3.34)$$

$$u_{0,\text{inlet}} C_{\text{inlet},T} c_p T_{\text{inlet}} = u_0 C_{g,T} c_p T_g - \lambda \frac{\partial T_g}{\partial z} \quad (3.35)$$

$z = L, \text{outlet:}$

$$\frac{\partial C_{g,i}}{\partial z} = 0 \quad (3.36)$$

$$P = P_{\text{outlet}} \quad (3.37)$$

$$\frac{\partial T_g}{\partial z} = 0 \quad (3.38)$$

The inlet for each bed is determined by the balance to the nodes for the SMB and hybrid simulations (Chapter 4, Chapter 6 and Chapter 7).

The mathematical model was then implemented into the *gPROMS* modelling platform, using the orthogonal collocation on finite elements method (OCFEM) to discretize the axial domain. The number of elements used depended on the system that was studied. This way, for the simulations performed in Chapter 4, both the polynomial order and the number of finite elements were adjusted depending on the adsorbent material to ensure numerical stability. For the simulations presented in Chapter 6, third-order polynomials were used, with the number of elements differing for each case. For the BPL activated carbon study (Section 6.2), the number of elements used was 8 with third-order polynomials (two interior collocation points). For the Maxsorb AC (Sections 6.3

and 6.4), second-order polynomials (one interior collocation point) and 13 discretisation intervals were used. For the hybrid process simulations performed in Chapter 7, second-order polynomials were applied using 12 discretization intervals.

To solve the system of ordinary differential equations that resulted from the discretization process, the Differential Algebraic Equation solver with Backward Differentiation (DAEBDF solver) was utilised, with an absolute tolerance of 10^{-5} .

The following equations are expressions used to calculate or estimate several parameters used in the mathematical model.

The particle specific area, a_p , is calculated by:

$$a_p = \frac{k_{sM}}{R_p} \quad (3.39)$$

where k_{sM} is the particle geometry factor and is considered 3 for sphere-like adsorbents, 2 for particles with a cylindrical geometry and 1 for particles with a slab shape.

The transfer parameters necessary in the mathematical model were calculated using the expressions presented below. These correlations, as well as the values displayed in Table 3.1 and Table 3.2 are available in the referenced literature [10-15]. The parameters were estimated at the feed conditions of the bed.

The pore diffusivity, $D_{p,i}$, is obtained using the following equation by Bosanquet [15]:

$$\frac{1}{D_{p,i}} = \tau_p \left(\frac{1}{D_{m,i}} + \frac{1}{D_{k,i}} \right) \quad (3.40)$$

where τ_p is the particle tortuosity and $D_{m,i}$ and $D_{k,i}$ are the molecular diffusivity and the Knudsen diffusivity for component i , respectively. These last two diffusivities can be calculated by the following equations:

$$D_{k,i} = 0.97 r_p \sqrt{\frac{T_g}{M_i}} \quad (3.41)$$

$$D_{m,i} = \frac{1 - y_i}{\sum_{j=1, j \neq i}^n \frac{y_j}{D_{i,j}}} \quad (3.42)$$

where r_p is the pore radius in centimeters, M_i is the molecular weight of the component i , y_i is the molar fraction of the component i and $D_{i,j}$ is the binary molecular diffusivity, calculated by the Chapman-Enskog equation:

$$D_{i,j} = \frac{2.66 \times 10^{-2} T^{\frac{3}{2}}}{P M_{ij}^{\frac{1}{2}} \sigma_{ij}^2 \Omega_D} \quad (3.43)$$

where M_{ij} is the molecular weight of the mixture between component i and j , σ_{ij} is the interaction value and Ω_D is the collision integral.

This parameter is a function of the Boltzman constant, k and the energy parameter, ε_i ($= f(\varepsilon_i/k)$) and is expressed by Equation (3.44):

$$\Omega_D = \frac{A_1}{\omega^{A_5}} + \frac{A_2}{\exp(A_6\omega)} + \frac{A_3}{\exp(A_7\omega)} + \frac{A_4}{\exp(A_8\omega)} \quad (3.44)$$

where A_1 to A_8 are constants tabled in the literature and ω is given by the following expression:

$$\omega = \frac{kT_g}{\varepsilon_i} \quad (3.45)$$

The values of σ and ε_i/k , denominated Lennard-Jones parameters, are also tabulated in the literature for various compounds. The values for the gases studied in this work are presented in Table 3.1.

Table 3.1 - Molecular weight and Lennard-Jones parameters for each compound.

Compound	M_i (g·mol ⁻¹)	σ (Å)	ε_i/k (K)
N ₂	28.014	3.798	71.4
CH ₄	16.043	3.758	148.6
CO ₂	44.010	3.941	195.2
Ar	39.948	3.542	93.3

σ_{ij} is obtained with the average of the values for the compounds present in the mixture.

The axial mass dispersion coefficient, D_{ax} , was estimated with the equation presented by Hsu and Haynes (1981) [12] (Equation (3.46)). The axial heat dispersion coefficient, λ , was determined by the correlation provides by Wakao and Funazkri (Equation (3.47)) [14].

$$D_{ax} = \frac{D_m}{\varepsilon} (0.76\varepsilon + 3.3) \frac{\text{Re Sc}}{1 + 13 \times 0.76 \left(\frac{\varepsilon}{\text{Re Sc}} \right)} \quad (3.46)$$

Where ε is the bed porosity, D_m is the molecular diffusivity of the gas mixture, obtained by a molar average and Sc and Re are the Schmidt and Reynolds numbers, respectively.

$$\frac{\lambda}{k_g} = 7 + 0.5 \text{ Pr Re} \quad (3.47)$$

Where Pr is the Prandtl number and k_g is the thermal conductivity of the mixture.

In order to obtain the thermal conductivity for the gas mixture, k_g , it is necessary to calculate the thermal conductivity for each pure component, $k_{g,i}$:

$$k_{g,i} = \left(\hat{c}_{P,i} + \frac{5}{4} \frac{R_g}{M_i} \right) \mu_i \quad (3.48)$$

This way, k_g is obtained using the following expression:

$$k_g = \sum_{i=1}^n \frac{y_i k_{g,i}}{\sum_{j=1}^n y_j \Phi_{ij}} \quad (3.49)$$

To assess the film mass and heat transfer coefficients between the gas phase and the solid particle, k_f and h_f , respectively, the Wakao and Funazkri correlations (Equation (3.50) and Equation (3.51)) were utilised [13, 14]:

$$\text{Sh} = \frac{k_f d_p}{D_m} = 2.0 + 1.1 \text{Re}^{0.6} \text{Sc}^{\frac{1}{3}} \quad (3.50)$$

$$\text{Nu} = \frac{h_f d_p}{k_g} = 2.0 + 1.1 \text{Re}^{0.6} \text{Pr}^{\frac{1}{3}} \quad (3.51)$$

where Sh and Nu are the Sherwood and Nusselt numbers.

The pure gas viscosity, μ_i , is obtained using Equation (3.52):

$$\mu_i = 2.669 \times 10^{-6} \frac{(M_i T_g)^{\frac{1}{2}}}{\sigma^2 \Omega_{\mu_i}} \quad (3.52)$$

where σ is the collision diameter and Ω_{μ_i} represents the collision integral for the viscosity which is expressed by Equation (3.53):

$$\Omega_{\mu_i} = \frac{A_1}{\omega^{A_4}} + \frac{A_2}{\exp(A_5 \omega)} + \frac{A_3}{\exp(A_6 \omega)} \quad (3.53)$$

where A_1 to A_6 are constants tabled in the literature and ω is given by Equation (3.45).

The mixture viscosity can then be calculated resorting to Equation (3.54):

$$\mu = \sum_{i=1}^n \frac{y_i \mu_i}{\sum_{j=1}^n y_j \Phi_{ij}} \quad (3.54)$$

where $\Phi_{i,j}$ are the Wilke's coefficients and are evaluated according to the expression presented below:

$$\Phi_{ij} = \frac{\left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{\frac{1}{2}} \left(\frac{M_j}{M_i} \right)^{\frac{1}{4}} \right]^2}{\left[8 \left(1 + \frac{M_i}{M_j} \right) \right]^{\frac{1}{2}}} \quad (3.55)$$

The molecular weight of the mixture between component i and j , M_{ij} , is given by the following equation:

$$M_{ij} = 2 \left[\frac{1}{M_i} + \frac{1}{M_j} \right]^{-1} \quad (3.56)$$

The heat capacity at constant pressure for the pure component, $c_{P,i}$, is obtained using the correlation presented below:

$$\frac{c_{P,i}}{R_g} = a_0 + a_1 T_g + a_2 T_g^2 + a_3 T_g^3 + a_4 T_g^4 \quad (3.57)$$

where a_0 to a_4 are constants tabled for each compound and are parameters of the polynomial equation. Their values for the gases used in this work are presented in Table 3.2.

The mixture's heat capacity at constant pressure, c_p , is then calculated by the molar average of the pure component heat capacity:

$$c_p = \sum_{i=1}^{NC} y_i c_{P,i} \quad (3.58)$$

Table 3.2 - Parameters of the polynomial equation for heat capacities calculation.

Compound	a_0	$a_1 \times 10^3$	$a_2 \times 10^5$	$a_3 \times 10^8$	$a_4 \times 10^{11}$
N ₂	3.539	-0.261	0.007	0.157	-0.099
CH ₄	4.568	-8.975	3.631	-3.407	1.091
CO ₂	3.259	1.356	1.502	-2.374	1.056
Ar	2.500	-	-	-	-

The heat capacity at constant pressure (per mass unit) for the pure component can be obtained by:

$$\hat{c}_{P,i} = \frac{c_{P,i}}{\sum_{i=1}^n y_i M_i} \quad (3.59)$$

The heat capacity at constant volume, c_V , is assessed by:

$$c_V = c_P - R_g \quad (3.60)$$

3.7. Simulated Moving Bed

The simulated moving bed (SMB) technology is based on the True Moving Bed (TMB) technology, where both fluid and solid phases flow continuously in countercurrent, in order to increase the mass transfer driving force, thus leading to better efficiency of the selected adsorbent material. However, the solid phase displacement poses some major drawbacks, such as equipment wearing, attrition between the adsorbent particles, difficulty in maintaining plug flow of the fluid phase, due to the solids movement and maintaining the solids plug flow, fluid velocity limited by the fluidization phenomena, pressure drop variations, etc. [16]. Given these problems, in the SMB technology, the solid is kept in a fixed position and the motion of the solid phase is simulated

through the periodical shifting of all inlet/outlet ports in the direction of the fluid flow, promoting the permanent contact between solid and fluid phases, according to a specified switching time.

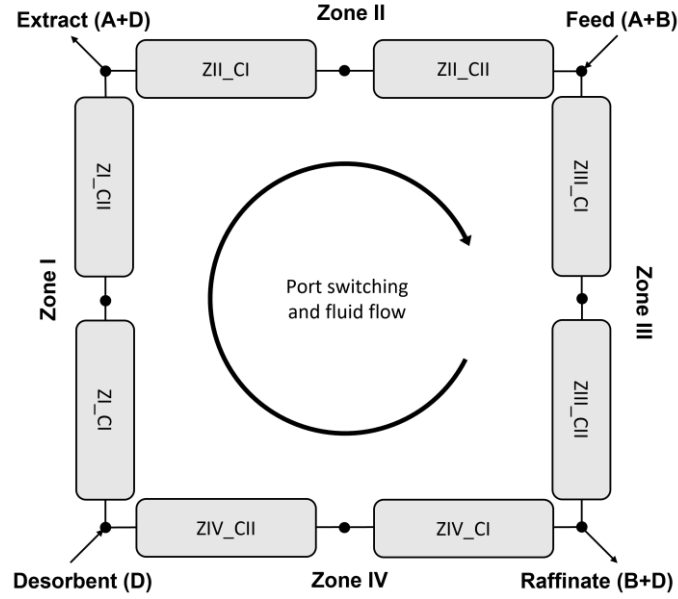


Figure 3.2 - Schematic representation for SMB operation with a classical 2-2-2-2 column configuration, where Z is the zone and C is the column.

In Figure 3.2, an eight column SMB unit, with the traditional 2-2-2-2 column configuration is presented, showing the different zones of the process. The SMB process is comprised of two inlet ports: the feed (F) and the desorbent (D) and two outlet ports: the extract (X) and the raffinate (R). The unit is divided by the ports into four zones, where each can operate at different flow rates. Zone I is comprised between the desorbent inlet and the extract outlet, where the adsorbent is regenerated by the desorbent. In Zone II, between the extract outlet and the feed inlet, the more retained component adsorbs onto the material, while the less retained component travels with the desorbent. The switching time should be defined to prevent the less adsorbed component from reaching the extract port. Zone III begins at the feed inlet and ends at the raffinate outlet. In this zone, the less retained species is carried by the eluent toward the raffinate port, enriching it in this compound. Again, the more retained species should not contaminate the raffinate stream. Zone IV starts at the raffinate outlet and ends at the desorbent inlet. In this section, the desorbent is cleaned by the adsorbent material so that the desorbent can be recycled back into Zone I [17].

The molar flow rates in each zone, F_j , in $\text{mol}\cdot\text{s}^{-1}$, are given by the node balances [17]:

$$F_I = F_D + F_{IV} \quad (3.61)$$

$$F_{II} = F_I - F_X \quad (3.62)$$

$$F_{III} = F_{II} + F_F \quad (3.63)$$

$$F_{IV} = F_{III} - F_R \quad (3.64)$$

where F_D , F_X , F_F and F_R is the desorbent, extract, feed, and raffinate stream molar flow rate, respectively. Similar balances can also be written in terms of Q_j , in SLPM, where the subscripts j remain the same as the equations above.

These flow rates can be presented as the dimensionless ratio of the interstitial fluid and solid velocities, v_j and u_s , respectively:

$$\gamma_j = \frac{v_j}{u_s} = \frac{F_j R_g T t^*}{P \varepsilon L A} \quad (3.65)$$

where ε is the bed porosity, A is the cross-section area of the bed, L is the bed length, t^* is the switching time.

During an SMB cycle, the feed stream, which contains the mixture to be separated, is continuously fed into the system, while the desorbent stream, which helps in desorbing the target components from the stationary phase, is fed into the regeneration zone. As both feed and desorbent flow through the columns, the adsorption and desorption processes occur simultaneously. The most retained species travels with the adsorbent material and is collected in the extract stream, alongside the desorbent, while the less retained species travels with the fluid phase and is collected in the raffinate stream mixed with the desorbent. This way, the SMB process essentially transforms a difficult separation into two easier ones [17]. After a certain number of cycles, the process operates in cyclic steady state [18]. The separation of the mixture can be achieved by controlling the temperature, pressure, inlet, and outlet flow rates, switching times, and the number of columns in each section (column configuration).

This technology can provide several advantages compared to other separation processes, offering almost isobaric and isothermal operation and high purity and throughputs with less adsorbent material. The main downside is the need to separate the downstream products from the desorbent species, which can be accomplished, for example, by PSA.

3.7.1. SMB modelling

To model and simulate the SMB process, in addition to the fixed-bed model presented above, it is necessary to model the nodes (or manifolds) that interconnect the SMB columns and account for the input and output streams of the process. These node balance equations are presented in Equations (3.66) to (3.77). If operating in open-loop mode, the section IV terms are removed from the equations in the desorbent node.

Desorbent node:

$$u_{0,inlet,I} C_{inlet,i,I} = u_{0,D} C_{D,i} + (u_{0,IV} C_{g,i,IV}) \Big|_{z=L_{IV}} \quad (3.66)$$

$$u_{0,inlet,I}C_{inlet,T,I} = u_{0,D}C_{D,T} + (u_{0,IV}C_{g,T,IV})\big|_{z=L_{IV}} \quad (3.67)$$

$$u_{0,inlet,I}C_{inlet,T,I}c_pT_{inlet,I} = u_{0,D}C_{D,T}c_pT_D + (u_{0,IV}C_{g,T,IV}c_pT_{g,IV})\big|_{z=L_{IV}} \quad (3.68)$$

Extract node:

$$C_{inlet,i,II} = C_{g,i,I}\big|_{z=L_I} \quad (3.69)$$

$$u_{0,inlet,II} = u_{0,I}\big|_{z=L_I} - u_{0,X} \quad (3.70)$$

$$T_{inlet,II} = T_{g,I}\big|_{z=L_I} \quad (3.71)$$

Feed node:

$$u_{0,inlet,III}C_{inlet,i,III} = u_{0,F}C_{F,i} + (u_{0,II}C_{g,i,II})\big|_{z=L_{II}} \quad (3.72)$$

$$u_{0,inlet,III}C_{inlet,T,III} = u_{0,F}C_{F,T} + (u_{0,II}C_{g,T,II})\big|_{z=L_{II}} \quad (3.73)$$

$$u_{0,inlet,III}C_{inlet,T,III}c_pT_{inlet,III} = u_{0,F}C_{F,T}c_pT_F + (u_{0,II}C_{g,T,II}c_pT_{g,II})\big|_{z=L_{II}} \quad (3.74)$$

Raffinate node:

$$C_{inlet,i,IV} = C_{g,i,III}\big|_{z=L_{III}} \quad (3.75)$$

$$u_{0,inlet,IV} = u_{0,III}\big|_{z=L_{III}} - u_{0,R} \quad (3.76)$$

$$T_{inlet,IV} = T_{g,III}\big|_{z=L_{III}} \quad (3.77)$$

Where C_T is the total molar concentration in each section/stream.

A hierarchical model is built in which eight instances of the fixed-bed model, and eight instances of the manifold model are defined. Each column is represented by an individual instance of the base fixed-bed model, with its inlet and outlet connected to corresponding manifold instances. The manifold model includes all node balance configurations described above, and a selector mechanism activates the appropriate one at each step. Then, a third model is used to construct the global process, which incorporates all eight columns and eight manifolds.

During a cycle, the synchronous switching of the inlet and outlet ports, according to the defined switching time, is performed using the *gPROMS* tasks, which also selects the appropriate operation mode of each manifold in accordance with the column configuration of the SMB.

3.7.2. Performance Parameters

To evaluate the performance of the SMB process for the separation of methane (A) and nitrogen (B), four parameters may be calculated: purity, recovery, productivity and desorbent consumption. The calculation of said criteria can be accomplished through Equations (3.78) to (3.84), admitting that the flow rates remain constant during the assay and so, its non-integral form can be used.

Desorbent-free extract and raffinate purity (%)

$$Pu_X = \frac{\bar{y}_X^A}{\bar{y}_X^A + \bar{y}_X^B} \times 100 \quad (3.78)$$

$$Pu_R = \frac{\bar{y}_R^B}{\bar{y}_R^A + \bar{y}_R^B} \times 100 \quad (3.79)$$

Extract and raffinate recovery (%)

$$Rec_X = \frac{\bar{y}_X^A Q_X}{y_F^A Q_F} \times 100 \quad (3.80)$$

$$Rec_R = \frac{\bar{y}_R^B Q_R}{y_F^B Q_F} \times 100 \quad (3.81)$$

Productivity (kg_{A,B}·m_{ads}⁻³·h⁻¹)

$$Prod_X = \frac{(\bar{y}_X^A Q_X P / R_g T) \times M^A}{V_s} \quad (3.82)$$

$$Prod_R = \frac{(\bar{y}_R^B Q_R P / R_g T) \times M^B}{V_s} \quad (3.83)$$

Desorbent consumption (m_{STP, desorbent}³·kg_A⁻¹)

$$DC = \frac{Q_D}{(\bar{y}_X^A Q_X P / R_g T) \times M^A} \quad (3.84)$$

3.7.3. Separation Region

The separation region is known as the area of a γ_{II} and γ_{III} plot (or Q_{II} and Q_{III} , if using molar flow rates in SLPM) in which extract and raffinate are considered pure, *i.e.*, obey the specified purity values for the product streams. Regardless of the system considered, the purity values in the extract outlet were set to be over 97% and in the raffinate outlet over 99%. These values correspond to the product specifications for the methane and nitrogen streams, respectively, but were fixed to compare the separation regions for different systems during the development of the SMB performance indicator. To compute the separation region, firstly, we need to ensure that the defined flow rate for section I is high enough to regenerate the adsorbent beds and for section IV is low enough so that the desorbent is cleaned to be recycled back into section I. Also, a switching time must be specified. The first points of the region are obtained by setting a low feed flow rate and simulating the SMB process for different values of extract flow rate until the product specifications are met. Once the limits are found for a particular feed flow rate, its value is increased, being the process repeated for progressively higher values, until the separation region is completely drawn.

To compute the separation regions, a *MATLAB* algorithm coupled with the *gPROMS* software was developed. The communication between *gPROMS* and *MATLAB* was facilitated using *goMATLAB*, an interface that enables data exchange between the two software environments. In this setup, *gPROMS* was responsible for simulating the SMB process, evaluating the separation performance based on the specified operating conditions received from *MATLAB*. On the other hand, *MATLAB* changes the feed/extract flow rates of the SMB system and receives the performance parameters from *gPROMS*. Based on the values received, the *MATLAB* program defines the next set of operating conditions to be sent to *gPROMS*. This bidirectional communication ensured an easier and more efficient search for the limits of the separation region.

When designing an SMB process, the operating point must reside inside the limits defined by this region and should be close to the vertex, which is the point at the boundary of the separation region farthest away from the diagonal $\gamma_{II} = \gamma_{III}$, where the productivity is maximized (since γ_F is higher and is proportional to the system productivity). An adsorbent/desorbent pair that exhibits a larger separation zone indicates that an easier separation of the target mixture can be achieved since a wider range of γ_{II} and γ_{III} values lead to pure product streams, while a higher $\gamma_{F, \max}$ is indicative of a higher system productivity.

3.8. SMB/PSA Hybrid Process

In a conventional SMB process, two output streams are produced: the extract stream, which contains the more retained species, and the raffinate stream, which contains the less retained species. Both streams are diluted with the desorbent, which is used for adsorbent regeneration and to aid in the separation. To obtain the pure products, two additional separation processes are required, separating the target components from the desorbent. To overcome this issue, an alternative method for adsorbent regeneration can be used, such as PSA. By using this approach, the desorbent can be effectively removed from the process entirely, simplifying the separation of the target mixture.

In the hybrid SMB/PSA process, the regeneration zone, designated as Section I, is decoupled from the SMB and the desorbent is replaced with a sequence of PSA steps that rely on pressure variations for the adsorbent regeneration.

While one column undergoes these PSA steps in section I, in parallel, the remaining columns operate in series and are divided into two zones, which operate at different flow rates and have different functions. In Section II, known as the displacement zone, located between the displacing gas inlet and the feed inlet, the heavy product acts as the eluent to enrich the beds in the more retained species through displacement chromatography. In the adsorption zone, Section III, located between the feed inlet and the light product outlet, the more retained species adsorbs preferentially to the solid material while the less retained species travels in the fluid flow direction, with the outlet stream being enriched in the latter. After a switching time, t^* , elapses, which

corresponds to the duration of one step, the inlets and outlets shift in the gas flow direction, promoting continuous mass transfer between solid and fluid phases. After the switch, the column that ended the PSA sequence in section I becomes the last column of section III, while the first column of section II becomes the column in section I to begin the PSA sequence. During a complete cycle of the SMB/PSA hybrid process, each column undergoes a total number of steps corresponding to the number of columns in the unit. Since the PSA sequence runs simultaneously to the SMB part of the process, to maintain synchronous operation of the process, the total duration of the PSA sub-steps (blowdown, counter-current purge, and co-current pressurization) must be equal to the switching time of the hybrid process, i.e., one step (Equation (3.85)).

$$t^* = t_{\text{blow}} + t_{\text{pg}} + t_{\text{press}} \quad (3.85)$$

The PSA sequence is comprised of the counter-current blowdown sub-step, during which the pressure is reduced, leading to the desorption of the more retained species and producing it at the column outlet. This is followed by a counter-current purge sub-step, where any residual impurities are removed using the light product as the purge stream. Then, a co-current pressurization sub-step is employed to restore the operating pressure, using the light product, ensuring the column is prepared to produce the less retained species in the following step.

Figure 3.3 shows a schematic of an SMB/PSA hybrid process for methane/nitrogen separation. An eight-column configuration was projected, with one column in Section I, two in Section II and five in Section III (1-2-5 column configuration). The number of columns allocated to the adsorption zone is due to the low adsorption selectivity of CH_4/N_2 , requiring a longer bed length to enhance the separation efficiency. Like the traditional SMB, the flow rate in each section of the SMB component of the process is given by the balance to the nodes, in SLPM.

$$Q_{\text{II}} = Q_{\text{Disp}} \quad (3.86)$$

$$Q_{\text{III}} = Q_{\text{II}} + Q_{\text{F}} \quad (3.87)$$

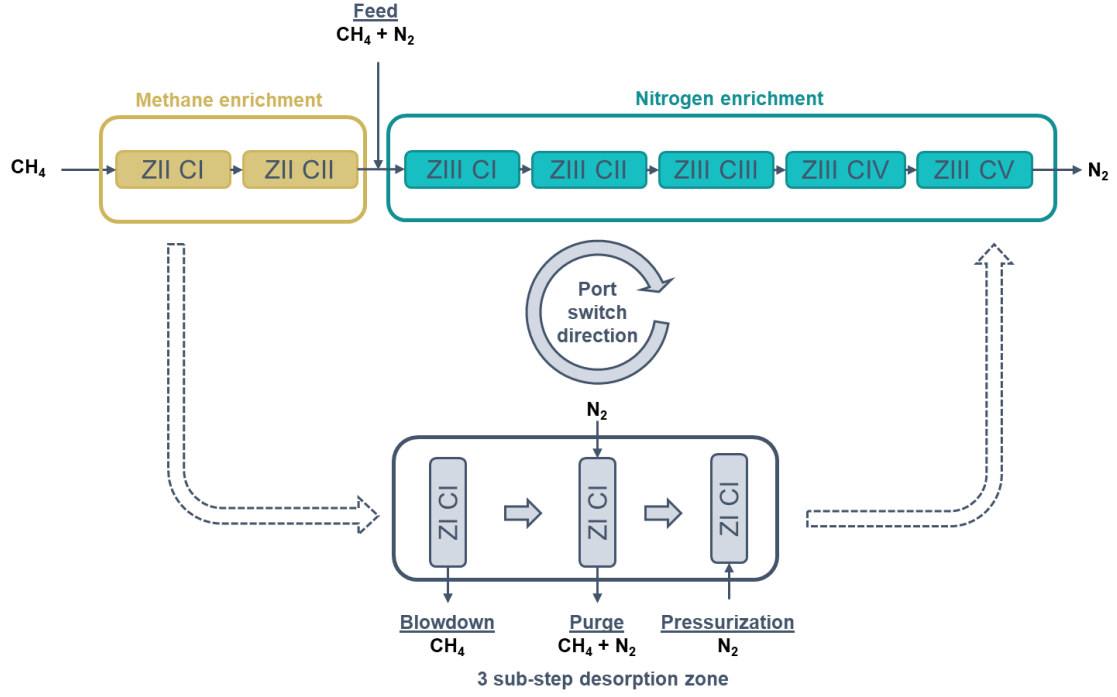


Figure 3.3 – Schematic of an SMB/PSA process with a 1-2-5 column configuration. Z corresponds to the section of the hybrid process and C corresponds to the column.

For the modelling of the hybrid process, the average composition of the product streams was considered for the recycle streams (displacement gas stream, purge gas stream, and pressurization gas stream).

By integrating SMB with PSA, this hybrid approach enhances separation efficiency, eliminates the need for a desorbent, and reduces additional purification steps, leading to a more cost-effective and streamlined process.

3.8.1. PSA sub-steps boundary conditions

The regeneration step of the SMB/PSA hybrid process involves a sequence of pressure swing sub-steps. Each sub-step is described by the fixed-bed dynamic model presented before with different boundary conditions, which depend on the characteristics of that sub-step. As such, coupled with the fixed-bed model (Equations (3.16 to (3.27))), the boundary conditions employed for each of the PSA sub-steps are given by the following equations:

Counter-current blowdown sub-step:

$$z = L:$$

$$\frac{\partial C_{g,i}}{\partial z} = 0 \quad (3.88)$$

$$u_0 = 0 \quad (3.89)$$

$$\frac{\partial T_g}{\partial z} = 0 \quad (3.90)$$

$z = 0$, outlet:

$$\frac{\partial C_{g,i}}{\partial z} = 0 \quad (3.91)$$

$$P = P_{\text{outlet}} \quad (3.92)$$

$$\frac{\partial T_g}{\partial z} = 0 \quad (3.93)$$

Counter-current purge sub-step (with the light product):

$z = L$, inlet:

$$u_{0,\text{inlet}} C_{\text{inlet},i} = u_0 C_{g,i} - \varepsilon D_{\text{ax}} C_{g,T} \frac{\partial y_i}{\partial z} \quad (3.94)$$

$$u_{0,\text{inlet}} C_{\text{inlet},T} = u_0 C_{g,T} \quad (3.95)$$

$$u_{0,\text{inlet}} C_{\text{inlet},T} c_P T_{\text{inlet}} = u_0 C_{g,T} c_P T_g - \lambda \frac{\partial T_g}{\partial z} \quad (3.96)$$

$z = 0$, outlet:

$$\frac{\partial C_{g,i}}{\partial z} = 0 \quad (3.97)$$

$$P = P_{\text{outlet}} \quad (3.98)$$

$$\frac{\partial T_g}{\partial z} = 0 \quad (3.99)$$

Co-current pressurization sub-step (with the light product):

$z = 0$, inlet:

$$u_{0,\text{inlet}} C_{\text{inlet},i} = u_0 C_{g,i} - \varepsilon D_{\text{ax}} C_{g,T} \frac{\partial y_i}{\partial z} \quad (3.100)$$

$$P = P_{\text{inlet}} \quad (3.101)$$

$$u_{0,\text{inlet}} C_{\text{inlet},T} c_P T_{\text{inlet}} = u_0 C_{g,T} c_P T_g - \lambda \frac{\partial T_g}{\partial z} \quad (3.102)$$

$z = L$:

$$\frac{\partial C_{g,i}}{\partial z} = 0 \quad (3.103)$$

$$u_0 = 0 \quad (3.104)$$

$$\frac{\partial T_g}{\partial z} = 0 \quad (3.105)$$

During the blowdown step, the outlet pressure (P_{outlet}) decreases exponentially over time, starting from the pressure at the end of column I of Section II at the end of the previous step and gradually reaching the blowdown pressure (P_{low}) due to the valve opening. In the case of the counter-current purge step, P_{outlet} is constant and is equal to P_{low} . For the co-current pressurization step, the inlet pressure (P_{inlet}) increases linearly over time, from P_{low} to the pressure at the end of Section III, P_{high} .

3.8.2. Performance Parameters

The performance of the SMB/PSA hybrid cycles was evaluated according to methane (A) and nitrogen (B) purity, product recovery, and process productivity, which are defined by the following equations. These parameters were evaluated at cyclic steady state, using data from one step (from time 0 to time t^*).

The heavy product is obtained during the blowdown sub-step. This way, the purity can be calculated by the amount of A that exits the column during this sub-step, divided by the total amount that exits the column (Equation (3.106)). The light product is produced at the end of Section III. As a result, the light product purity is obtained by dividing the amount of B that exits this column during a step, divided by the total amount that exits the column (Equation (3.107)).

Also, a portion of the heavy product is utilised as displacement gas in Section II. Thus, the methane recovery can be obtained by subtracting the amount of methane used as displacement gas during the step from the amount of methane produced and dividing it by the amount of methane fed to the system (Equation (3.108)).

The purge and pressurization sub-steps are performed with part of the nitrogen product as the inlet gas. This way, the nitrogen recovery is calculated by subtracting the amount of nitrogen used during these sub-steps from the amount of nitrogen produced during a step at the end of Section III and dividing it by the amount of nitrogen fed at the feed inlet (Equation (3.109)).

Accordingly, the heavy and light component productivity can be obtained through Equations (3.110) and (3.111).

Heavy and light component purity (%)

$$Pu_A = \frac{\int_0^{t_{\text{blow}}} C_{A,\text{blow}} u_0 \Big|_{z=0,I} dt}{\sum_{i=1}^{NC} \left(\int_0^{t_{\text{blow}}} C_{i,\text{blow}} u_0 \Big|_{z=0,I} dt \right)} \times 100 \quad (3.106)$$

$$Pu_B = \frac{\int_0^{t^*} C_B u_0 \Big|_{z=L_{III}} dt}{\sum_{i=1}^{NC} \left(\int_0^{t^*} C_i u_0 \Big|_{z=L_{III}} dt \right)} \times 100 \quad (3.107)$$

Heavy and light component recovery (%)

$$Rec_A = \frac{\int_0^{t_{\text{blow}}} C_{A,\text{blow}} u_0 \Big|_{z=0,I} dt - \int_0^{t^*} C_{A,\text{disp}} u_0 \Big|_{z=0,II} dt}{\int_0^{t^*} C_{A,F} u_{0,F} \Big|_{z=0,III} dt} \times 100 \quad (3.108)$$

$$Rec_B = \frac{\int_0^{t^*} C_B u_0 \Big|_{z=L_{III}} dt - \int_0^{t_{\text{pg}}} C_B u_0 \Big|_{z=L_I} dt - \int_0^{t_{\text{press}}} C_{B,\text{press}} u_0 \Big|_{z=0,I} dt}{\int_0^{t^*} C_{B,F} u_{0,F} \Big|_{z=0,III} dt} \times 100 \quad (3.109)$$

Heavy and light component productivity (kg_{A,B}·m_{ads}⁻³·h⁻¹)

$$Prod_A = \frac{\left[\int_0^{t_{\text{blow}}} C_{A,\text{blow}} u_0 \Big|_{z=0,I} dt - \int_0^{t^*} C_{A,\text{disp}} u_0 \Big|_{z=0,II} dt \right] \times M^A}{V_s t^*} \quad (3.110)$$

$$Prod_B = \frac{\left[\int_0^{t^*} C_B u_0 \Big|_{z=L_{III}} dt - \int_0^{t_{\text{pg}}} C_B u_0 \Big|_{z=L_I} dt - \int_0^{t_{\text{press}}} C_{B,\text{press}} u_0 \Big|_{z=0,I} dt \right] \times M^B}{V_s t^*} \quad (3.111)$$

To increase the methane recovery was considered the possibility of a fraction of the purge outlet stream being recovered as heavy product, while the methane purity is kept above the 97 % specification. The fraction of the purge duration where the purged methane is recovered is defined as $t_{\text{int, pg}}$. This way, only the gas purged from $t_{\text{int, pg}}$ to t^* is considered as waste. In this case, the purity, recovery and productivity of the heavy component are calculated by the equations provided below.

Heavy component purity, with purge recovery (%)

$$Pu_A = \frac{\int_0^{t_{\text{blow}}} C_{A,\text{blow}} u_0 \Big|_{z=0,I} dt + \int_0^{t_{\text{int,pg}}} C_{A,\text{pg,out}} u_0 \Big|_{z=0,I} dt}{\sum_{i=1}^{NC} \left[\int_0^{t_{\text{blow}}} C_{i,\text{blow}} u_0 \Big|_{z=0,I} dt + \int_0^{t_{\text{int,pg}}} C_{i,\text{pg,out}} u_0 \Big|_{z=0,I} dt \right]} \times 100 \quad (3.112)$$

Heavy component recovery, with purge recovery (%)

$$Rec_A = \frac{\int_0^{t_{\text{blow}}} C_{A,\text{blow}} u_0 \Big|_{z=0,I} dt + \int_0^{t_{\text{int,pg}}} C_{A,\text{pg,out}} u_0 \Big|_{z=0,I} dt - \int_0^{t^*} C_{A,\text{disp}} u_0 \Big|_{z=0,II} dt}{\int_0^{t^*} C_{A,F} u_{0,F} \Big|_{z=0,III} dt} \times 100 \quad (3.113)$$

Heavy component productivity, with purge recovery (kg_A·m_{ads}⁻³·h⁻¹)

$$Prod_A = \frac{\left[\int_0^{t_{\text{blow}}} C_{A,\text{blow}} u_0 \Big|_{z=0,I} dt + \int_0^{t_{\text{int,pg}}} C_{A,\text{pg,out}} u_0 \Big|_{z=0,I} dt - \int_0^{t^*} C_{A,\text{disp}} u_0 \Big|_{z=0,II} dt \right] \times M^A}{V_s t^*} \quad (3.114)$$

3.8.3. Power consumption

As previously mentioned, a portion of the CH_4 produced during the blowdown sub-step is used to displace the adsorbed phase in Section II. This way, a compressor is required to raise the low-pressure gas to the higher pressure at the inlet of the first column. The power consumption of this compressor was calculated assuming adiabatic and single stage compression. An efficiency of 85% was considered for the compressor. The compression power required for the displacement gas, W_{disp} , was determined with the following equation:

$$W_{\text{disp}} = \frac{1}{\eta} F_{\text{disp}} R_g T_{\text{in}} \frac{\gamma}{\gamma - 1} \left[\left(\frac{P_{\text{out}}}{P_{\text{atm}}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (3.115)$$

where F_{disp} is the molar flow rate of the displacement gas, T_{in} is the inlet temperature, P_{atm} and P_{out} are the atmospheric pressure and outlet pressure, respectively, and γ is the ratio between the heat capacity of the gas mixture at constant pressure and the heat capacity of the gas mixture at constant volume, $\gamma = c_p/c_v$.

For the blowdown sub-step, since sub-atmospheric pressures were used, a vacuum pump is necessary. For the vacuum pump, an efficiency of 60% was considered. In this case, multiple stages with equal pressure ratios, and negligible pressure drop between stages were considered. Also, the inlet temperature was assumed to remain constant across stages. For the calculation of the power consumption of the blowdown, W_{blow} , a similar equation is employed:

$$W_{\text{blow}} = \frac{1}{\eta} F_{\text{blow}} R_g T_{\text{blow}} \frac{\gamma}{\gamma - 1} \left[\left(\frac{P_{\text{atm}}}{P_{\text{low}}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (3.116)$$

Where η is the pump efficiency, F_{blow} is the average molar flow rate of the blowdown sub-step, and T_{blow} is the temperature of the blowdown sub-step.

The used of a vacuum pump during the purge step is also necessary. To obtain the power consumption of the purge sub-step, W_{pg} , the following equation was used:

$$W_{\text{pg}} = \frac{1}{\eta} F_{\text{pg,out}} R_g T_{\text{pg}} \frac{\gamma}{\gamma - 1} \left[\left(\frac{P_{\text{atm}}}{P_{\text{low}}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (3.117)$$

where $F_{\text{pg,out}}$ is the average molar flow rate at the outlet during the purge sub-step, and T_{pg} is the temperature of the purge sub-step.

The total power consumption is then calculated by the sum of the power consumption obtained for each sub-step, considering only the time percentage each pump is on:

$$W_T = W_{\text{disp}} + \frac{t_{\text{blow}}}{t^*} W_{\text{blow}} + \frac{t_{\text{pg}}}{t^*} W_{\text{pg}} \quad (3.118)$$

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CHAPTER 4 – SMB PERFORMANCE INDICATOR (SPI)

This chapter is based on the following publication: Dias R.O.M., Nogueira I.B.R., Ferreira A.F.P., Rodrigues A.E., Ribeiro A.M., A performance indicator for the screening of adsorbent/desorbent pairs for gas-phase simulated moving bed applications. AIChE J. 2023; 69(6):e18074. doi:10.1002/aic.18074

4.1. Introduction

As mentioned in Section 3.7, in an SMB process, the regeneration is accomplished by the introduction of a third species, the desorbent, which is later recovered by two downstream separations. As such, the choice of a proper adsorbent/desorbent pair is critical to ensure the effectiveness of the SMB process. While this can be done by comparing the separation region for each system, the computational effort required is extremely high. By developing a parameter that uses readily available literature data, the selection process is sped up and can be easily accomplished.

This said, an SMB performance indicator (SPI) is suggested in this chapter. The aim of this new metric is to be able to select the most suitable adsorbent/desorbent pair for the studied separation by SMB through simple calculations.

4.2. Multicomponent adsorption equilibrium

To develop the SPI, the first step was to perform multicomponent adsorption equilibrium predictions. To do so, pure component adsorption data over different materials was collected from the literature. This chapter studied the methane/nitrogen separation, using carbon dioxide as the desorbent. As such, 55 materials were screened and categorized by type, and their adsorption equilibrium data for the pure adsorbates at 303 K was tabled. These materials include carbon-based materials (activated carbons and carbon molecular sieves), zeolites, a commercial activated alumina, and metal-organic frameworks (MOFs) for possible application in a gas-phase SMB process for the CH₄/N₂ separation. In Table 4.1, information regarding the shape and manufacturer of the adsorbent can be consulted. When the manufacturer is not mentioned, the adsorbent sample was synthesized in the laboratory by the author(s) of the respective work. The experimental data of adsorption isotherms of pure nitrogen, methane, and carbon dioxide is presented in Appendix A in Table A.1, Table A.2, and Table A.3, respectively. The method used to obtain the equilibrium data is also depicted in the referred tables, either volumetric (V), gravimetric (G), or *via* breakthrough curves (BT).

Table 4.1 – Screened adsorbents for the CH₄/N₂ separation.

Adsorbent	Manufacturer	Form	Ref.
Carbon-based materials			
2GA-H2J	Kuraray Chemical Co.	Pellets	[1]
AC	Sutcliffe Speakman	Pellets	[2]
AC Beads	East China University of Science and Technology	Pellets	[3]
BPL	Calgon Carbon Co.	Pellets	[4]
CMS 3A	Takeda Co.	Pellets	[5]
CMS 3K	Takeda Co.	Pellets	[6]
DARCO	Cabot Co.	Granules	[7]
Degussa F30-470	Degussa	Pellets	[8]
Norit R1 Extra	Cabot Co.	Pellets	[9]
Norit R2030	Cabot Co.	Pellets	[10]
Norit RB3	Cabot Co.	Pellets	[11, 12]
Maxsorb	Kansai Coke Chemical Co.	Powder	[13]
PCB	Calgon Carbon Co.	Pellets	[14]
WV1050	WestRock Co.	Pellets	[15]
Xtrusorb A754	Calgon Carbon Co.	Pellets	[16, 17]
Activated aluminas / Silica Gel			
AA-300	Alcan	Spheres	[16, 17]
Zeolites			
4A (Binderless)	Chemiewerk Bad Köstritz GmbH	Granules	[18]
5A	Union Carbide	Pellets	[16, 17]
5A	Takeda Co.	Pellets	[19]
13X	CECA Arkema Group	Spheres	[20]
13X	Honeywell UOP	Pellets	[21]
CaX	Zeochem	Spheres	[16, 17]
Chabazite	Zeox Corporation	Granules	[22]
Clinoptilolite (Raw)	Ash Meadows Zeolite LLC	Powder	[23]
Sr ²⁺ Clinoptilolite	-	Powder	[23]
Cs ⁺ Clinoptilolite	-	Powder	[23]
Fe ³⁺ Clinoptilolite	-	Powder	[23]
DD3R	Exxon Mobil	Powder	[24]
H-β	Süd-Chemie	Pellets	[25]
HiSiv3000	Honeywell UOP	Pellets	[26]
LiX	Zeochem	Spheres	[1]
H-Mordenite	CU Chemie Uetikon AG	Powder	[27]
NaY	Nankai University	Powder	[28]
ZSM-5	Süd-Chemie	Powder	[29]

Table 4.1 (cont.) – Screened adsorbents for the CH₄/N₂ separation.

Adsorbent	Manufacturer	Form	Ref.
Metal-Organic Frameworks			
CAU-1	KIEL	Powder	[19]
CuBTC	KRICT	Spheres	[30]
Cu-MOF	-	Powder	[31]
MIL-53(Al)	BASF	Powder	[32, 33]
MIL-100(Al)	KRICT	Powder	[19]
MIL-100(Fe)	KRICT	Spheres	[19]
MIL-101(Cr)	-	Powder	[34]
MIL-125(Ti)	KRICT	Powder	[19]
MIL-125(Ti)-NH ₂	KRICT	Granules	[35]
MIL-127(Fe)	KRICT	Spheres	[19]
MOF-508b	-	Powder	[36]
Ni-MOF-74	-	Powder	[7]
Co-MOF-74	-	Powder	[7]
Mg-MOF-74	-	Powder	[7]
MOF Al-Fumarate	BASF	Pellets	[37]
UiO-66(Zr)	KRICT	Spheres	[19]
UiO-66(Zr)-NH ₂	KRICT	Spheres	[19]
UiO-66(Zr)-(COOH) ₂	KRICT	Granules	[38]
UTSA-16	-	Pellets	[39]
ZIF-8	BASF	Powder	[40]
ZIF-94	-	Powder	[41, 42]

Analysis of the pure component adsorption equilibrium isotherms indicates that, at the defined temperature of the isotherms (303 K for most of the adsorbents), for all screened materials, the order is CO₂ > CH₄ > N₂ from highest to lowest adsorption capacity. Also, the screened materials are all selective towards methane ($\alpha_{\text{CH}_4/\text{N}_2} > 1$) based on the ideal selectivity. Physisorption is controlled by dispersion-repulsion forces (van der Waals forces) and electrostatic forces, with the dispersion forces being always present and prevailing when stronger forces are non-existent, establishing the adsorption equilibrium [43]. The adsorbed amount increases further depending on the electrostatic nature of the adsorbent surface and the adsorbates, as well as their polarizability. The properties of the studied gases are presented in Table 4.2 [44, 45]. Since methane exhibits larger polarizability than nitrogen, even though both molecules have a null dipole moment, its interaction is stronger on non-polar adsorbent surfaces. The existent strong permanent quadrupole moment on the CO₂ and the N₂ molecules also negatively affects their affinity towards these surfaces. As a result, activated carbons have a weaker performance for CO₂ adsorption. On the other hand, and for the same reason, CO₂ strongly adsorbs on the surface of polar materials

such as zeolites (4A, 5A, 13X, CaX, LiX), which might be detrimental to an SMB process, exhibiting a steeper isotherm.

Table 4.2 - Physiochemical properties of the studied gases [44, 45].

Adsorbate	Kinetic Diameter ($\times 10^{-8}$ cm)	Dipole Moment (esu·cm)	Quadrupole Moment ($\times 10^{-26}$ esu·cm ²)	Polarizability ($\times 10^{-24}$ cm ³)
CH ₄	3.80	0	0	2.593
N ₂	3.64	0	1.52	1.740
CO ₂	3.30	0	4.30	2.911
Ar	3.40	0	0	1.641

Having collected the adsorption equilibrium isotherms of pure gases on various adsorbents, the next step was to predict the adsorption behaviour of a ternary mixture composed of the compounds that take part in the process. As such, the multi-component adsorption equilibrium was computed resorting to the IAS theory by inputting the pure component isotherms at the specified temperature. To solve the system of equations, the total pressure and the gas phase composition were also given as input parameters. A pressure range of 0 to 500 kPa and a molar fraction of $y_{\text{CO}_2}=0.5$ and $y_{\text{CH}_4} = y_{\text{N}_2} = 0.25$ was used, which is a typical composition at the feed inlet of an SMB process when the cyclic steady state is reached [46]. These inputs are inserted into a macro-enabled spreadsheet, and the system is solved with an algorithm programmed in *Visual Basic for Applications* in combination with *Excel*, as described elsewhere [47]. By solving the system of equations depicted in Section 3.2 for the IAST calculations, the co-adsorption data for the ternary mixture is obtained and the selectivity of CH₄ over N₂ in the presence of the desorbent (CO₂) can be easily calculated by the quotient of the amount adsorbed of each component (since the mixture is equimolar for these two components). To ensure the suitability of the calculations, ternary adsorption equilibrium data was taken from the literature for NORIT R1 Extra [9], at 298 K, and MOF-508b [36], at 303 K, and compared to the results obtained by IAST calculations. The comparison is available in Figure A.1 and Figure A.2.

As an example, the predicted multicomponent adsorption equilibrium results for one of the activated carbons, 2GA-H2J, are presented below, in Figure 4.1. This calculation was performed considering a molar ratio of 0.5:0.25:0.25 for the CO₂/CH₄/N₂ ternary mixture at 303 K. To evaluate the effect of the desorbent composition on the adsorption selectivity, three compositions ($y_{\text{CO}_2}=0.35, 0.6$ and 0.75 and $y_{\text{CH}_4}=y_{\text{N}_2}=0.325, 0.2$ and 0.125), which are representative of the compositions inside the separation zone, were also considered. The total pressure of the system was fixed at 185 kPa. The results obtained are illustrated for the 2GA-H2J adsorbent in Figure 4.2. The results obtained for the remaining materials can be observed in Appendix A, from Figure A.3 to Figure A.56.

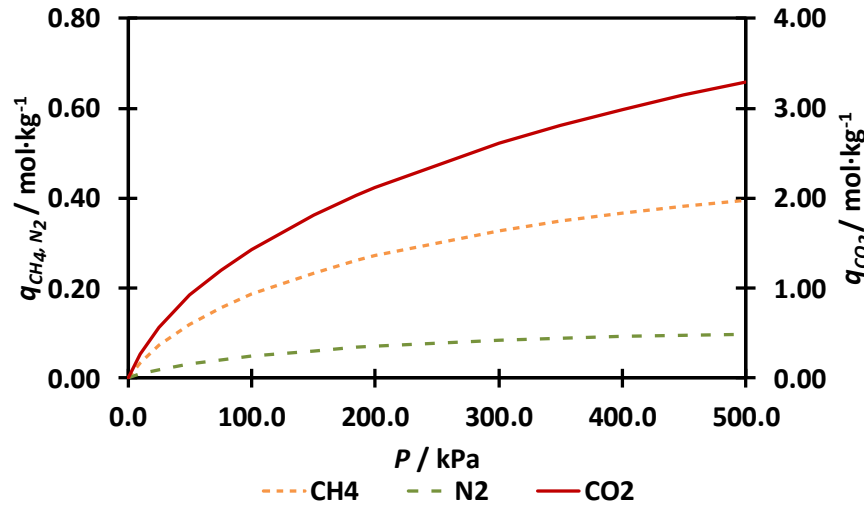


Figure 4.1 - Ternary adsorption equilibria of CO₂ (straight line), CH₄ (dashed line), and N₂ (spaced dashed line) on the commercial activated carbon 2GA-H2J at 303 K, for a 0.5:0.25:0.25 gas-phase composition.

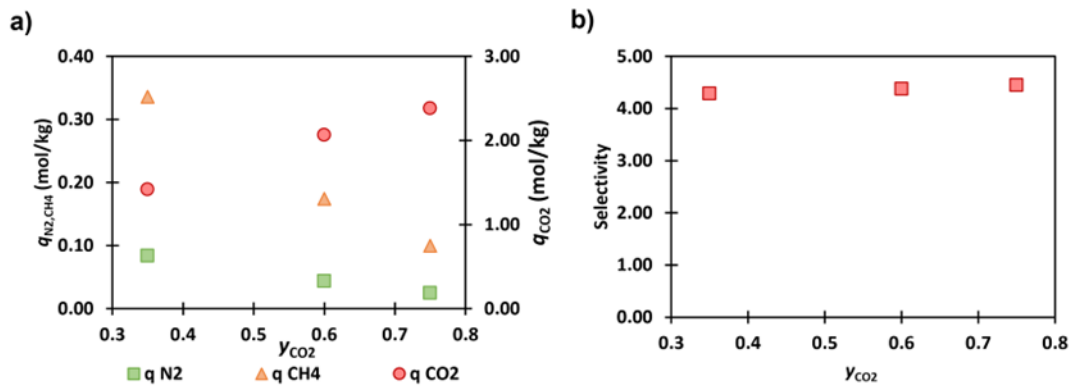


Figure 4.2 – Effect of the desorbent fraction on a) the amount adsorbed and b) CH₄/N₂ adsorption selectivity for the commercial activated carbon 2GA-H2J at 303 K and 185 kPa.

Firstly, the results obtained for the multicomponent adsorption data are in accordance with the pure component isotherms, in the way that CH₄ remains the heavier component when compared to N₂, even in the presence of CO₂, for all pressures considered and at the defined bulk compositions. The only exception is the raw clinoptilolite, which becomes selective toward nitrogen and discarded from the analysis since the comparison with the remaining adsorbents is invalid.

For most of the materials, the selectivity of the adsorbent remains constant when the desorbent fraction in the gas phase increases, with a deviation of less than 5%. Materials that exhibit very low adsorption quantities of methane and nitrogen, such as AA300, zeolite 13X, CaX, LiX, and Cs⁺-clinoptilolite, show larger deviations due to the tolerance error used in the calculations. Although these materials present a seemingly high selectivity, they also offer an inferior performance

regarding methane uptake. This is because CO_2 is preferentially adsorbed over the other two components that compose the gas mixture, due to the stronger interaction of this molecule towards the polar surface of these materials.

For clarity and more accessible analysis of the adsorbent performance, the methane/nitrogen selectivity in the presence of CO_2 *versus* methane uptake at 185 kPa for a 50% CO_2 /25% CH_4 /25% N_2 ternary mixture is compiled in Figure 4.3, where the squares, circles, and triangles represent zeolites, carbonaceous materials, and MOFs, respectively.

Most materials exhibit an adsorption selectivity that falls in the 2-6 range, with some outliers, such as the Cu-MOF, showing the highest selectivity among the screened materials of 11.2 for the inputted conditions. The least selective material reviewed in this study is the MOF-508b, exhibiting a selectivity close to the unity (1.04). Among the adsorbents studied, the material that offers the least methane adsorption capacity is the Cs^+ exchanged clinoptilolite, which mostly adsorbs carbon dioxide. On the other hand, the one that provides the largest uptake of CH_4 is Norit R1 Extra, adsorbing 0.349 mmol/g for the defined conditions (note that a slightly lower temperature of 298 K was used for this material). It can also be observed that most of the zeolite-type adsorbents perform poorly in terms of methane adsorption capacity, which is explained, as aforementioned, by the nature of the surface of these materials. Activated carbons, contrarily, exhibit the best performance in terms of methane uptake, given their weaker interaction with the desorbent. Regarding the MOFs, their performance in terms of methane adsorption and selectivity is variable, as can be seen in Figure 4.3 by the triangles spread through both axes. This said, materials that provide high selectivities, and high adsorption capacities are desired for adsorptive processes, as they lead to not only pure product streams but also high productivities.

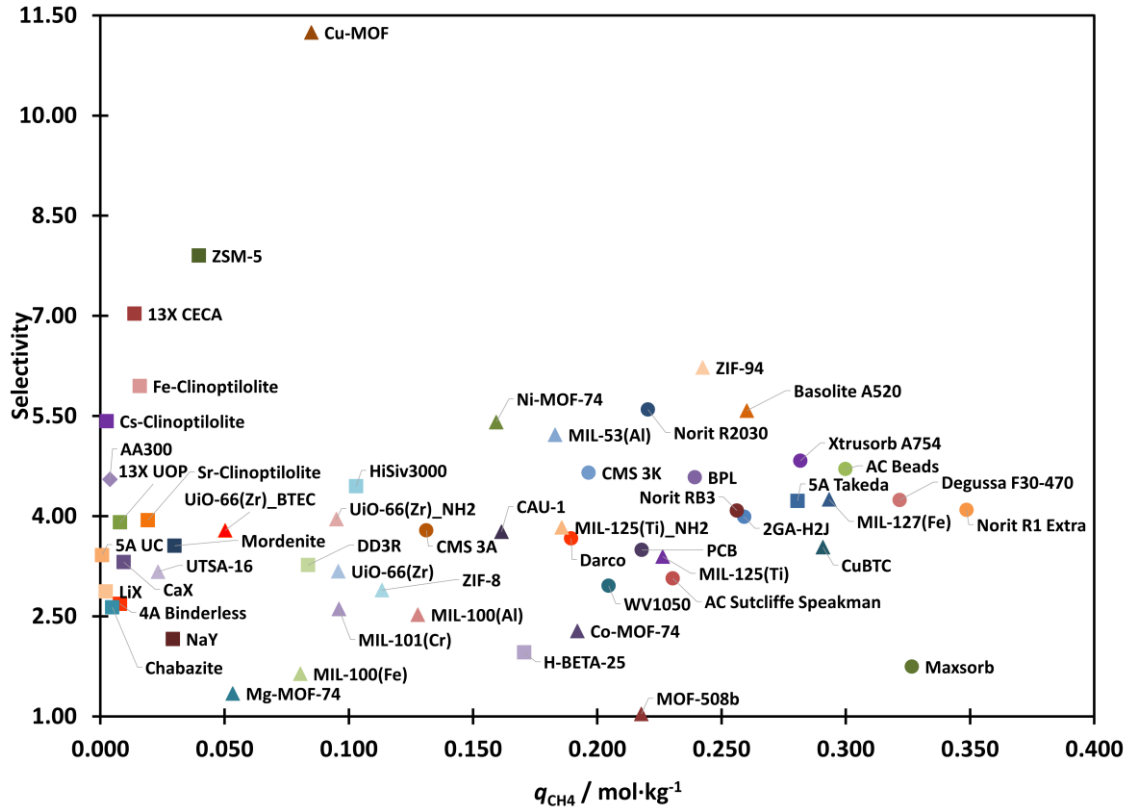


Figure 4.3 - Methane/nitrogen selectivity in the presence of CO₂ versus methane uptake at 185 kPa for a 50% CO₂/25% CH₄/25% N₂ ternary mixture.

While the previously shown calculations can provide an insight into which material is best suited for a specific gas mixture separation, it can still be challenging to know which one will provide the best performance when integrated into an SMB process. Considering only the adsorption selectivity is not a suitable parameter to predict the performance of the adsorbent materials, as can be seen in Figure A.57 and Figure A.58. In the case of an SMB process, it has some particularities due to the presence of the desorbent. This leads to different selectivity requirements to those observed in a PSA process. Furthermore, using existing metrics to screen materials for an SMB process is not optimal, as the process nature is not taken into consideration, *i.e.*, the material-process nexus is disregarded [48].

4.3. SMB Performance Indicator

To further evaluate the screened materials for a gas-phase SMB process and to facilitate the selection of the most efficient one, an SMB performance indicator (SPI) was developed. This parameter can provide a preliminary selection of the most promising adsorbent/desorbent pair before dynamic tests are performed and SMB cycles are executed. Among the tested expressions for the calculation of the SPI, the presented metric was the one that offered the best correlation when compared to the results given in this section.

The proposed SPI is based on the Adsorption Performance Indicator (API) developed by Wiersum *et al.* [19], comprising three adsorbent properties that can be obtained from readily available pure isotherms data. The equation that allows the computation of the SPI is expressed in Equation (4.1).

$$SPI = \frac{\alpha_{AB} \times q_A^2 \times \frac{\Delta H_A}{\Delta H_D}}{\frac{\Delta H_B}{\Delta H_D}} = \frac{\alpha_{AB} \times q_A^2}{\frac{\Delta H_B}{\Delta H_A}} \quad (4.1)$$

where A is the more retained species, B is the less retained species, α_{AB} is the selectivity of A over B, q_A is the amount adsorbed of A when multicomponent adsorption behaviour is considered, and ΔH_B and ΔH_A are the heat of adsorption of components B and A, respectively.

The adsorption selectivity of the most retained species (CH_4 - A) over the less retained species (N_2 - B) in the presence of the desorbent gas (D) and the amount adsorbed of the more retained species were obtained from the IAST multicomponent adsorption equilibrium predictions. For these calculations, a molar composition of $y_D=0.5$ and $y_A = y_B = 0.25$ was used at 303 K and total pressure of 185 kPa. The heat of adsorption is factored in the expression since the heat generated during the adsorption is unfavourable to the process, as it is indicative of the strong affinity of the adsorbates to the solid phase, leading to regeneration impediments in an SMB process. In this case, the reasoning behind the ratio of the isosteric heat of adsorption of the heavy and light components is two-fold: 1) a higher adsorption affinity of the more adsorbed species and a lower adsorption affinity of the less retained species is preferred and 2) the relative strength of the desorbent to the components of the mixture is important for the displacement of the adsorbed phase. In this study, the values of the isosteric heat of adsorption were obtained from the equation derived for the DSL isotherm model by D. Do [47] (Equation (3.14)). The second-order power in the amount adsorbed of the more retained species is introduced in the SPI to adjust the relative importance to the other factors used in the expression.

To validate the proposed SPI for the selection of a material for the cyclic adsorption separation by gas-SMB, ten commercial materials were selected, with largely different adsorption performances (based on the previous IAS theory calculations): 2GA-H2J, AC (Sutcliffe Speakman), BPL, Norit RB3, H-BETA zeolite, silicalite HiSiv3000, CuBTC, MIL-53(Al), Al-Fumarate MOF, and UiO-66(Zr)₂(COOH)₂. As such, the separation region for each material was determined with the complete model at 303 K, pressure range between 171 and 206 kPa, 8 beds with a configuration 2-3-2-1 in a closed-loop, and a switching time of 50 s for purity values in the extract outlet over 97% and raffinate outlet over 99%, with a *MATLAB* algorithm coupled with the *gPROMS* tool. The Q_1 flow rate (CO_2) was defined as 0.800 SLPM, considering an equimolar feed composition of CH_4/N_2 . The pure adsorption equilibrium data was readjusted to the Dual-Site Langmuir model for easier computation of the separation regions. The new fitting parameters for each adsorbate

are presented in Table A.4 to Table A.6. The values from the previous IAST calculations, which are necessary for attaining the SPI value for each adsorbent, are summarised in Table 4.3.

The separation regions for the ten selected materials, under the defined conditions, are presented in Figure 4.6 to Figure 4.13. For each of the computed regions, two values were calculated which are related to the performance of the adsorbent/desorbent pair, the square root of the area of the separation region ($\sqrt{\text{Area}}$) and the maximum γ_F ($\gamma_{F,\text{max}}$). The area of the triangle is intrinsically related to the ease of separation of a gas mixture and the $\gamma_{F,\text{max}}$ is associated with the productivity of the process. The area of the region was determined by numerical integration through the trapezoidal rule, while $\gamma_{F,\text{max}}$ corresponds to the value of γ_F in the vertex. To correlate the SPI with both values simultaneously, the square root of the area was used instead of the value of the area, converting it to the same dimensional space as the maximum γ_F .

Table 4.3 – Adsorption selectivity, CH₄ uptake resultant from the IAST calculations, and isosteric heat of adsorption of the mixture species.

Adsorbent	Selectivity	q_{CH_4} (mol·kg ⁻¹)	ΔH_{N_2} (J·mol ⁻¹)	ΔH_{CH_4} (J·mol ⁻¹)
2GA-H2J	3.86	0.26	17206	23930
AC Sutcliffe Speakman	2.99	0.23	11401	16513
BPL	5.43	0.27	19287	21228
Norit RB3	3.97	0.26	13624	17010
H-BETA-25	1.96	0.17	6613	10410
HiSiv3000	3.60	0.09	3945	11181
CuBTC	3.53	0.22	12514	16584
MIL-53(Al)	5.41	0.19	14790	19950
Al-Fumarate	5.59	0.26	13891	14467
UiO-66(Zr)-(COOH) ₂	3.79	0.05	15382	24317

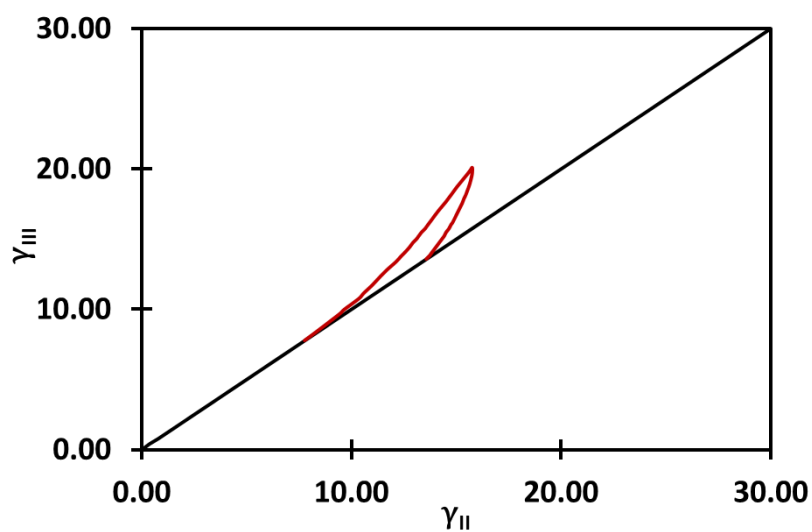


Figure 4.4 - Separation region computed for the 2GA-H2J adsorbent material.

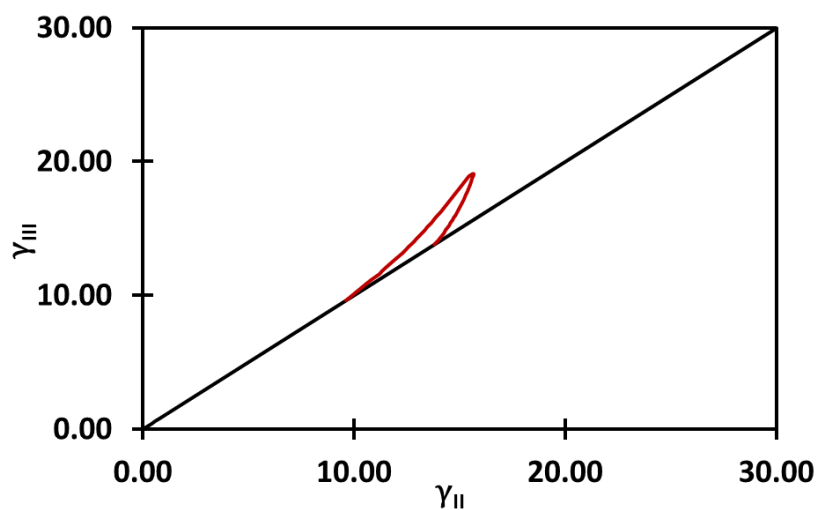


Figure 4.5 - Separation region computed for the AC Sutcliffe Speakman adsorbent material.

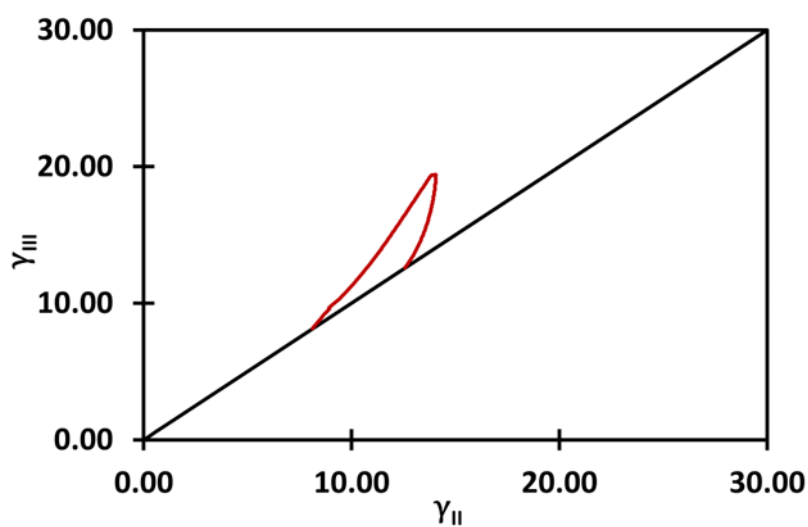


Figure 4.6 – Separation region computed for the AC BPL adsorbent material.

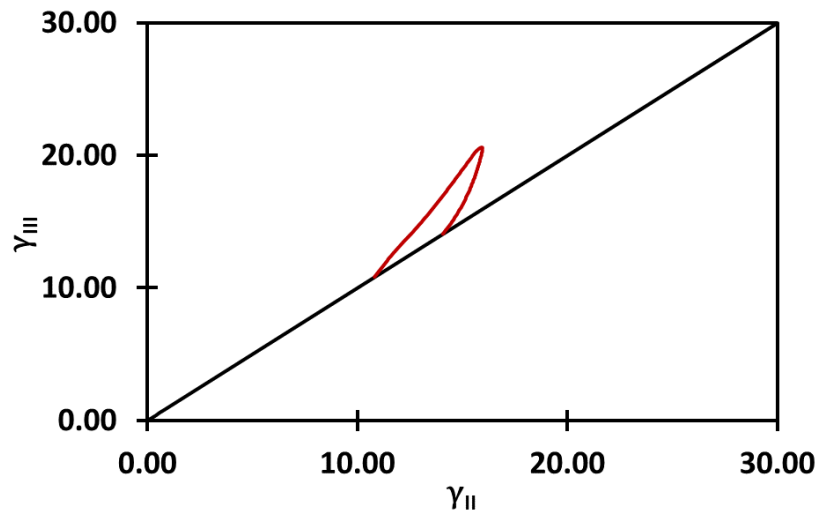


Figure 4.7 - Separation region computed for the Norit RB3 adsorbent material.

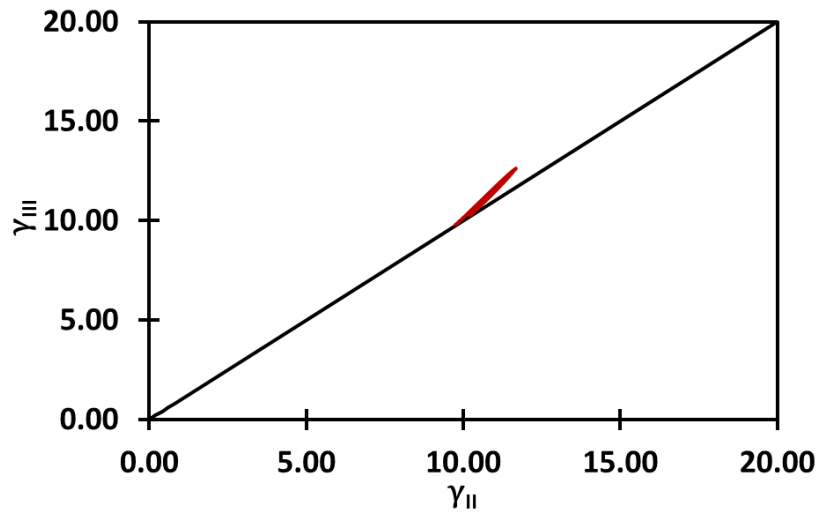


Figure 4.8 - Separation region computed for the H-BETA adsorbent material.

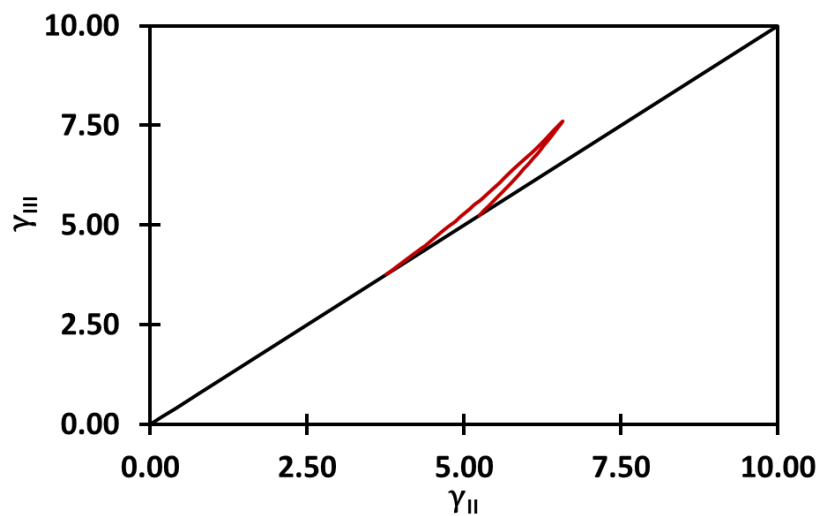


Figure 4.9 - Separation region computed for the HiSiv3000 adsorbent material.

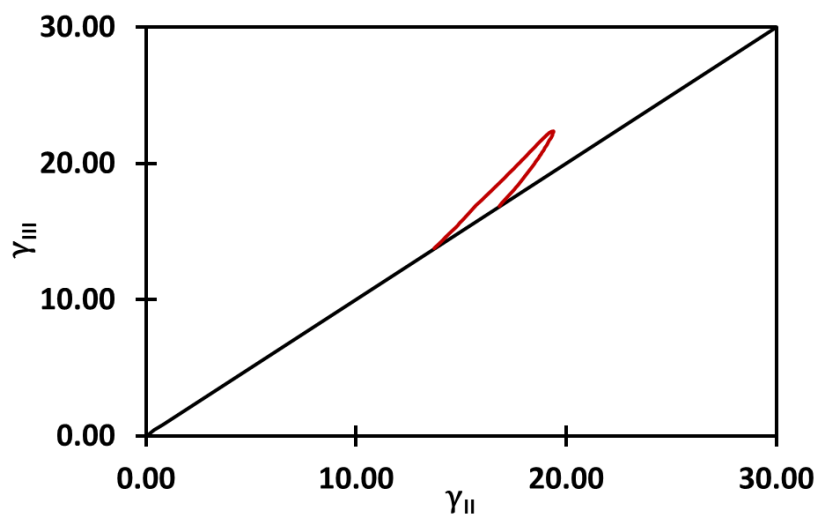


Figure 4.10 - Separation region computed for the CuBTC adsorbent material.

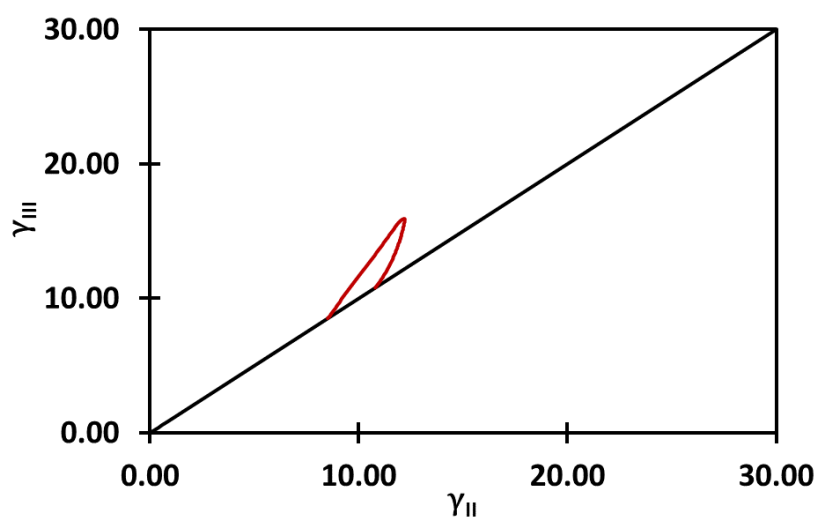


Figure 4.11 - Separation region computed for the MIL-53(Al) adsorbent material.

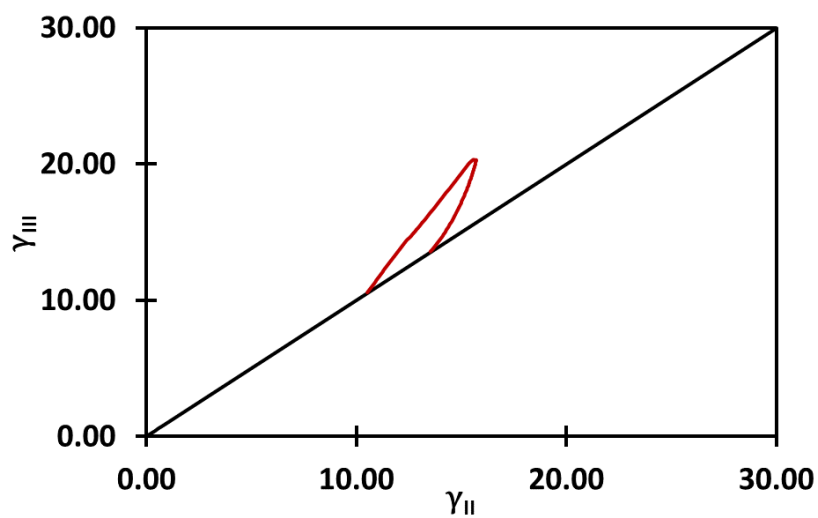


Figure 4.12 - Separation region computed for the Al-Fumarate adsorbent material.

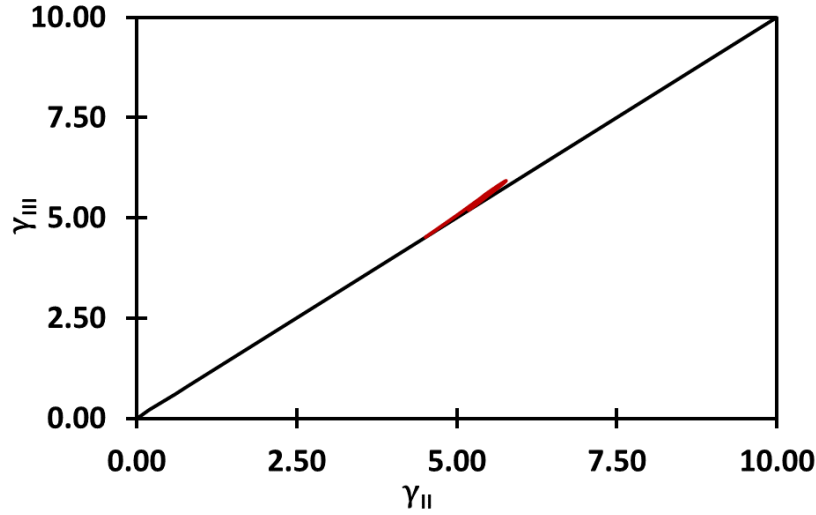


Figure 4.13 - Separation region computed for the UiO-66(Zr)-(COOH)₂ adsorbent material.

Once the separation regions are computed and the square root of the area and maximum γ_F are calculated, the results can be compared with the values obtained for the SPI to identify a possible correlation between the efficiency of the material, given by the analysis of the separation region, and the value of the SPI, which is obtained simply from the results provided by the IAST calculations with data from the literature. As can be observed, the separation regions obtained for each material are significantly different, with the largest triangle corresponding to the AC BPL, followed by the MOF Al-Fumarate, Norit RB3, 2GA-H2J, CuBTC, AC from Sutcliffe Speakman, MIL-53(Al), HiSiv3000, H-BETA, and lastly, UiO-66(Zr)-(COOH)₂. For the latter, the conditions that allow us to obtain separation lay in a very narrow interval when CO₂ is utilised as the desorbent gas. Regarding the $\gamma_{F,max}$, the order is as follows: BPL > Norit RB3 $\approx$ Al-Fumarate > 2GA-H2J > MIL-53(Al) > AC Sutcliffe Speakman > CuBTC > HiSiv3000 > H-BETA > UiO-66(Zr)-(COOH)₂.

Also, for the materials in which CO₂ has a stronger affinity to the stationary phase, the values of γ_{II} and γ_{III} for complete separation of the target mixture are lower than when a material with weaker desorbent interaction is used, as pointed out by Mazzotti *et al.* [49]. This, coupled with the narrower regions observed for these materials, leads to practical problems, as these conditions may be challenging to achieve during experimental assays.

The performance values taken from the separation region, as well as the value of the SPI for each material, are presented in Table A.7. In Figure 4.14 and Figure 4.15, the SPI results were compared with the square root of the area of the separation region and the maximum productivity obtained for each material, represented by each experimental point.

According to the obtained results, the most promising material among the ten selected materials is the adsorbent BPL.

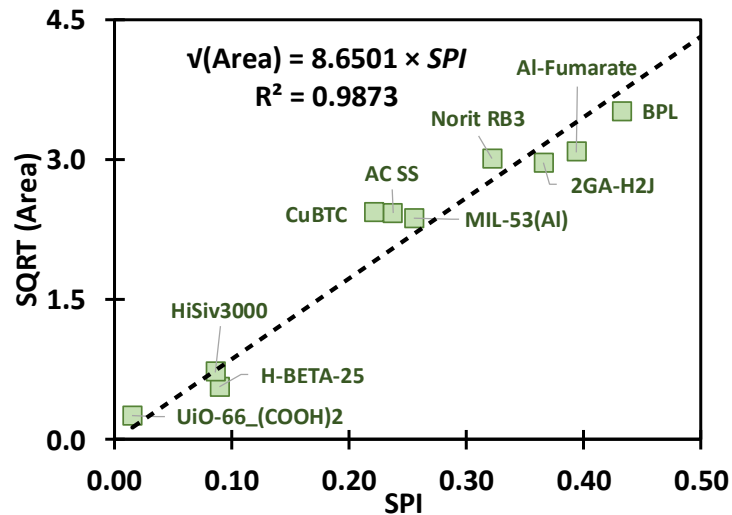


Figure 4.14 – Comparison of the SPI value with the square root of the area of the separation region for each material.

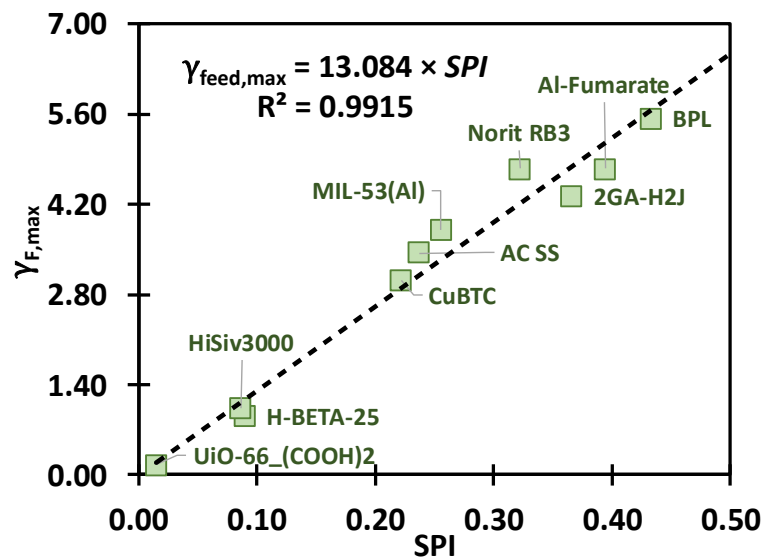


Figure 4.15 - Comparison of the SPI value with the maximum γ_F .

By crossing the data obtained from the separation regions with the SPI value calculated for each material, it is possible to observe that there is evidence of the existence of a proportional correlation between the indicator and the performance values, indicating that the higher the SPI for a certain material, the more efficient it is for the separation of the case study mixture by SMB, more easily obtaining high purity extract and raffinate streams with higher throughputs.

Similar plots were drawn to observe the relation between the CH_4/N_2 adsorption selectivity and the performance of each material, since calculating it would be the most straightforward approach for the selection of a material. The competitive selectivity, calculated considering the presence of a desorbent species, and ideal selectivity, without competition, were both considered and the results obtained can be seen in Figure A.57 and Figure A.58. As observed, neither calculations can

predict the results obtained from the simulations of the separation regions, i.e., their effectiveness when integrated into the SMB process. Furthermore, they can also not provide the ranking of the materials in terms of performance. One material, the UiO-66_(COOH)₂, has a good adsorption selectivity but performed the worst among the tested materials, as exhibited by the obtained values of the square root of the area and maximum γ_F under the specified operating and bed conditions.

With the equation obtained through the linear regression of the acquired data for the ten materials in Figure 4.15, the square root of the area and maximum γ_F were calculated for three new different materials, DD3R, MIL-125(Ti)_NH₂, and Norit R2030 by computing the respective separation regions. The values obtained were compared to the ones calculated by the linear regression equation to validate the SPI for the herein studied system. As observed in Figure 4.16, the proposed SPI can accurately predict the values for the separation of CH₄/N₂ using CO₂ as the desorbent.

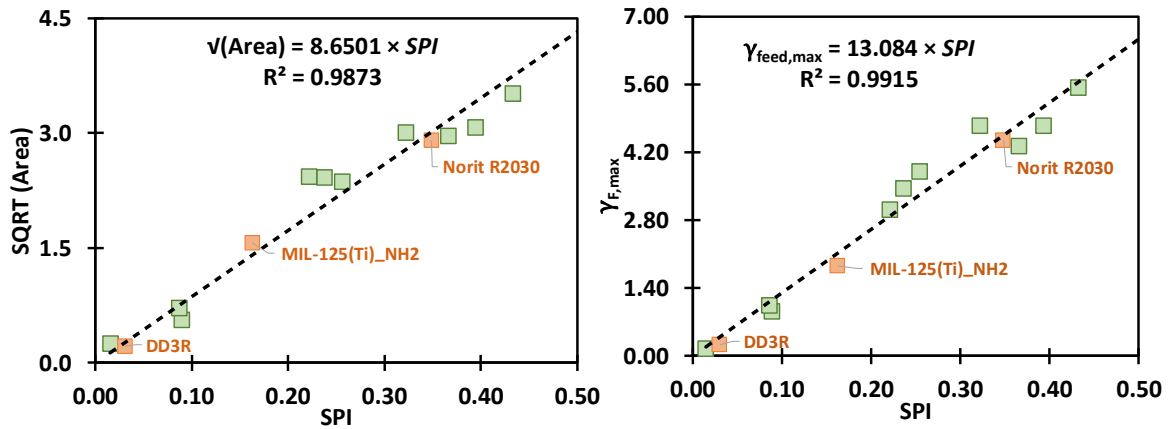


Figure 4.16 – Validation of the SPI for the CH₄/N₂/CO₂ system.

4.3.1. Influence of the feed molar fraction

To study the influence of the feed molar fraction, the CO₂ fraction considered for the simulations was kept constant (50 %). At the same time, the methane and nitrogen content were changed to 10% and 40%, and vice versa. As such, the separation region was determined for three materials for the CH₄/N₂/CO₂ system, and the performance values were taken and crossed with the SPI value obtained for each case. The results obtained are presented in Figure 4.17.

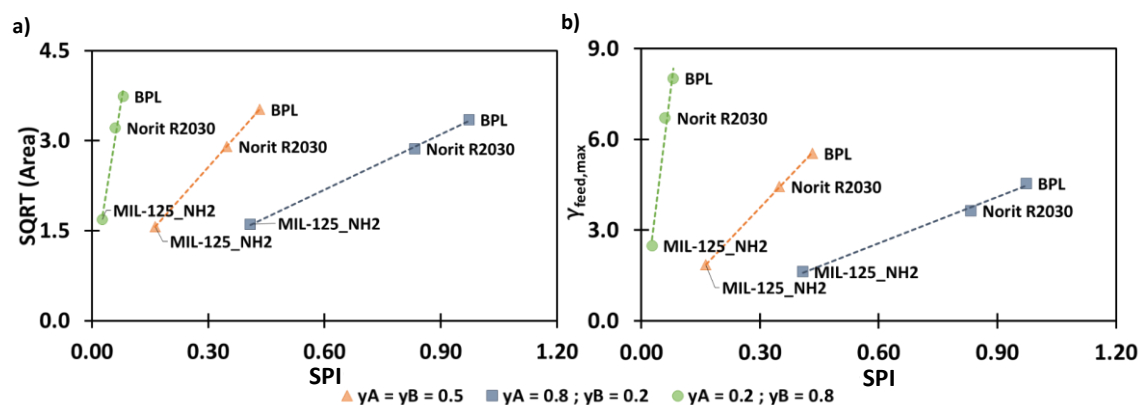


Figure 4.17 – Influence of the feed composition on the indicator effectiveness: a) square root of the area vs. SPI and b) maximum γ_F vs. SPI.

While the correlation for each molar composition is different, the material that shows the best performance when integrated into an SMB process is the BPL, despite the molar fraction of each component inserted in the simulation. A linear tendency can still be observed, with the slope decreasing for a higher molar fraction of the heavy component. This suggests that even with different molar fractions in the feed stream, the ranking remains unchanged, allowing the SPI, calculated with the base composition, to be used as a reliable tool for decision-making.

The effect of the feed composition in the competitive selectivity was also verified and can be observed in Figure A.59. The effect of the composition in the competitive selectivity is not very noticeable, remaining practically identical for the MIL-125(Ti)₂NH₂ material, while a slight increase is observed for the other two materials when the mixture is not equimolar. Similar selectivity values can be noted for the two carbonaceous materials. This supports the conclusion drawn in the results presented in Figure 4.17.

4.3.2. Influence of the pressure

The procedure was repeated for a higher pressure, 485 kPa, for the same three materials to validate the proposed parameter for different pressure conditions inside an SMB process. The data acquired can be observed in Figure 4.18.

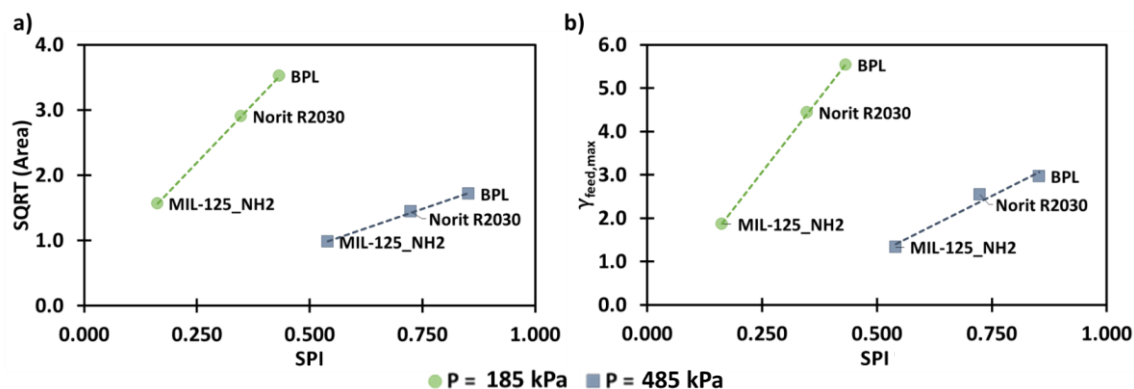


Figure 4.18 - Influence of the pressure on the SPI effectiveness: a) square root of the area vs SPI and b) maximum γ_F vs SPI.

Similar to that observed in the previous section, the increase in the system pressure decreases the slope of the regression, while maintaining the order of the materials regarding their performance in an SMB cycle. Comparing different pressure conditions using the indicator is not possible, as a higher SPI value, observed when the pressure is increased, does not lead to a better performance of the material. However, the parameter predicts the BPL material as the best adsorbent material for both pressure values, which agrees with the results obtained through the simulations. This way, the proposed SPI can indicate the best adsorbent for this separation regardless of the pressure of the system.

4.3.3. Other systems

The next step was verifying the performance indicator's validity and reliability for different systems, firstly by changing the desorbent gas to argon, which weakly adsorbs to the stationary phase. Afterward, the proposed equation was used to predict the performance of several adsorbent/desorbent pairs for olefin/paraffin separation by gas-SMB, with equilibrium data obtained from the literature.

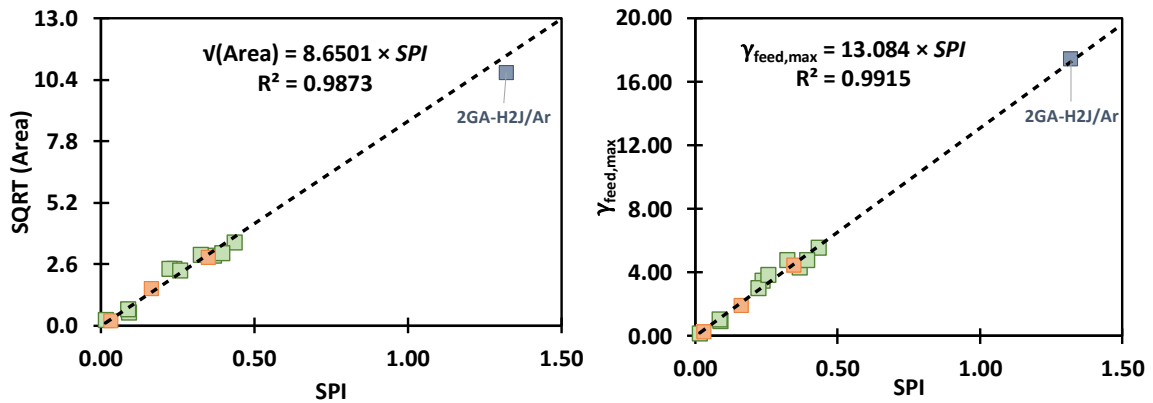


Figure 4.19 - Validation of the SPI for the $\text{CH}_4/\text{N}_2/\text{Argon}$ system.

Figure 4.19 shows the point corresponding to the 2GA-H2J/argon adsorbent/desorbent pair for separating methane and nitrogen. The conditions and parameters utilised for the simulation of the separation region were the same as when CO_2 was utilised, altering only the desorbent adsorption equilibrium data and gas properties. As can be observed, even when a weaker desorbent is used for the separation of the same mixture, the correlation previously shown can predict both the $\sqrt{\text{Area}}$ and the maximum γ_F from the SPI value with good accuracy. This is valuable as desorbents with different affinity strength to the stationary phase can also be introduced into the screening process for a specific separation, as long as the pure adsorption equilibrium data for that species is available and the pretended operating conditions for the SMB

process are defined. As a result, when designing the SMB process, not only can the adsorbent be selected by this method, but also the desorbent gas.

To study whether the proposed SPI can be utilised to screen the adsorbent/desorbent pair for the separation of different mixtures, literature data for ethane/ethylene separation by SMB was retrieved. Both olefin-selective and paraffin-selective materials were considered. The separation regions were computed using the same parameters and conditions as before. Four adsorbent/desorbent pairs were studied: ZIF-8/CO₂, ZIF-8/Propane, binderless zeolite 13X/Propane, and CuBTC/Propane [50-52]. The performance results were crossed with the value calculated for the SPI, as shown in Figure 4.20.

Analysis of the graphic shows that for the binderless 13X/Propane pair, the values predicted deviate slightly from the actual values obtained through the separation regions, especially for the square root of the area of the obtained separation region. The indicator accurately estimates these values for the remaining pairs, which may indicate a lack of data for higher values of the SPI. Also, the indicator can accurately predict the best performing adsorbent/desorbent pair for the ethane/ethylene separation among the tested combinations.

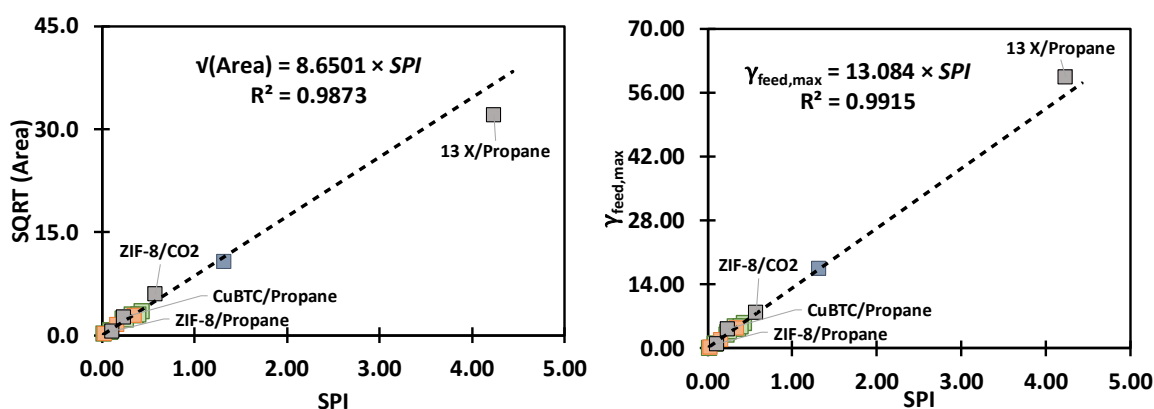


Figure 4.20 - Validation of the SPI for the separation of other gas-phase applications: separation of ethane/ethylene.

As a final remark, the proposed SPI can be used for screening a suitable adsorbent and desorbent pair for a specific gas-phase separation application by SMB. By defining the temperature, pressure, and feed composition *a priori*, the best pair can be selected from multicomponent adsorption equilibrium without the necessity of more comprehensive research. Afterward, a more in-depth study will determine the optimal operating conditions and the design of the SMB cycles for the separation at hand.

4.4. References

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CHAPTER 5 – MATERIALS AND EXPERIMENTAL METHODS

5.1. Introduction

Selecting the proper adsorbent material is of utmost importance when designing a simulated moving bed process, not only to ensure that a separation of the mixture is achieved, but also from an economic standpoint. When selecting an adsorbent material for a cyclic adsorption process, some criteria should be considered, such as the adsorbent capacity, selectivity, difficulty to regenerate, kinetics, compatibility and cost [1].

After the selection of the solid material, the next step is the shaping of the material. Adsorbents in their powder form lead to high pressure drops, poor mechanical stability, and challenges in handling during operation, hindering the mass and heat transfer and reducing the process efficiency. To overcome these limitations, structured materials such as pellets, monoliths, or 3D-printed structures are produced. These shaped forms enhance mechanical strength and minimize pressure drops, while providing controlled porosity and uniform flow distribution [2, 3].

Afterward, textural characterization of these materials is necessary to determine their physical properties (porosities, pore size distribution, densities, *etc.*), and verify the effect of the shaping process on these properties. Then, the adsorption equilibrium and multicomponent adsorption dynamics need to be assessed as they are essential for the design of the cyclic process.

In this chapter, the materials' textural characterization methods are described, as well as the experimental set-ups and protocols utilised for the measurement of the isotherms and dynamic tests.

5.2. Adsorbent Materials

The SPI shown in the previous chapter was utilised to ensure that efficient adsorbent materials were selected. For the separation of nitrogen from methane streams, activated carbons, such as BPL and Norit RB3, presented the highest SPI values and so, are expected to outperform the remaining materials. Also, Maxsorb, due to its carbonaceous nature, high surface area, and high adsorption capacity at the studied conditions, is also predicted to be a very promising option for the stationary phase.

This said, in this work, a commercial activated carbon, BPL, and in-house extruded Maxsorb pellets were used as the adsorbent materials. Also, the Maxsorb AC was utilised to produce 3D-printed monoliths, and its performance was tested for the studied separation. For the pellet and monolith production, a binder, carboxymethylcellulose (CMC), was utilised. The extrusion method to produce the pellets, as well as the 3D-printing process of the monoliths used in this thesis are briefly described in the following subsections.

Textural characterization of the materials was performed, which included mercury porosimetry, helium pycnometry, N_2 physisorption isotherm at 77 K, and CO_2 physisorption isotherm at 273 K. These methods are introduced and described in the Section 5.3.

5.2.1. BPL AC

The commercial activated carbon, BPL, was supplied and manufactured by Chemviron Carbon, in its granular form. The granulates were sieved to eliminate smaller particles, obtaining a particle size between 1.68 and 4.00 mm. The granulates can be seen in Figure 5.1.



Figure 5.1 - BPL activated carbon granulates, supplied by Chemviron Carbon.

5.2.2. Pelletised Maxsorb AC

Maxsorb activated carbon, acquired from Kansai Coke and Chemicals Co, Ltd., in the form of powder, was used as a raw material for the manufacturing of the pellets utilised in this thesis.

The detailed procedure for pellet production is well established and can be found in previous works from the group [4, 5]. Briefly, the pellets were prepared in multiple batches with 20 g of activated carbon and 10 %wt CMC (VWR Chemicals), which was used as a binder. The dry powders were mixed at 60 rpm for 30 minutes to homogenise the mixture. Then, approximately 48 ml of distilled water was added, drop by drop, until the wet powders started to aggregate. When the wet mixing step was complete, the mixture was extruded through a 2 mm diameter die with a screw that rotated at 12/14 rpm. The prepared extrudates were then manually split into pellets with a length between 3 and 5 mm. This procedure is schematised in Figure 5.2, where the produced extrudates can be observe on the right.



Figure 5.2 - Schematic of the extrusion process of the pelletised Maxsorb AC.

5.2.3. 3D-printed Maxsorb AC monoliths

Maxsorb activated carbon was purchased from Kansai Coke and Chemicals Co, Ltd. and it was used as the adsorbent to produce the 3D-printed monoliths. CMC served as a binder and plasticiser additive in the printable paste. Distilled water was used as the solvent.

Formulating a printable ink involved using distilled water as the solvent, with a composition of 90 %wt. of Maxsorb activated carbon and 10 %wt. of CMC. The mixture was performed in the mixing chamber of the *Caleva Multi Lab* extruder. Initially, the dry powders were blended for one hour. Then, distilled water was added dropwise until a printable ink was obtained. More details can be seen in Pereira *et al.* [6].

Several monoliths were developed using direct ink writing. The printed monoliths have approximately constant size, each measuring approximately 1 cm in height. These monoliths were then used to pack six columns, with a total bed length of 8 cm each. Consequently, a total of 48 monoliths were produced for this purpose. An additional monolith was also produced to measure adsorption equilibrium data to compare to the previous results. The detailed procedure for printing the monolith is presented in the referenced work [6].

The schematic in Figure 5.3 shows the 3D-printing of one of the monoliths, as well as the packing process of a fixed bed.



Figure 5.3 - Schematic of the 3D-printing process of a Maxsorb monolith and packing of a column.

5.3. Textural characterization

5.3.1. Mercury porosimetry

The mercury porosimetry test involves the intrusion of mercury into the pores of the solid material while measuring the pressure required to penetrate the mercury into the pores. The pressure required to fill the pores is directly related to the pore size, with smaller pores requiring higher pressures for intrusion. As a controlled mercury pressure is applied to the adsorbent, the volume that intruded the pores is recorded. This way, it provides valuable information about the size, distribution, and volume of pores within the material. At low pressure, the mercury is not able to penetrate the pores of the material, giving information regarding the apparent density of the material. This method is more suitable for the measurement of macropores and mesopores and is usually destructive [7].

In this thesis, mercury porosimetry was carried out using a *Micromeritics AutoPore IV 9500* (V1.10). Prior to the test, the sample was activated under vacuum. These tests were performed by the *Laboratorio de Sólidos Porosos* at the *Departamento de Química Inorgánica* from the University of Malaga (UMA).

5.3.2. Helium pycnometry

Helium pycnometry is a method used to measure the solid density of adsorbent materials. Helium gas is used since it is inert, and so, it does not adsorb onto the surface of the material and is small enough to penetrate even the smaller pores.

Firstly, a known mass of adsorbent is placed into a chamber with known volume and the sample is degassed, under vacuum. This chamber is connected to a dosing cell, with known volume, with a valve in between the two cells. The dosing cell is filled with helium at a specific pressure and the initial pressure is recorded. Then, the helium is allowed to flow into the sample cell by opening the valve. Once the pressure stabilizes, the equilibrium pressure is measured. Using the ideal gas law, the solid volume can be calculated. Finally, the solid density is determined by dividing the mass of the sample by the volume obtained.

Helium pycnometry was performed in the equipment described in Section 5.5.1, using a similar procedure to the measurement of an adsorption equilibrium isotherm.

5.3.3. Physisorption isotherms

Adsorption is a mass transfer operation between a fluid phase and a solid adsorbent phase. In this process, the molecules and atoms bind to the surface of a porous adsorbent material, either weakly interacting with it through van der Waals' forces, which include quadrupole, permanent dipole and induced dipole attraction (physisorption) or by exchanging or sharing electrons, leading to the formation of chemical bonds (chemisorption). As aforementioned, the physisorption of the adsorbate onto the adsorbent surface is essential for the design of cyclic processes.

According to IUPAC, the physisorption isotherms can be classified as shown in Figure 5.4 [8].

Type I isotherms are characteristic of very microporous solids. The steep uptake at low relative pressures is due to the fast filling of narrow micropores, reaching a plateau at higher pressures according to the accessible pore volume. For this type of materials, no hysteresis is observed, which occurs when the adsorption and desorption curves do not overlap. The difference between Type I(a) and Type I(b) is the pore size distribution, where the first is given by materials with primarily narrow micropores and the latter having a wider pore size distribution, which include large micropores and narrow mesopores [8].

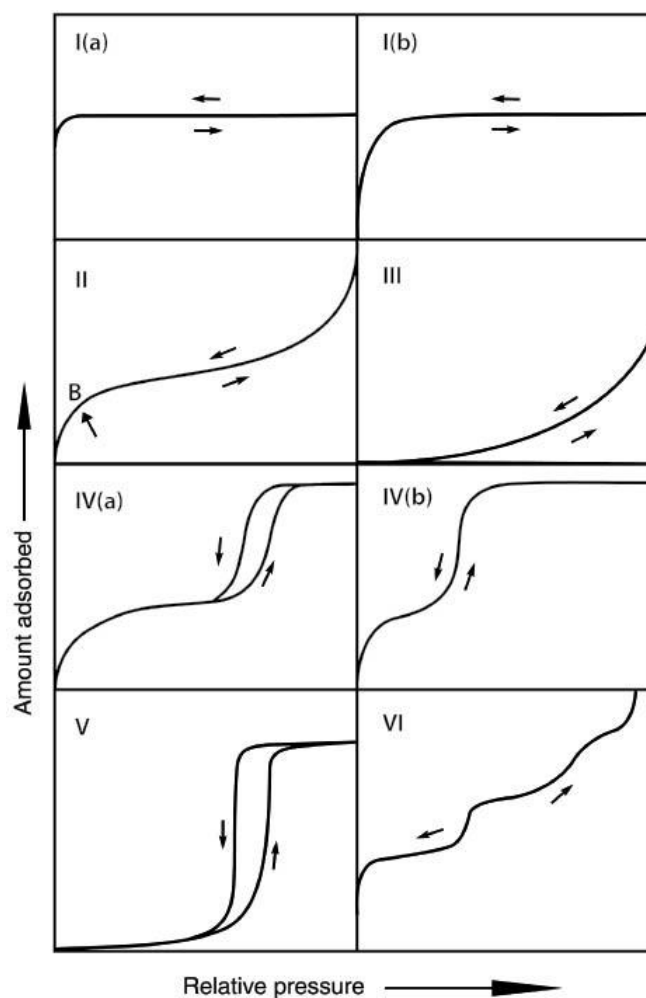


Figure 5.4 - Classification of the physisorption isotherms. Adapted from [8].

Type II isotherms are characteristic of non-porous or macroporous solids, where firstly the adsorbate interacts with the surface of the material, forming a monolayer (completion given by point B) and multilayer adsorption occurs as the relative pressure increases [8].

Type III isotherms are also characteristic of non-porous or macroporous adsorbents, however, there is no observable formation of a monolayer and the adsorbate interacts with the most favourable sites on the solid surface [8].

Type IV isotherms are characteristic of mesoporous solids. In this case, monolayer formation occurs at low relative pressures inside the mesoporous, giving the first observed plateau, followed by multilayer adsorption, as is the case with Type II isotherms. At higher relative pressures, capillary condensation ensues, giving the second plateau. If hysteresis is observed, the isotherm is classified as Type IV(a). Otherwise, it is classified as Type IV(b) [8].

Type V is similar to Type III isotherms, with the difference being the occurrence of pore condensation at higher relative pressures [8].

Type VI isotherms are identified in highly homogeneous non-porous materials, where layer-by-layer adsorption occurs, with each plateau corresponding to the amount adsorbed in each layer [8].

For the determination of the physisorption isotherms, a manometric method, where the amount of gas removed from the gas phase is measured, or a gravimetric method, where the adsorbent mass variation is measured, can be utilised.

For the assessment of the surface area and the pore size distribution of an adsorbent material, the selection of the proper adsorptive is important, with the most common being N_2 at 77 K, Ar at 87 K and CO_2 at 273 K. The interpretation of the physisorption isotherm allows the determination of the adsorption mechanism and most importantly, it provides essential adsorbent properties such as the surface area of the material and the pore size distribution [9]. If the surface of the material is functionalized or has exposed ions, Ar at 87 K should be performed instead of N_2 at 77 K, due to the permanent quadrupole moment of the N_2 molecule, which can lead to incorrect results. Complementing the N_2 adsorption at 77 K and the Ar adsorption at 87 K, CO_2 adsorption at 273 K can be performed. Due to the cryogenic temperature of the test for the first two adsorptives, the gas diffusion inside the pores is very slow and poses some limitations when the material has very narrow micropores. In this case, a CO_2 physisorption isotherm at 273 K assay can be performed, with the diffusion being much faster, allowing the analysis of pores with <1 nm. This way, it is utilised to characterize microporous carbon-based materials except for microporous solids with polar surface groups, since the quadrupole moment is larger than that of N_2 [10].

To evaluate the porosity of the materials, physisorption of N_2 at 77 K and CO_2 at 273 K was performed. N_2 adsorption/desorption at 77 K and CO_2 isotherms at 273 K were determined at *Laboratorio de Sólidos Porosos* of the University of Málaga with a *Micromeritics Analyzer ASAP 2420* (V2.09.02J) and an *ASAP 2020* (V4.02) equipment, respectively. Before the measurements, the samples were degassed at 423 K under vacuum.

5.4. Adsorbates

To perform all the breakthrough tests and the simulated moving bed experiments, four gases were utilised: CH_4 (99.995 %, Linde), N_2 (99.999 %, Air Liquide), CO_2 (99.998 %, Air Liquide), and Ar (99.999 %, Air Liquide). For the activation of the adsorbent material and the single and binary breakthrough curves, helium (99.999%, Air Liquide) was also used. All gases were used as received without any further pretreatment.

5.5. Adsorption Equilibrium Isotherms

For measuring adsorption equilibrium isotherms, there are two common methods that can be used volumetric and gravimetric methods. The volumetric method involves measuring the change in pressure of the gas phase to determine the amount of adsorbate adsorbed onto the solid surface.

The gravimetric method involves the measurement of the small changes in mass that occur when the adsorbate adsorbs to the solid material, providing a direct measurement of the adsorption amount.

In this thesis, the volumetric method was used for the acquirement of the isotherms for the BPL, pelletised Maxsorb, and different fragments of the 3D-printed Maxsorb monoliths. For the latter, the equilibrium data acquired was compared to previously measured equilibrium data, determined through a gravimetric method. The volumetric equipment utilised in this thesis is described below.

5.5.1. Volumetric Method

In this lab-scale unit, two cells, the dosing cell and the adsorption cell, connected by a pneumatic valve, are inserted into a convection oven to operate the system at a constant temperature. Two pressure transducers (0-350 mbar and 0-2.5 bar) are installed in parallel, connected to the dosing cell to monitor and record the system pressure variations. A vacuum pump allows the exhaustion of the cells and the depressurization of the system for the measurement of the desorption data. To correctly measure the isotherm data, it is vital that the volume of the dosing cell, which accounts for the volume from the transfer lines, as well as the volume of the adsorption cell, are accurately determined *a priori*. The schematic of the apparatus is presented in Figure 5.5.

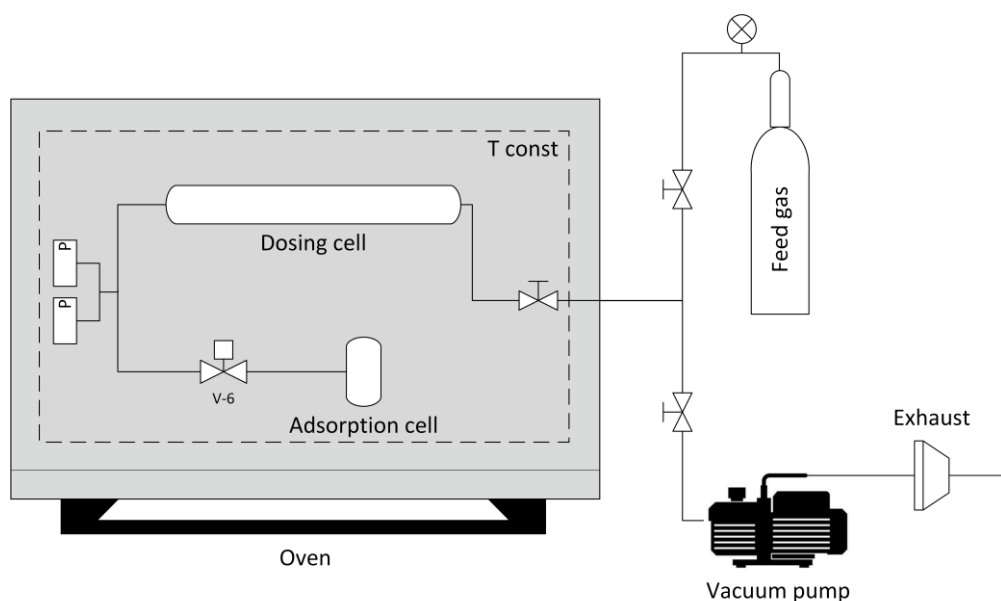


Figure 5.5. Schematic of the volumetric unit for the measurement of the equilibrium data.

Firstly, the adsorbent sample is inserted in the adsorption cell and activated at a constant temperature (for both carbonaceous materials, a temperature of 393 K was used) with a heating tape to avoid damaging the electric components of the system. To start the measurement of an isotherm, the sample cell must be under vacuum, while the dosing cell is pressurized with the pure

adsorbate, and the valve connecting the two cells closed. The number of moles, n , present in the dosing cell can be obtained with the ideal gas law:

$$n = \frac{PV_{\text{dos}}}{R_g T} \quad (5.1)$$

where P is the pressure, V_{dos} is the volume of the dosing cell, R_g is the ideal gas constant and T is the temperature.

The valve is then opened, allowing the expansion of the gas into the adsorption cell. Equilibrium is achieved once the pressure stabilizes. The amount of moles adsorbed, n_{ads} , in each step, j , is obtained by Equation (5.2).

$$n_{\text{ads}} = \frac{1}{R_g T} \left(P_{f,j-1} (V_{\text{ads}} - V_s) + P_{i,j} V_{\text{dos}} - P_{f,j} (V_{\text{dos}} + V_{\text{ads}} - V_s) \right) \quad (5.2)$$

where V_{ads} is the volume of the adsorption cell, V_s is the volume occupied by the solid material, obtained by helium pycnometry, and the index i and f indicate the initial and final pressure, before the opening of the pneumatic valve and after equilibrium is reached for each adsorption point, respectively.

After obtaining the first equilibrium point, the procedure is repeated until the desired upper pressure is reached. Afterward, the desorption points are obtained by depressurizing the cells with the vacuum pump. For each measurement, the amount adsorbed, q , is given by the quotient of the uptake, n_{ads} , and the adsorbent mass, m_{ads} :

$$q = \frac{n_{\text{ads}}}{m_{\text{ads}}} \quad (5.3)$$

5.6. Fixed Bed and SMB Experiments

The breakthrough curve and SMB experiments were performed in a pilot gas-phase simulated moving bed unit (Figure 5.6a). The apparatus can be comprised of up to eight stainless steel columns, packed with the adsorbent material, which is supported by a metal mesh placed at the bottom of the column. To prevent damage to the equipment, which may happen due to the release of fines from the particles resulting from the adsorbent attrition, glass wool is placed upstream and downstream of the adsorbent. The columns are located inside a convection oven, in a circle formation (Figure 5.6b), in which the temperature can be set between 303 and 523 K, with an accuracy of ± 2 K. The columns are interconnected in serial with a check valve to prevent the gas from flowing in the opposite direction. To monitor the temperature inside each bed, a K-type thermocouple (± 2.2 K accuracy) is inserted in the middle (both lengthwise and in the radial direction) of the column. The pressure is regulated via a back-pressure regulator (BPR) located at the end of section IV. This BPR allows the unit to be operated at a maximum pressure of 5 bar (accuracy of ± 0.025 bar), creating a pressure drop between consecutive beds, ensuring the desired

flow direction. The system pressure is measured by four pressure transducers placed every two columns. These transducers are capable of measuring pressures within a range of 0 to 7 bar $\pm$ 0.003 bar.

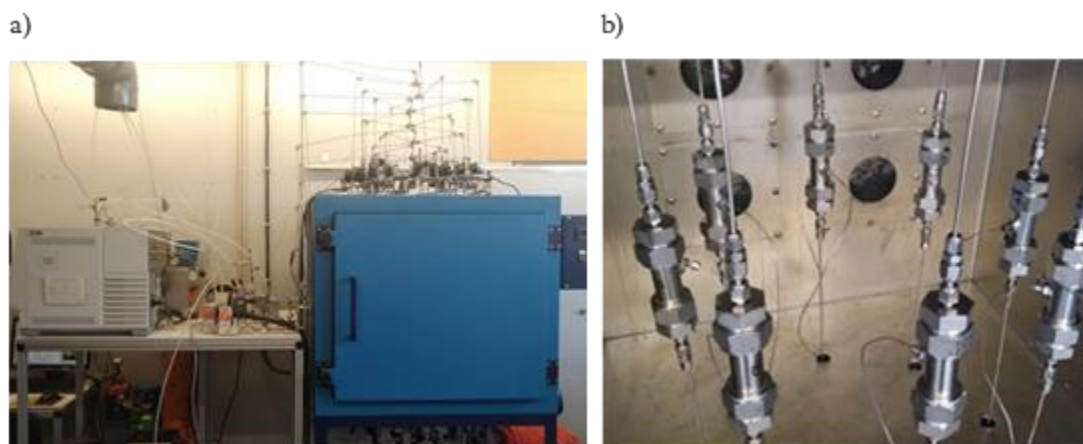


Figure 5.6 - a) Gas-phase SMB unit, coupled with a GC system and b) columns inside the SMB oven.

As described in Section 3.7, the SMB unit is comprised of two inlet streams (the desorbent and feed inlets) and two outlet streams (the extract and raffinate outlets), plus a recycle stream which is used when the unit is operated in closed loop mode, *i.e.*, with the desorbent recycle loop from zone IV to zone I. For each stream, two five-way manifolds allow the splitting of the inlets into eight individual ports or the convergence of the eight ports into one in the case of an outlet stream. To control the gas entry and exit of each column, sixty-four solenoid valves are controlled by an *OMRON CPlE* programmable logic controller (PLC), functioning automatically, through the *CX Programmer* computer interface, in accordance with the specified switching time. Depending on which valves are open and closed at a given time, the column configuration is also specified. Before starting any experiments, the columns must be saturated with the desorbent gas.

Each inlet and outlet stream has a designated mass flow controller (MFC) that allows the flow rate to be tuned ($\pm$ 0.5% of reading plus $\pm$ 0.1% full scale accuracy). The feed stream can consist of up to three gases, which converge at the mixing node. Two of the MFC allow a feed flow rate between 0.4 and 200 SCCM and one between 0.1 and 2 SLPM, merging into a single feed stream in a mixing node. The desorbent stream is also controlled by an MFC, up to a maximum flow rate of 2 SLPM.

The analysis of the composition of the outlet streams is done by gas chromatography (GC), a *Shimadzu GC-2010 Plus*, equipped with a thermal conductivity detector (TCD) and a flame ionisation detector (FID). The samples are taken at the end of column 6 and are stored in a sample collector, comprised of a 6-port, two-position sampling valve, equipped with ten 50 μ l loops. This sampling system is used to assess the composition profile, allowing the storage and analysis of multiple samples taken at different times. Depending on the gases used in the experiments, different columns are used. When CO₂ is present in the gas sample, a *Supelco CARBOXEN 1010*

PLOT 30 m $\times$ 0.53 mm capillary column is used. In the case where Ar is present instead, a Molsieve 5A capillary column is utilised. Before use, the column must be properly conditioned. The capillary column is placed inside the GC oven, which can operate at a maximum temperature of 423 K. The method is configured in the GC Solution software, where the operating temperature of the oven, the TCD and FID, the carrier gas flow rate and the split ratio are set. The methods employed are presented in Table 5.1.

Table 5.1 - Methods utilised for the analysis of the outlet composition by gas chromatography.

Column	Gases analysed	T _{oven} K	Column flow ml·min ⁻¹	T _{inj} K	T _{TCD} K	T _{FID} K
Carboxen 1010	CH ₄ , N ₂ , CO ₂	393	4.42	453	453	453
Molsieve 5A	CH ₄ , N ₂ , Ar	333	2.12	473	453	453

This unit is controlled with a *Labview* interface, which allows the operator to input the pretended set-points for the feed, eluent, raffinate, and extract flow rates, as well as monitor the temperature inside each column and the oven, the pressure signals from the four pressure sensors and the measured flow rates given by each MFC. At the end of the experiment, the software generates a file with all the collected data. From this interface, the operator also gives the command to open the sampling valve, to analyse the stream composition during the experiment, and obtain the internal profile of the columns at a given moment during a cycle.

The breakthrough curves were performed using three of the packed columns (column 4 to column 6) for the BPL and pelletised Maxsorb materials and two columns (column 5 and column 6) for the Maxsorb monoliths. The single component breakthrough experiments start by feeding the desired adsorbate into the columns, which are initially filled with helium, at the desired pressure, temperature, and flow conditions. Once both adsorption and thermal equilibrium are achieved, the desorption step starts by feeding pure helium into the columns at the same operating conditions, until the beds are completely regenerated. Binary fixed-bed experiments are performed similarly, with the beds filled with helium, while an equimolar mixture of nitrogen and methane is fed into the columns at the desired operating conditions. For the ternary experiments, the columns are initially saturated with the desorbent gas and a mixture of 25% methane, 25% nitrogen and 50% of the desorbent is fed into the columns at the set pressure, temperature and flow rate. The desorption step is performed by feeding pure desorbent to regenerate the adsorbent.

For all materials, single-component, binary, and ternary experiments are conducted to evaluate both pure component and multicomponent dynamic behaviour of the adsorption process and validate the estimated transport parameters and the proposed model equations. Additionally, the

ternary fixed bed experiments will allow the analysis of the behaviour of the mixture in the presence of the desorbent, *i.e.*, if the desorbent is able to displace the mixture and vice-versa. The experimental conditions of each run, for each material, can be found in the respective section of Chapter 6.

The SMB cycles can be performed without desorbent recycle, *i.e.*, operating in open-loop mode, with a third outlet stream at the end of Section IV or in closed loop operation mode, where the stream from Section IV is recycled into Section I. For the BPL and Maxsorb extrudates studies, two runs were conducted with the two selected desorbent species: carbon dioxide and argon, in open-loop mode. The experiments were performed at 303 K, with the BPR set at 1.5 bar and a switching time of 50 s. All eight columns were utilised for both materials. Regarding the cycles with the 3D-printed Maxsorb monolith, only six out of the eight columns were used. Similarly to the other materials, two assays were performed, with the two desorbent candidates, operating without desorbent recycle. A third cycle was carried out in closed-loop mode, using Ar as the desorbent gas. A switching time of 110 s was utilised for these runs.

The target purity for the extract and raffinate stream, on a desorbent free basis, is 97% and 99%, respectively, to meet the pipeline specifications.

5.7. References

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CHAPTER 6 — GAS-PHASE SIMULATED MOVING BED

This chapter is based on the following publications:

Dias R.O.M., Ferreira A.F.P., Rodrigues A.E., Ribeiro A.M., Gas-Phase Simulated Moving Bed for Methane/Nitrogen Separation Using a Commercial Activated Carbon. Ind. Eng. Chem. Res. 2022 61 (34), 12739-12753. doi: 10.1021/acs.iecr.2c01436

Dias R.O.M., Regufe M.J., Pereira A.A., Ferreira A.F.P., Rodrigues A.E., Ribeiro A.M., Methane upgrading on pelletised Maxsorb activated carbon by gas-phase simulated moving bed. Adsorption 31, 7 (2025). doi: 10.1007/s10450-024-00563-7

Pereira, A., Dias, R. O. M., Lourenço, D., Regufe, M. J., Ribeiro, A. M., Rodrigues, A., and Ferreira, A. F. P., Methane and nitrogen separation by Gas-SMB in activated carbon monoliths manufactured via 3D-printing. Chemical Engineering Journal, 2025. 512: p. 162315. doi: 10.1016/j.cej.2025.162315

6.1. Introduction

This chapter focuses on designing and developing a simulated moving bed (SMB) process for the separation of CH_4 and N_2 mixtures. As previously mentioned, three adsorbent systems were studied: a commercial BPL activated carbon, extruded Maxsorb activated carbon pellets, and in-house 3D-printed Maxsorb monoliths. Two potential desorbent gases, argon (Ar) and carbon dioxide (CO_2), were evaluated to determine their effectiveness.

The performance of each adsorbent was assessed through adsorption equilibrium and dynamic behaviour studies. Pure component adsorption isotherms for N_2 , CH_4 , Ar, and CO_2 were measured using a volumetric apparatus at 303, 323, and 343 K in a pressure range of 0–2.5 bar. CO_2 exhibited the highest affinity to the stationary phase, followed by CH_4 , N_2 , and Ar for all materials. Fixed-bed experiments were conducted for single, binary, and multicomponent mixtures, providing dynamic adsorption data and enabling validation of the proposed mathematical model.

For each material/desorbent pair, the SMB process was designed and operated to separate an equimolar CH_4/N_2 mixture. The SMB cycles show that this technology is able to effectively separate the target mixture, producing high purity and recovery streams. Also, the use of a weaker desorbent allows to treat higher feed flow rates, increasing the productivity.

This chapter emphasizes the potential of activated carbon adsorbents and the conventional gas-phase SMB technology for efficient methane/nitrogen separation, providing both experimental and simulation results that would allow the scale-up of the process to be implemented at an industrial scale.

6.2. BPL activated carbon

6.2.1. Material characterization

The BPL activated carbon material was characterized by mercury porosimetry, helium pycnometry, N_2 physisorption at 77 K and CO_2 physisorption at 273 K.

The N_2 adsorption/desorption at 77 K and CO_2 sorption at 273 K isotherms are presented in Figure 6.1 and Figure 6.2, respectively. Some of the most essential properties obtained through these characterization methods are shown in Table 6.1.

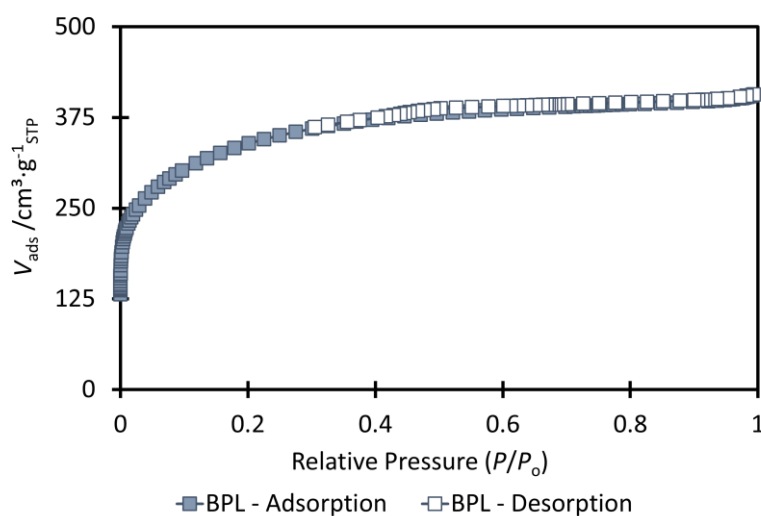


Figure 6.1 - N_2 adsorption equilibrium isotherm on BPL granulates at 77 K. Closed and open symbols correspond to the adsorption and desorption branches, respectively.

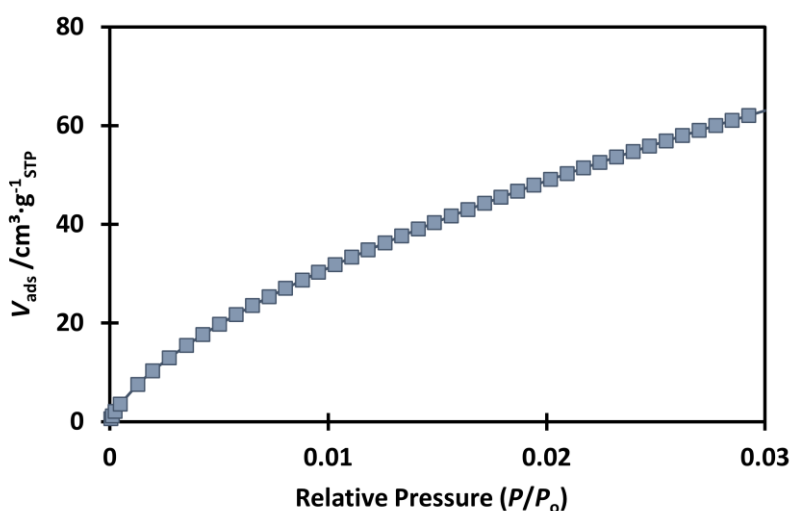


Figure 6.2 - CO_2 adsorption equilibrium isotherm on BPL granulates at 273 K.

According to IUPAC classification, the N_2 equilibrium data at 77 K shows a type I isotherm characteristic of very microporous solids. The observed steep uptake at low relative pressures results from the fast filling of the narrow micropores, reaching a plateau at higher pressures according to the accessible pore volume. The calculated micropore volume, V_{micro} , and BET surface

area, S_{BET} , are $0.491 \text{ cm}^3/\text{g}$ and $1204 \text{ m}^2/\text{g}$, respectively. Analysis of the desorption branch indicates that no hysteresis is observed, meaning that the adsorption step is fully reversible. The CO_2 sorption measured at 273 K shows a pore volume of $0.115 \text{ cm}^3/\text{g}$ for pores with a diameter of less than $7.97 \text{ \AA}$.

The skeleton density of the granules, ρ_s , was determined by helium pycnometry, the apparent density, ρ_p , and the pore size distribution were determined by mercury porosimetry. The values obtained for the average pore size, $\bar{d}_{\text{pore}}$, and ρ_p are summarised in Table 6.1.

Table 6.1 - Textural Properties of the BPL granulates.

Properties	Value
Shape	Granulates
Dimensions	1.68 – 4.00 mm diameter
$S_{BET} (\text{m}^2 \cdot \text{g}^{-1})$	1204
$V_{\text{micro}} (\text{cm}^3 \cdot \text{g}^{-1})$	0.49
$\rho_s (\text{kg} \cdot \text{m}^{-3})$	2136
$\rho_p (\text{kg} \cdot \text{m}^{-3})$	672
$\bar{d}_{\text{pore}} (\text{nm})$	52.1

6.2.2. Pure component adsorption equilibrium data

The adsorption isotherms of pure components N_2 , CH_4 , CO_2 , and Ar at 303, 323, and 343 K over the BPL activated carbon were measured in a pressure range up to 2.5 bar. The collected isotherms are presented in Figure 6.3, where the points represent the experimental data, and the solid lines represent the DSL model (Equation (3.3)). The reported equilibrium data has a maximum uncertainty of 7.0% associated with the uncertainty of the pressure transducer measurements. Figure 6.4 compares the measured isotherms at 303 K. The model parameters are presented in Table 6.2 and were obtained by minimizing the sum of the squared residuals by resorting to the Solver tool.

Analysis of the desorption data shows no evidence of hysteresis, indicating that the adsorption is fully reversible. Furthermore, for the entire range of pressure and temperature presented, carbon dioxide has a higher affinity toward the surface of the adsorbent material, due to the higher polarizability and higher quadrupole moment of the molecule compared to the other adsorbates. Also, for the explored temperature and pressure range, the presented isotherms do not exhibit a plateau, especially for N_2 and Ar, indicating that the adsorption capacity will increase at higher pressures until the saturation capacity is achieved, given by the sum of $q_{m,1,i}$ and $q_{m,2,i}$.

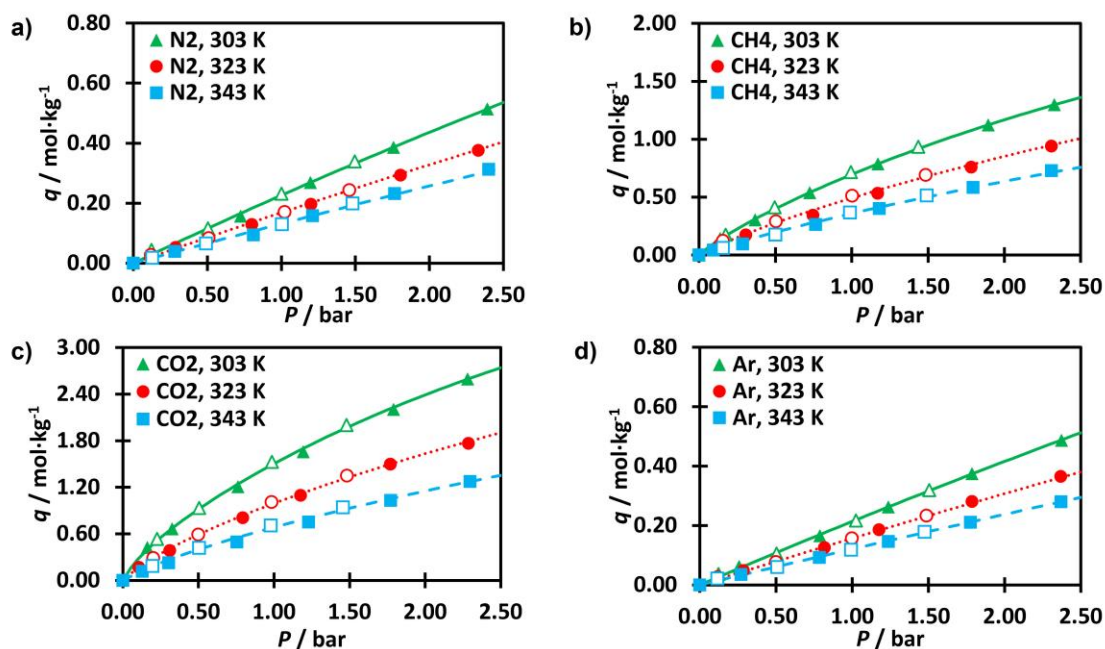


Figure 6.3 - Amount adsorbed of a) N_2 , b) CH_4 , c) CO_2 and d) Ar on BPL carbon at 303 ($\blacktriangle$), 323 ($\bullet$) and 343 K ($\blacksquare$). Closed symbols correspond to adsorption and open symbols to desorption. Lines represent the DSL fitting.

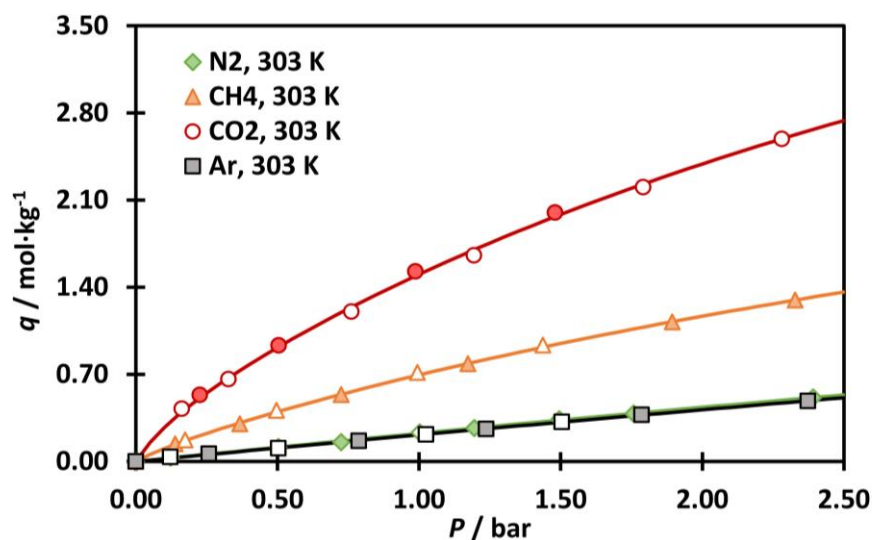


Figure 6.4 - Amount adsorbed of each adsorbate on the BPL carbon at 303 K.

Table 6.2 - Fitting parameters of the DSL model for N_2 , CH_4 , CO_2 , and Argon adsorption equilibrium on the BPL activated carbon.

Species	$q_{m,1}$ mol·kg ⁻¹	$q_{m,2}$ mol·kg ⁻¹	$b_{0,1} \times 10^4$ bar ⁻¹	$b_{0,2} \times 10^4$ bar ⁻¹	$-\Delta H_1$ J·mol ⁻¹	$-\Delta H_2$ J·mol ⁻¹
N_2	6.78	0.66	3.33	2.03	10856	15648
CH_4	4.72	0.40	1.76	2.98	16310	20595
CO_2	7.12	0.32	0.30	0.80	22199	28433
Ar	8.19	0.46	2.04	1.34	11790	16214

6.2.3. Isosteric heat of adsorption

For the estimation of the isosteric heat of adsorption, the Clausius-Clapeyron equation was used (Equation (3.2)). The results obtained are displayed in Figure 6.5, with the dashed lines representing the enthalpic parameters of the DSL model. For N_2 and Ar, the isosteric heat of adsorption indicates that the energetic nature of the surface of the adsorbent is homogeneous. This is not the case for CH_4 and CO_2 , where the results imply heterogeneity of the solid surface, with the isosteric heat varying between 16.5-26.3 kJ/mol and 22.1-31.7 kJ/mol for the adsorption of CH_4 and CO_2 , respectively. While this might indicate that a single site Langmuir equation could be used to fit the experimental data for the weakly adsorbed species, the lack of information on the plateau at higher pressures might affect the observed results. Also, the isosteric heat of adsorption values should be between those enthalpic parameters, which is not observed for the CO_2 and CH_4 adsorbates at lower values of q_i . This said, the fitting parameters will be validated to some degree with the dynamic tests once they can accurately predict the multicomponent capacity inside the adsorber.

The values are in good agreement with some results reported in the literature for the BPL carbon (13.8, 17.1, and 21.9 kJ/mol for N_2 , CH_4 , and CO_2 , respectively) [1] and other commercial activated carbons (CO_2 : 20-26 kJ/mol; CH_4 : 16-21 kJ/mol; N_2 : 12-16 kJ/mol; Ar: 15 kJ/mol) [2, 3].

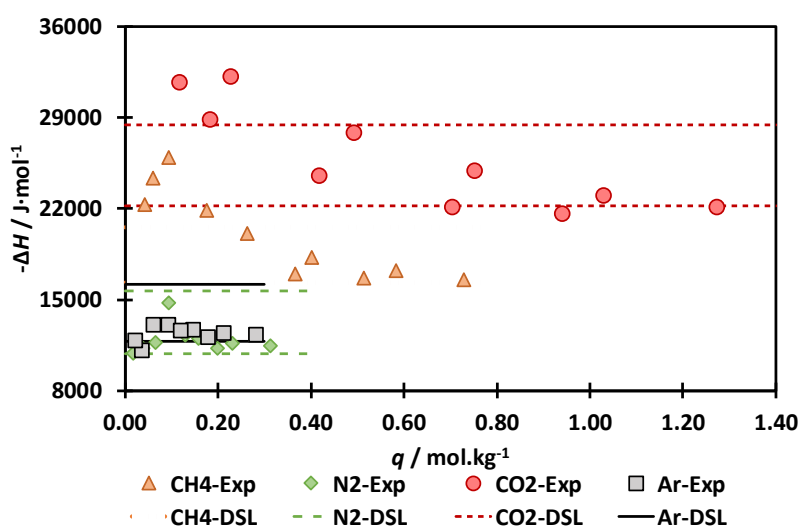


Figure 6.5 - Isosteric heat of adsorption for carbon dioxide, methane, nitrogen, and argon on the BPL activated carbon. Lines represent the enthalpic parameters of the DSL model.

6.2.4. Fixed Bed Experiments

To study the system single and multicomponent adsorption dynamics, single, binary, and ternary breakthrough curves were performed in the SMB unit described in Section 5.6 at 303 K and 1.5 bar. The columns were packed with the adsorbent material and activated overnight at 393 K with a constant helium flow (0.2 SLPM).

The fixed bed experiments were carried out in columns 4 to 6, where the back-pressure regulator, located at the column 6 outlet, ensured the pressure was constant during each assay. The characteristics of the beds are presented in Table 6.3. The initial conditions of the beds, the feed composition, the flow rate, and the adsorption and desorption time steps for each experiment are presented in Table 6.4. In each experiment, the desorption step began once mass and thermal equilibrium were reached to ensure complete saturation of the adsorbent beds.

Table 6.3 - Characteristics of the fixed beds.

	Value	Unit
Mass (m)	12.3	g
Internal diameter (d_w)	2.15	cm
Bed length (L)	8.5	cm
Bed porosity (ϵ)	0.41	
Bulk density (ρ_b)	396.6	kg·m ⁻³

Table 6.4 - Experimental conditions of the fixed bed experiments performed at 303 K and 1.5 bar.

	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5	Exp. 6	Exp. 7
Total flow rate (SLPM)	0.200	0.200	0.200	0.200	0.200	0.200	0.200
Feed composition	N ₂ : 1.0	CH ₄ : 1.0	Ar: 1.0	CO ₂ : 1.0	N ₂ : 0.5 CH ₄ : 0.5	N ₂ : 0.25 CH ₄ : 0.25 Ar: 0.5	N ₂ : 0.25 CH ₄ : 0.25 CO ₂ : 0.5
Initial conditions	He	He	He	He	He	Ar	CO ₂
Desorption gas	He	He	He	He	He	Ar	CO ₂
Desorption starting time (s)	2700	2600	2500	3800	3800	3800	3800

The obtained experimental data was used to validate a mathematical model through simulation using the *gPROMS* modelling software. The mass and heat transfer parameters implemented in the mathematical model are displayed in Table 6.5 and Table 6.6. These values were obtained using the referenced correlations in Section 3.6. The values of h_w and U were fitted having in consideration the temperature history. The values presented in Table 6.6 were calculated based on a correlation for the BPL activated carbon available in the literature [4].

Table 6.5 - Transport parameter values used in the simulations.

	$D_{ax} \times 10^5$ (m ² ·s ⁻¹)	$k_f \times 10^2$ (m·s ⁻¹)	λ (W·m ⁻¹ ·K ⁻¹)	h_f (W·m ⁻² ·K ⁻¹)	$D_{p,i} \times 10^6$ (m ² ·s ⁻¹)	U (W·m ⁻² ·K ⁻¹)	h_w (W·m ⁻² ·K ⁻¹)
Exp. 1	9.0	1.77	0.19	28.9	N ₂ : 2.82	100	50
Exp. 2	9.0	1.75	0.25	36.8	CH ₄ : 3.59	100	50
Exp. 3	9.0	1.76	0.15	22.7	Ar: 2.42	100	50
Exp. 4	9.0	1.90	0.14	22.8	CO ₂ : 2.27	100	50
Exp. 5	9.0	1.76	0.22	33.1	N ₂ : 2.82 CH ₄ : 3.59	100	50
Exp. 6	9.0	1.76	0.22	27.9	N ₂ : 2.82 CH ₄ : 3.59	100	50

Exp. 7	9.0	1.84	0.18	27.6	Ar: 2.42	100	50
					N ₂ : 2.82		
					CH ₄ : 3.59		
					CO ₂ : 2.27		

Table 6.6 - Transport parameter values used in the simulations (cont.).

Adsorbate	$D_{\text{micro},i} \text{ (s}^{-1}\text{)}$
N ₂	2.32×10^{-9}
CH ₄	1.42×10^{-9}
CO ₂	3.49×10^{-10}
Ar	1.71×10^{-9}

The pure component breakthrough experiments are presented in Figure 6.6 to Figure 6.9. The presented molar fractions have a maximum relative uncertainty of 2.1% associated with the GC calibration. Analysis of the curves indicated that the breakthrough time for N₂, CH₄, Ar, and CO₂ is 95, 220, 90, and 415 s, respectively. This way, the pure component adsorption order is CO₂>CH₄>N₂≈Ar, corroborating the equilibrium data at 303 K and 1.5 bar. The temperature histories show a positive/negative thermal peak during the adsorption/desorption step since the adsorption process is exothermic. The largest increase in temperature (15 K) is observed for CO₂, given its higher heat of adsorption. Sharp concentration fronts can be noted for the adsorption step, because of the favourable nature of the isotherm. As the isotherm becomes unfavourable during the desorption step, broad and tailing curves can be seen. The simulations predict well both the mass and heat fronts.

The binary fixed bed results are displayed in Figure 6.10. A roll-up effect can be observed for the N₂ front once CH₄ breaks at the 6th column outlet. Since methane is preferably adsorbed, it exhibits a slower concentration front relative to N₂ and, therefore, causes the displacement of the adsorbed nitrogen. Two thermal peaks can be detected in the temperature histories as a result of the adsorption of each component of the mixture. The simulation results are in good agreement with the binary experimental data.

Figure 6.11 and Figure 6.12 show the breakthrough curves and temperature histories of a nitrogen (25%)/methane (25%)/argon or carbon dioxide (50%) mixture adsorption and desorption over a fixed bed adsorbent saturated and regenerated with argon/carbon dioxide, respectively. The purpose of these experiments is to study the adsorption behaviour of the mixture when the bed is saturated with the desorbent gas, to evaluate the ability of the mixture to displace the desorbent and *vice versa*, which is a requirement for an efficient SMB process. Close analysis of the first experiment (with Ar) shows that during the adsorption of the mixture, the mass front of methane is sharp as a result of the higher affinity toward the adsorbent material. However, since N₂ and Ar exhibit similar adsorption equilibrium at the experimental conditions, both the adsorption and desorption of N₂ are steep, while the desorption of CH₄ is dispersive. As a result, a single thermal

peak is observed in the temperature history once the breakthrough of methane occurs since the enthalpic constant is similar for both N_2 and Ar. Contrastingly, in the case of carbon dioxide, the concentration fronts of the components are dispersive during the adsorption of the mixture and compressive when the bed is saturated with CO_2 since it has a higher affinity toward the solid surface. For the same reason, a roll-up is observable once methane is desorbed. During the desorption step, three plateaus are clearly defined in the CO_2 concentration front, with two transitions, corresponding to the breakthrough of both N_2 and CH_4 . In this case, the adsorption of the mixture ensues two negative thermal peaks resulting from the lower adsorption enthalpy of its components. Nevertheless, in both cases, the desorbent is easily displaced by the mixture and is equally able to displace the adsorbed phase. This way, a continuous SMB process seems feasible, using either of the tested desorbent gases.

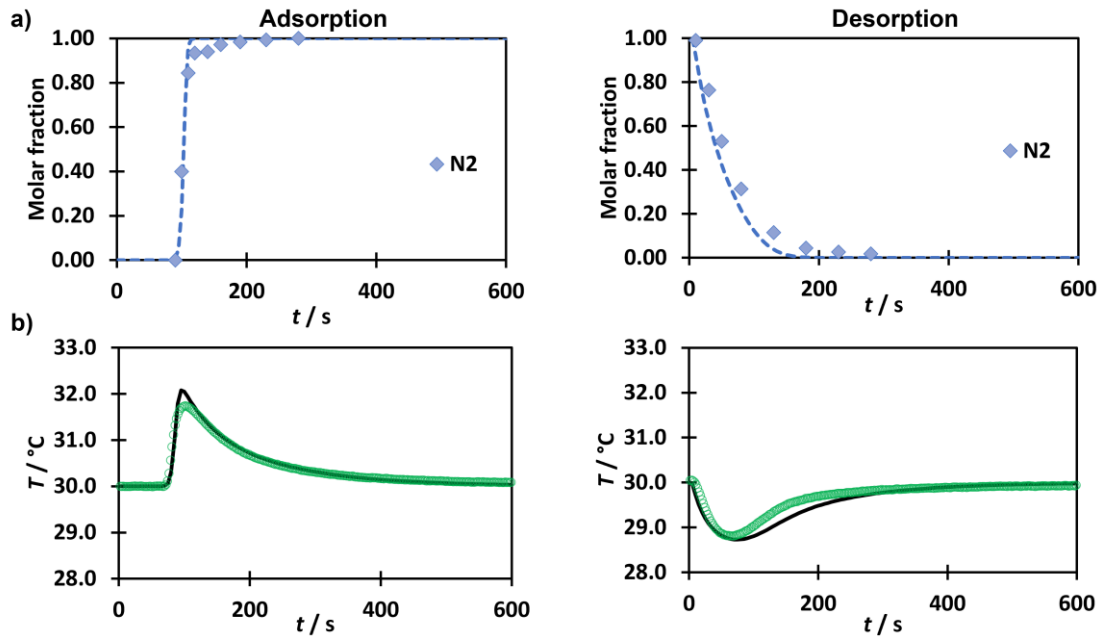


Figure 6.6 - Adsorption of nitrogen over a BPL fixed bed initially regenerated with helium: a) molar fraction at the 6th column outlet; b) temperature history in the middle of the 6th column. Lines represent the simulation results.

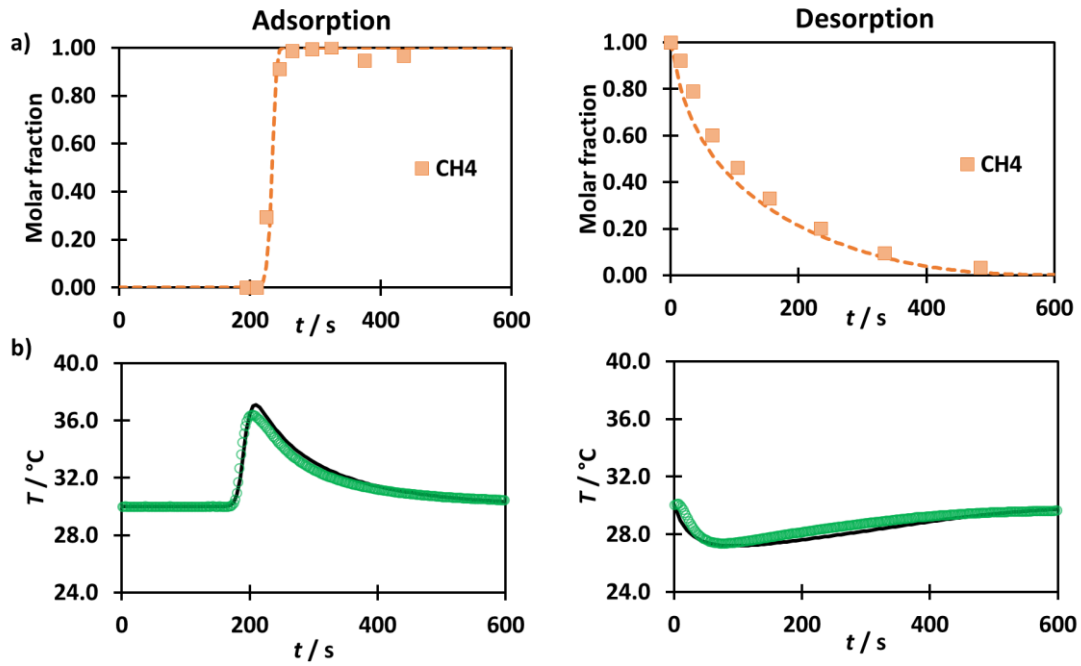


Figure 6.7 - Adsorption of methane over a BPL fixed bed initially regenerated with helium: a) molar fraction at the 6th column outlet; b) temperature history in the middle of the 6th column. Lines represent the simulation results.

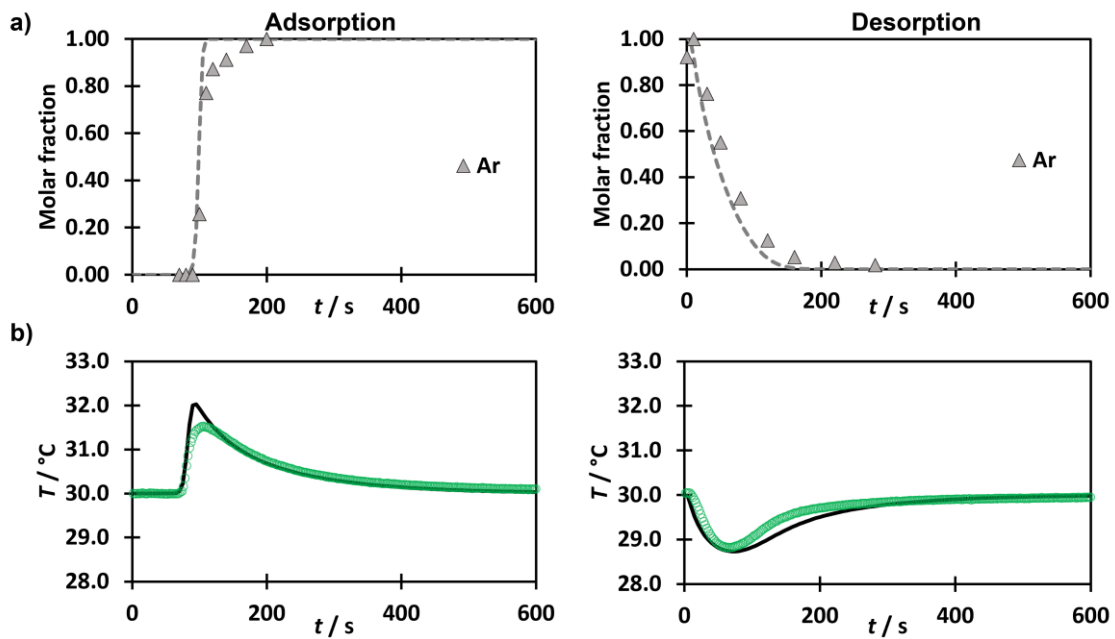


Figure 6.8 - Adsorption of argon over a BPL fixed bed initially regenerated with helium: a) molar fraction at the 6th column outlet; b) temperature history in the middle of the 6th column. Lines represent the simulation results.

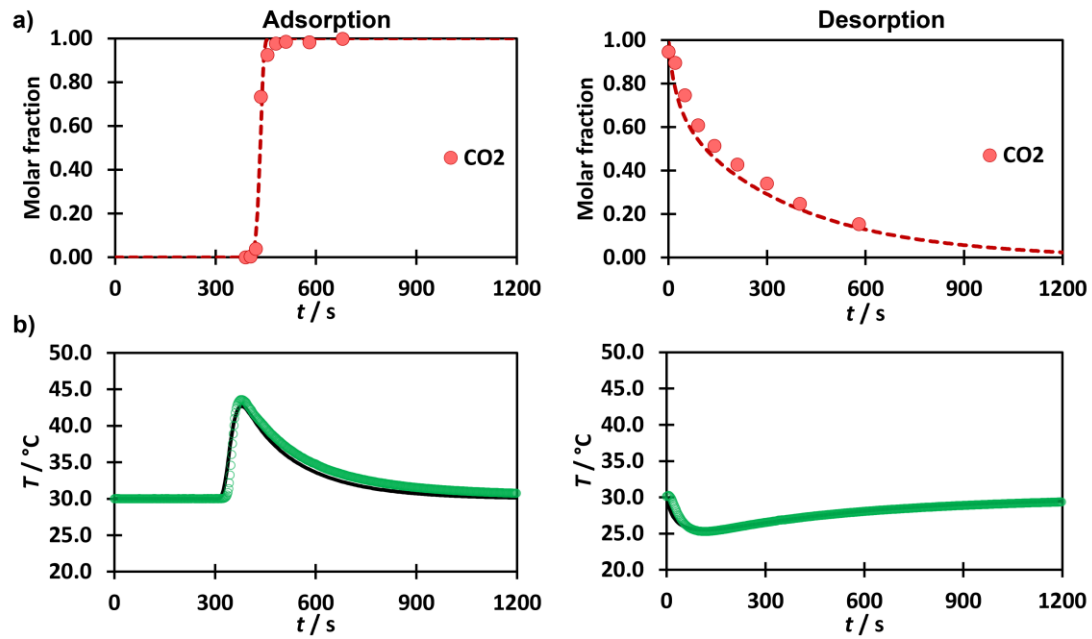


Figure 6.9 - Adsorption of carbon dioxide over a BPL fixed bed initially regenerated with helium: a) molar fraction at the 6th column outlet; b) temperature history in the middle of the 6th column. Lines represent the simulation results.

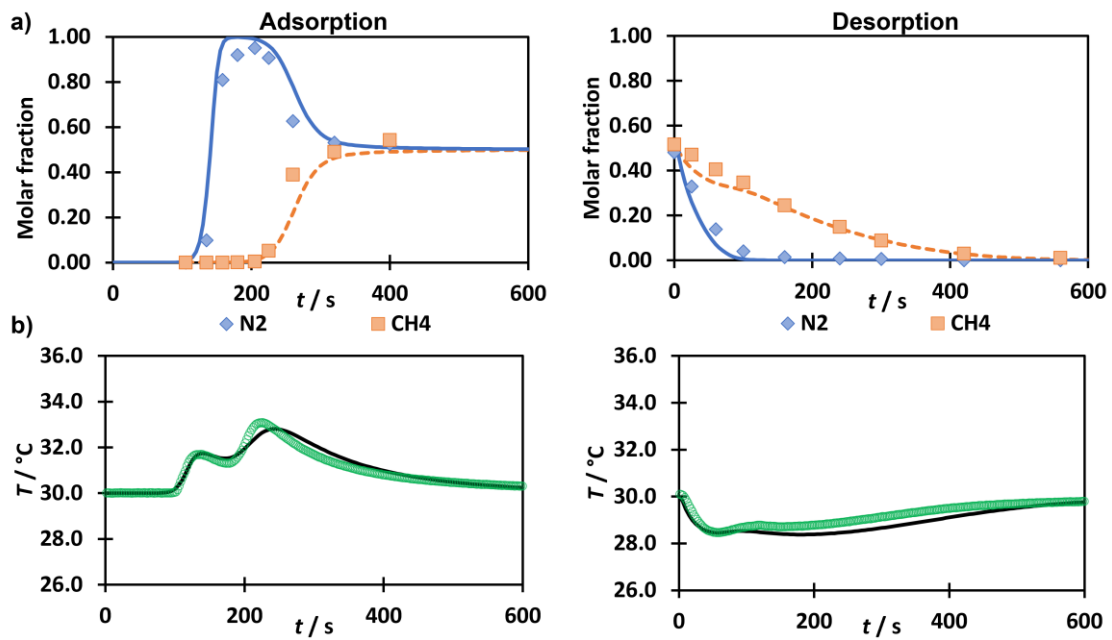


Figure 6.10 - Adsorption of a nitrogen/methane mixture (equimolar) over a BPL fixed bed initially regenerated with helium: a) molar fraction of each component at the 6th column outlet; b) temperature history in the middle of the 6th column. Lines represent the simulation results.

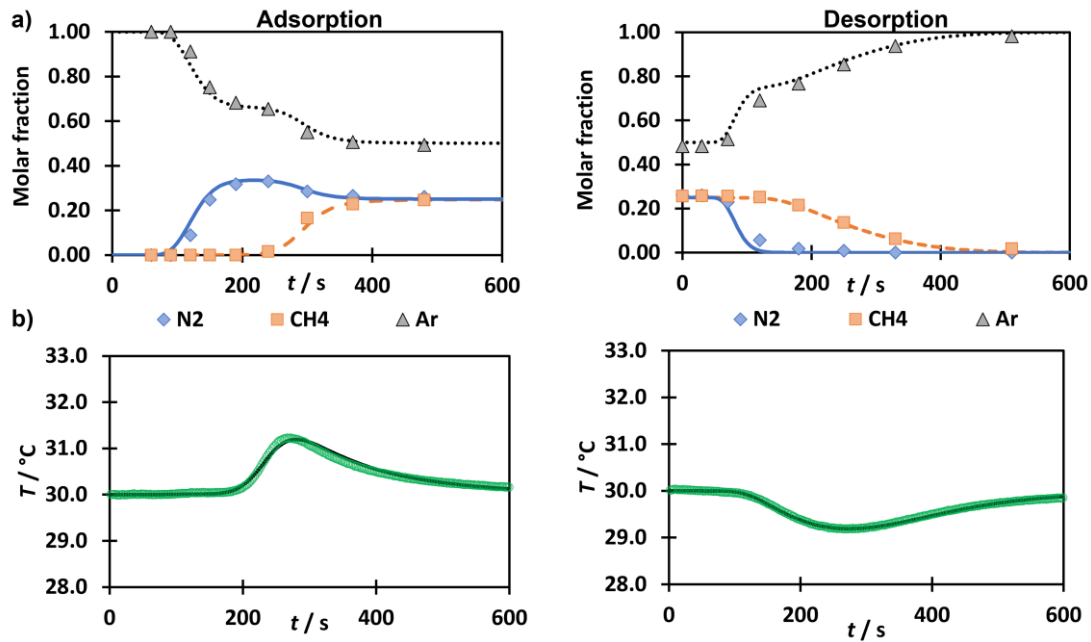


Figure 6.11 - Adsorption of a nitrogen/methane/argon mixture (25 %/25 %/50 %) over a BPL fixed bed initially saturated with argon: a) molar fraction of each component at the 6th column outlet; b) temperature history in the middle of the 6th column. Lines represent the simulation results.

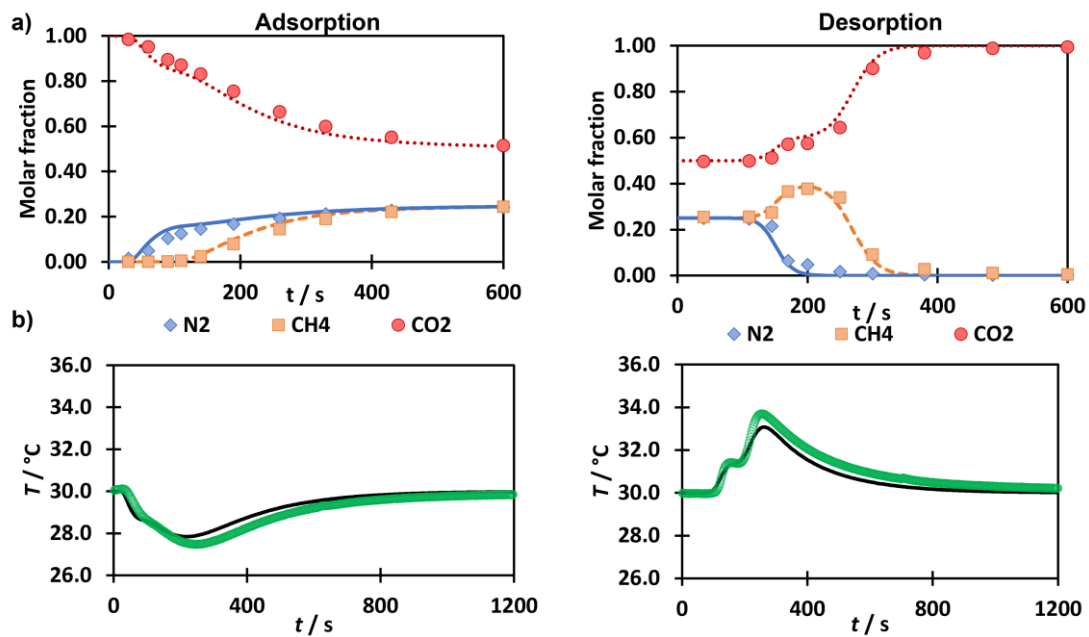


Figure 6.12 - Adsorption of a nitrogen/methane/carbon dioxide mixture (25 %/25 %/50 %) over a BPL fixed bed initially saturated with carbon dioxide: a) molar fraction of each component at the 6th column outlet; b) temperature history in the middle of the 6th column. Lines represent the simulation results.

6.2.5. SMB Cycles

After the equilibrium and dynamic tests, two SMB cycles were performed with each of the considered desorbents to assess their CH_4/N_2 separation performance using the BPL carbon material. The experiments were carried out in an open loop mode, with no desorbent recycle. A 2-3-2-1 four-zone system configuration was considered, with a switching time of 50 s. The SMB

unit was operated at 303 K and in a pressure range between 151 and 220 kPa for case 1 and 151 and 187 kPa for case 2. To ensure the adsorbent is cleaned in the zone I, the desorbent flow rate was set as 0.966 SLPM for case 1 and 0.50 SLPM for case 2. The feed composition for both cases was 50% CH₄ and 50% N₂, with a feed stream of 0.19 SLPM for case 1 and 0.06 SLPM for case 2. To obtain the initial operating conditions, an expected pressure history at the column outlet is used in the simulations to obtain a preliminary separation region. These conditions are then tuned during the experiment until complete separation of the mixture is attained. The operating conditions for each experiment are summarised in Table 6.7, where T and P are the system temperature and pressure, t^* is the switching time, and Q_D , Q_F , Q_X , Q_R , and Q_{IV} are the desorbent, feed, extract, raffinate, and zone IV flowrates, respectively.

Table 6.7 - Operating conditions for the performed SMB cycles.

Run	T (K)	P (bar)	t^* (s)	Desorbent	Config.	Q_D (SLPM)	Q_F (SLPM)	Q_X (SLPM)	Q_R (SLPM)	Q_{IV} (SLPM)
1	303	151- 220	50	Ar	2-3-2-1	0.97	0.19	0.81	0.22	0.13
2	303	151- 187	50	CO ₂	2-3-2-1	0.50	0.06	0.16	0.27	0.13

Once cyclic steady state is achieved, the internal composition profile can be acquired. The results are shown in Figure 6.13 and Figure 6.14, for case 1 and case 2, respectively. The performance parameters obtained for each case are also displayed in Table 6.8. The equations used to obtain these values are available in Section 3.7.2.

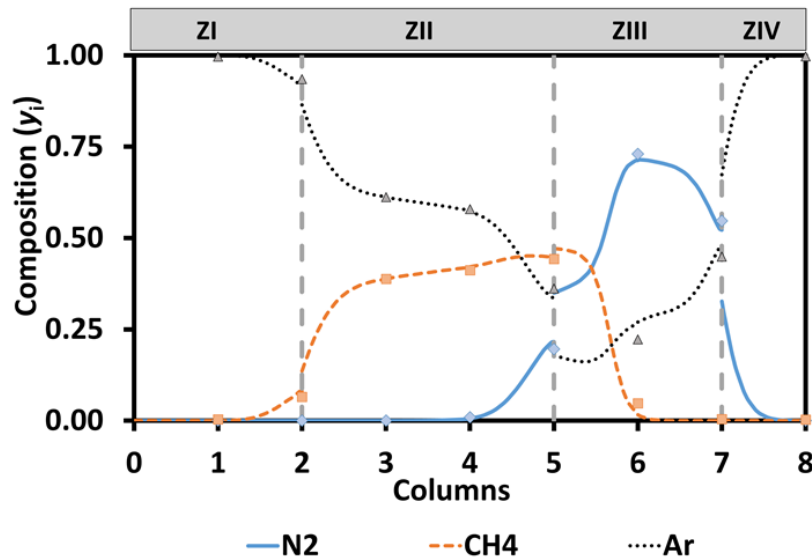


Figure 6.13 - Internal profile in function of the column number for the argon experiment, collected at half switching time. Points represent experimental data and lines represent the simulation results.

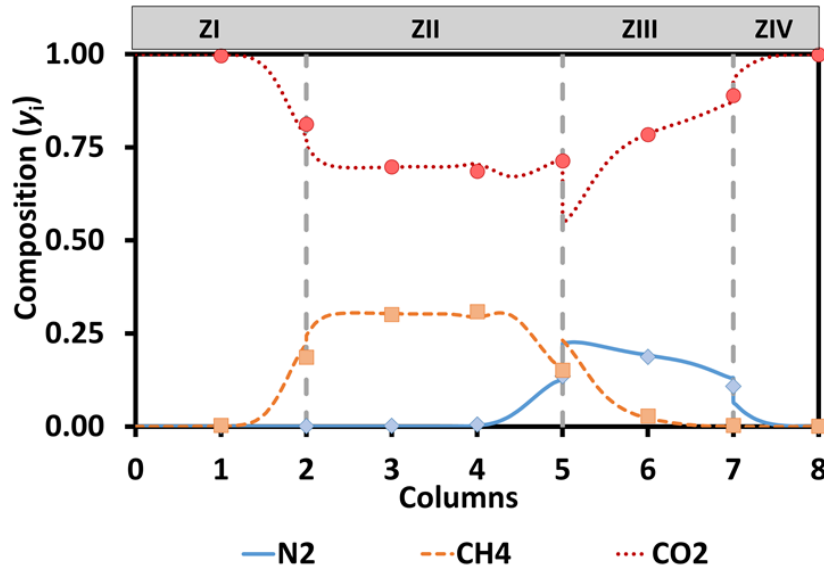


Figure 6.14 - Internal profile in function of column number for the CO₂ experiment, collected at half switching time. Points represent experimental data and lines represent the simulation results.

It can be observed that both desorbents allow for the complete separation of the mixture, with similar purity values being achieved. However, when carbon dioxide is used, the productivity value is lower than when argon is used due to the much lower feed flow rate treated during the cycle. Regarding desorbent consumption, case 2 shows a better performance, as the eluent flow rate used for the separation is halved. The experimental results are in good agreement with the simulation results obtained with the complete model, as shown in Figure 6.13 and Figure 6.14.

Table 6.8 - Performance parameters for both SMB cycles.

	Case 1 - Argon		Case 2 – Carbon Dioxide	
	Extract	Raffinate	Extract	Raffinate
Average N₂ molar fraction (%)	0.004	0.451	0.005	0.101
Average CH₄ molar fraction (%)	0.096	0.009	0.169	0.007
Purity (%)	96.2	98.0	97.4	93.4
Recovery (%)	97.4	96.9	92.7	97.2
Productivity (kg·m⁻³_{ads}·h⁻¹)	22.9	49.8	7.83	13.8
Desorbent Consumption (m³_{STP,desorbent}·kg⁻¹)	15.0		19.2	

In both experiments, the mixture is fed into the system in the node between sections II and III. In section II, between the extract outlet and the feed inlet, the more adsorbed species, methane, is retained in the material. In contrast, the less adsorbed species, nitrogen, is carried by the eluent. In section III, which begins at the feed inlet and ends at the raffinate outlet, the nitrogen content increases. The flow rate in section I is high enough to guarantee that the adsorbent is cleaned, ensuring that section IV is not contaminated after the switch. The nitrogen content decreases in section IV, with pure desorbent being obtained at the outlet, which can be recycled back into

section I when operating in a closed loop mode, which would decrease the desorbent consumption. Also, it can be observed that a traditional configuration of 2-2-2-2 could be used instead of the presented configuration, with the internal profiles showing that using the third column in Section II is unnecessary, since the nitrogen content decreases rapidly.

The extract and raffinate stream composition histories during a switching time for each experiment are displayed in Figure 6.15. It can be noticed that when argon is used as the desorbent gas, the molar fraction varies between 0.19 and 0.01, exhibiting a more tailing curve when compared to the extract history for case 2 (composition ranging from 0.28 to 0.02). This observation is explained by the difference in desorbent strength for each case. During the regeneration of the adsorbent material in zone I, the desorption of methane is dispersive for case 1 and compressive for case 2, as a result of the weaker and stronger affinity of argon and carbon dioxide, respectively. Also, it can be seen that the desorbent flow rate could be decreased for both cases while maintaining the flow rate in section II, increasing the methane content in the extract stream and further improving the performance of the adsorber in terms of desorbent consumption. Analysis of the raffinate outlet history shows a sharper front for the argon SMB cycle, once again due to the favourable nitrogen breakthrough, with its content increasing up to 0.76. It can be observed through the simulations that for the CO₂ experiment, a slighter lower zone III flow rate should be used to avoid contamination of the raffinate stream.

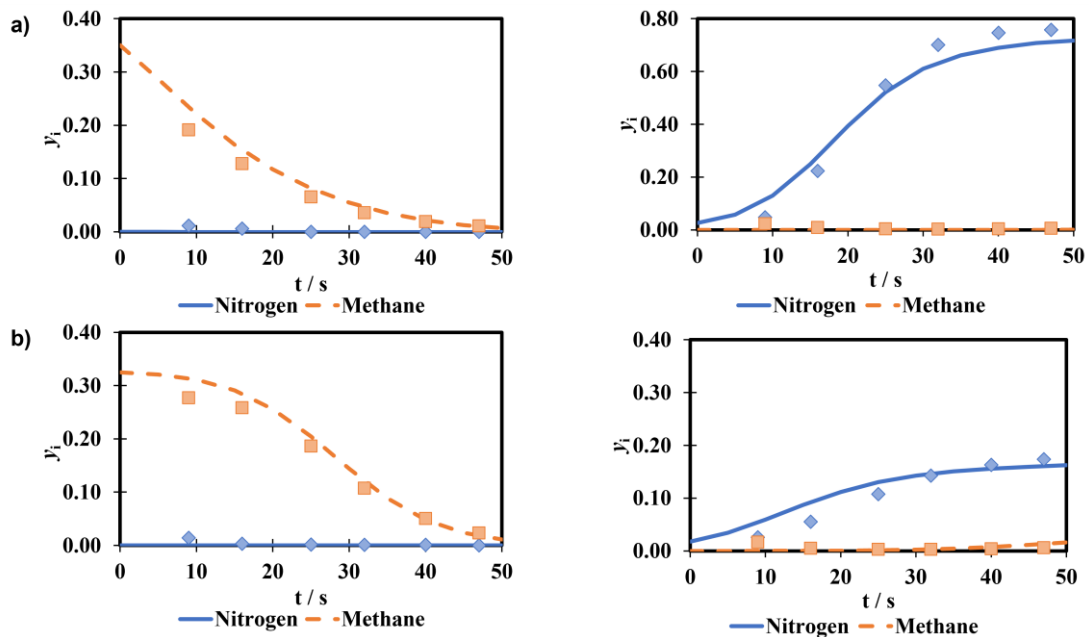


Figure 6.15 - Extract (ZI_CII, left) and Raffinate (ZIII_CII, right) molar fraction history at the exit of the respective column, during one step for a) Case 1 and b) Case 2. Points correspond to experimental data and lines to simulation data.

To further investigate the impact of the desorbent strength, the separation regions for each of the studied desorbents were computed, which can also be used to redefine the operating conditions and improve the experimental results. To obtain the separation regions, the purity values were

defined to be over 97% for the extract outlet and over 99% for the raffinate outlet, to meet the product specifications. The switching time and desorbent flow rate values used were equal to the experimental conditions. To compute the separation region, the procedure described in Section 3.7.3 was used. The drawn separation regions are presented and compared in Figure 6.16, where the operating points from each experiment are also represented.

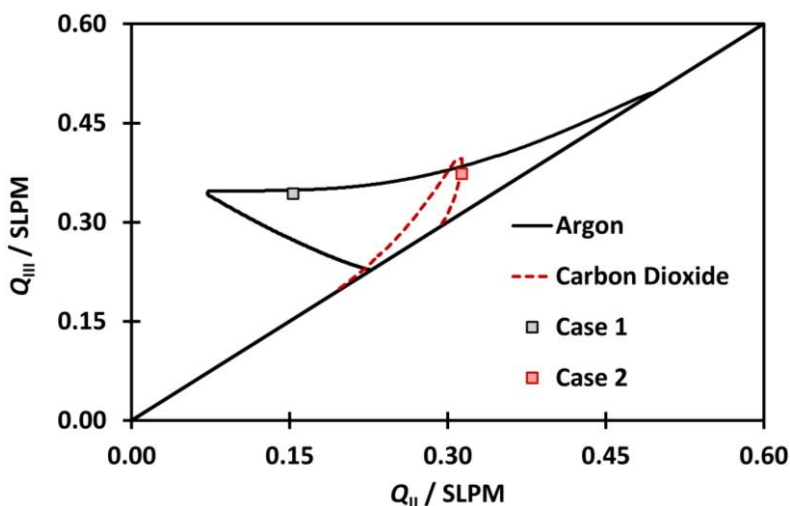


Figure 6.16 - Separation region for CH_4/N_2 separation in BPL determined with the complete model, with a 2-3-2-1 configuration, switching time of 50 s, temperature of 303 K, and extract and raffinate purity of 97 and 99 %, respectively, using argon (full line) and carbon dioxide (dashed line) as the desorbent gas. Operating points for cases 1 and 2.

Firstly, the operating point for case 1 lies within the separation region drawn using argon as the desorbent gas, whereas for case 2, it lies on the boundary of the computed region for the respective desorbent, which could explain the lower purity grade observed in the raffinate stream for this experiment. Comparing the computed regions, it is clear that both the shape and area are very different. Because carbon dioxide strongly adsorbs to the solid surface, it hinders the performance of the SMB process, especially in terms of the maximum feed flow rate that can be treated, and consequently limits the productivity of the process. Achieving optimal operating conditions for complete separation can also be challenging when using a strong eluent, as the separation region can be much narrower. Regarding the shape of the regions, when treating larger feed streams, a higher section II flow rate is needed when a strong desorbent is used, contrary to what occurs when a weak desorbent is utilised, which is in agreement with the shape predicted by the equilibrium theory [5]. Martins *et al.* [6] also studied the impact of a strong and a weak desorbent on the separation of an ethane/ethylene mixture and obtained similar results. However, in the cited work, the interaction between the desorbent, propane, and the adsorbent material was so strong that the optimal conditions for complete separation were unfeasible, with the optimal conditions lying in an extremely narrow region. In the present work, although CO_2 is more retained than the components of the mixture, total separation can still be achieved, suggesting that a strong desorbent with extremely favourable isotherm (sharp increase at low pressures) leads to inefficient SMB processes.

6.3. Pelletized Maxsorb activated carbon

6.3.1. Material characterization

Some representative properties of the pelletised material prepared in this work are presented in Table 6.9. The information presented in the table was gathered from a series of assays performed to characterise the adsorbent sample: adsorption isotherms of N_2 and CO_2 at 77 and 273 K, respectively, porosimetry by mercury intrusion, and helium pycnometry. The particle porosity, ϵ_p , was calculated with the apparent and solid density and is also presented in Table 6.9.

Table 6.9 - Properties of the solid material

Properties	Value
Shape	Extrudates/cylinders
Dimensions	2 mm in diameter, 3 to 5 mm in length
$S_{Langmuir} (m^2 \cdot g^{-1})$	2513
$V_{micro} (cm^3 \cdot g^{-1})$	1.19
$\rho_s (kg \cdot m^{-3})$	1876
$\rho_p (kg \cdot m^{-3})$	581.9
ϵ_p	0.690
$\bar{d}_{pore} (nm)$	31.1

To evaluate the microporosity of the extrudates, physisorption of N_2 at 77 K and CO_2 at 273 K was performed. Before the measurements, the sample was degassed at 423 K under vacuum. The obtained data can be observed in Figure 6.17 and Figure 6.18.

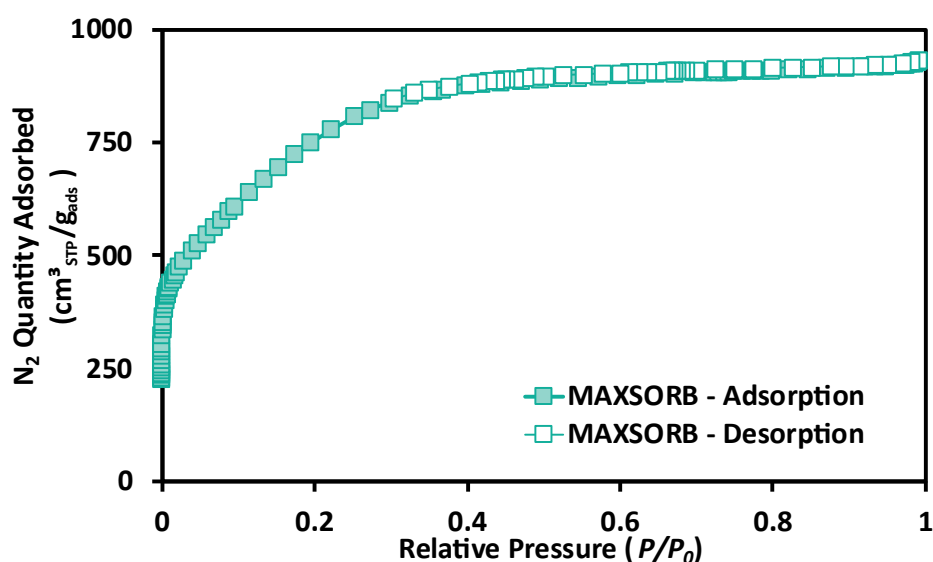


Figure 6.17 - N_2 adsorption equilibrium isotherm on Maxsorb pellets at 77 K. Closed and open symbols correspond to the adsorption and desorption branches, respectively.

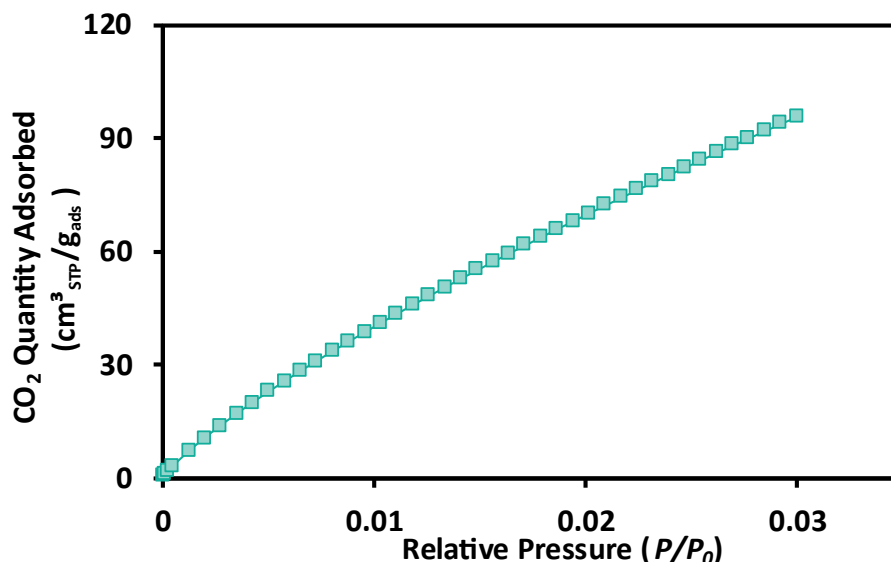


Figure 6.18 - CO₂ adsorption equilibrium isotherm on Maxsorb pellets at 273 K.

The N₂ equilibrium data at 77 K shows a type I(b) isotherm, which is commonly observed for materials with a broader pore size distribution, having both micropores and narrow mesopores [7]. For low relative pressures, a sharp increase in adsorption is visible due to the presence of micropores. As the pressure increases, a gradual saturation of the adsorbent occurs, leading to a plateau in the isotherm once the accessible sites are fully occupied. No hysteresis is observed since there is an overlap of the adsorption and desorption branches. This indicates that the adsorption/desorption process is entirely reversible. The micropore volume and Langmuir surface area are 1.19 cm³·g⁻¹ and 2513 m²·g⁻¹, respectively.

From the CO₂ adsorption at 273 K, presented in Figure 6.18, the pore volume for a pore diameter lower than 7.97 Å can be obtained, giving a value of 0.176 cm³·g⁻¹.

The mercury porosimetry test was carried out to obtain valuable information about the pore size, distribution, and volume of pores within the material. At low pressure, since the mercury is not able to penetrate the pores of the material, it also gives information regarding the apparent density, ρ_{ap} , of the material. The values obtained for the average pore size, $\bar{d}_{pore}$ and ρ_{ap} are presented in Table 6.9. Figure 6.19 provides the pore size distribution of the Maxsorb pellets given by mercury porosimetry.

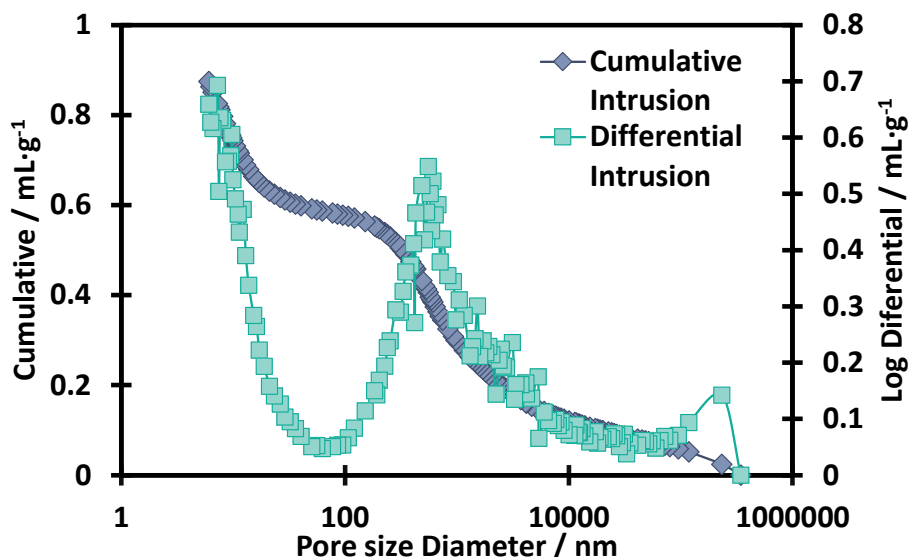


Figure 6.19 - Pore size distribution of the Maxsorb pellets.

Analysis of Figure 6.19 indicates a broad pore size distribution, with the presence of both meso and macropores, which can be attributed to the interparticle voids.

6.3.2. Pure component adsorption equilibrium data

The pure component adsorption capacity for N_2 , CH_4 , CO_2 , and Ar on the pelletised Maxsorb was obtained over a pressure range of 0-2.5 bar at 303, 323, and 343 K. The experimental points are presented in Figure 6.20, where the closed and open symbols correspond to the adsorption and desorption points, respectively. The Langmuir model was used to fit the collected data, where the best-fit model parameters were determined by minimising the sum of the squared residuals between the measurements and the calculated capacities. The lines presented in Figure 6.20 correspond to the equilibrium data model predictions. The obtained model parameters for each of the adsorbates are shown in Table 6.10.

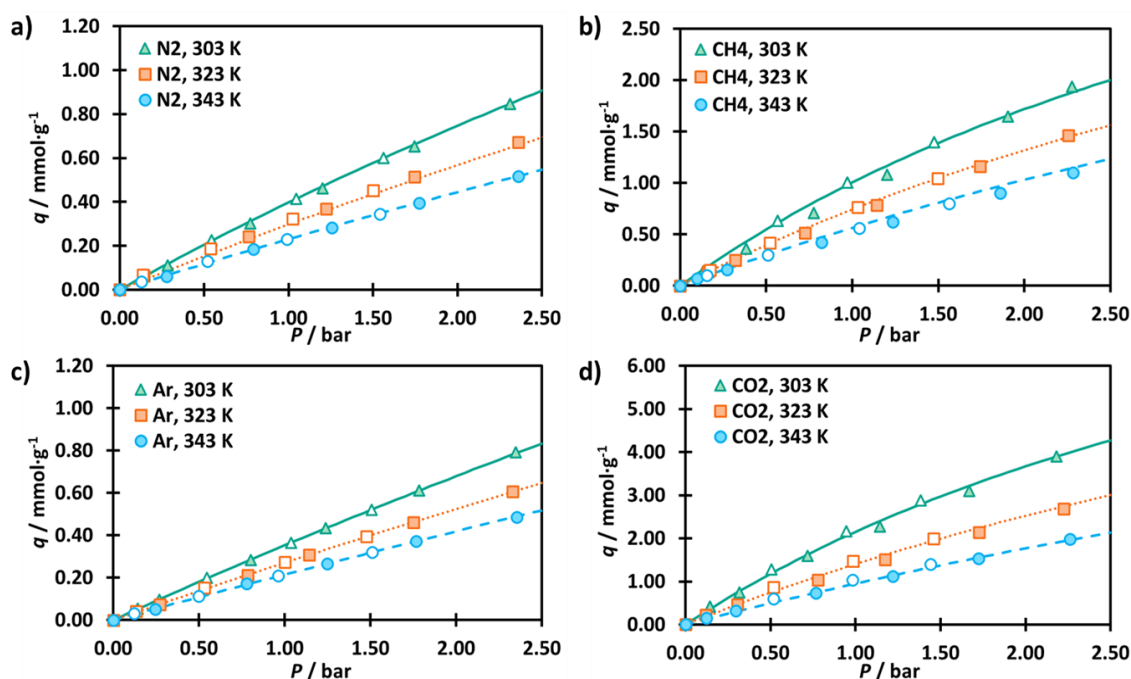


Figure 6.20 - Adsorption isotherms of a) N_2 , b) CH_4 , c) Ar, and d) CO_2 over the pelletised Maxsorb carbon at 303 ($\blacktriangle$), 323 ($\blacksquare$), and 343 K ($\bullet$). Lines represent the fitting with the Single-site Langmuir model.

Table 6.10 - Fitting parameters of the Langmuir model for N_2 , CH_4 , CO_2 , and Argon adsorption equilibrium on the Maxsorb pellets.

Adsorbate	$q_m / \text{mol} \cdot \text{kg}^{-1}$	$b_0 \times 10^4 / \text{bar}^{-1}$	$-\Delta H / \text{J} \cdot \text{mol}^{-1}$
N_2	6.09	5.79	12049
CH_4	5.93	8.09	13897
CO_2	12.47	0.89	19481
Ar	8.98	5.55	10805

The experimental data indicates that, for the four components, the adsorption process is reversible as there are no signs of hysteresis in the desorption branch. The adsorption capacity for CO_2 is the highest over the studied range of temperatures/pressures, followed by CH_4 , N_2 , and Ar. Due to the higher uptake relative to the target species, it is expected that carbon dioxide will behave as a strong desorbent when integrated into an SMB process, while argon will act as a weak desorbent.

In Figure 6.21, the N_2 and CO_2 isotherms at 303 K were compared with the equilibrium data measured in a previous work by our group for Maxsorb pellets with 5% binder [8]. Note that the binder percentage was increased in this work to enhance the mechanical stability of the produced pellets. To compare the results, the capacities obtained for the extrudates with 5% binder were converted to a 10% binder basis. As expected, both materials exhibit similar adsorption capacity for both adsorbates.

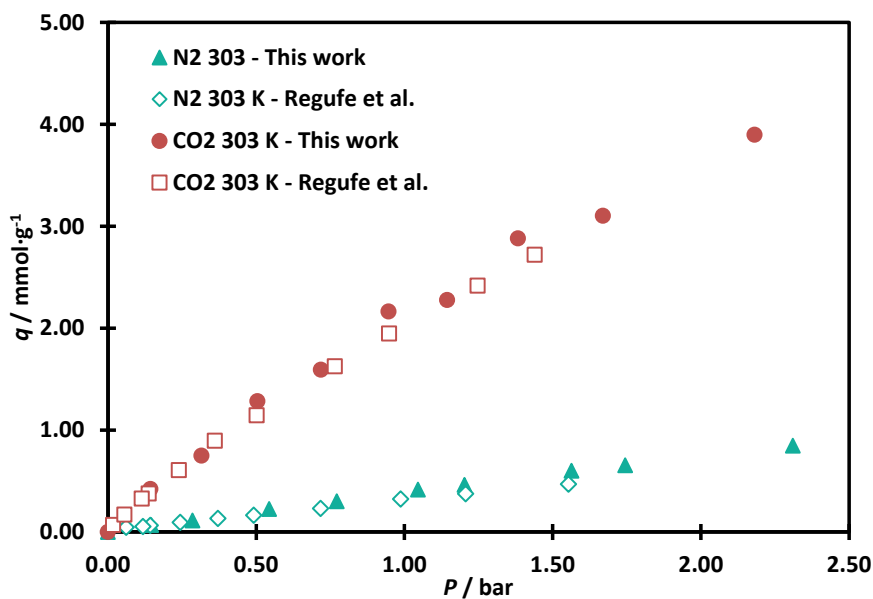


Figure 6.21 - Comparison of the adsorption equilibrium data at 303 K for N_2 and CO_2 with the adsorption equilibrium isotherms reported for Maxsorb extrudates with 5% binder (basis converted to 10% binder content). Data taken from Regufe *et al.* [8].

6.3.3. Isosteric heat of adsorption

To validate the heat of adsorption values obtained through the Langmuir fitting, the isosteric heat of adsorption was calculated and compared. The isosteric heat of adsorption can provide valuable insights into the interaction strength between the gas and the surface of the solid [9]. The experimental value can be estimated through the adsorption equilibrium data by using the Clausius-Clapeyron equation (Equation (3.2)).

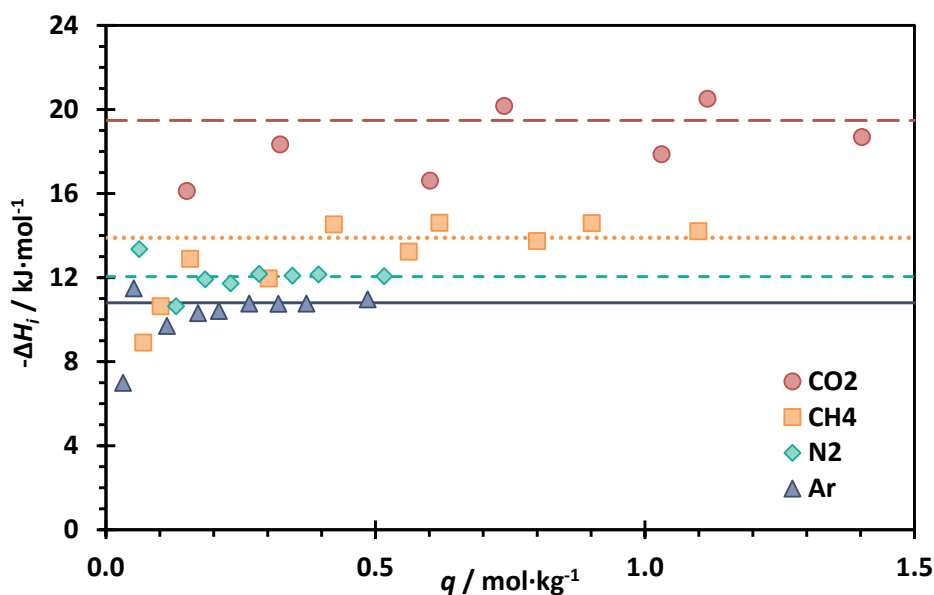


Figure 6.22 - Isosteric heat of adsorption for carbon dioxide, methane, nitrogen, and argon on the pelletised Maxsorb. Lines represent the value calculated with the Langmuir model fitting.

In Figure 6.22, the isosteric heat of adsorption is plotted as a function of the amount adsorbed for each component. The lines correspond to the values obtained through the Langmuir fitting. The experimental data is in good agreement with the fitted values. The results suggest a homogeneous adsorbent surface. The observed increase in the heat of adsorption at low coverage can be attributed to interactions between the molecules in the adsorbed phase. CO₂ exhibits a stronger affinity toward the adsorbent, with heat of adsorption of 19.5 kJ·mol⁻¹. CH₄, N₂, and Ar show a heat of adsorption of 13.9, 12.0, and 10.8 kJ·mol⁻¹, respectively. The heat of adsorption values are comparable to those found in the literature for the Maxsorb material and adsorbents of a similar nature [3, 10].

6.3.4. Fixed Bed Experiments

The single component, binary, and ternary experiment results are presented in Figure 6.23 to Figure 6.29. The fixed bed characteristics can be found in Table 6.11. The experimental conditions of each assay can be found in Table 6.12. The experimental data was compared with the simulation results for all runs. The required transport parameters for the data modelling can be found in Table 6.13. A value of 1.2 s⁻¹ was used for the micropore mass transfer coefficient, $k_{\text{micro},i}$. In each figure, subplot a) shows the molar fraction variation of each component at the column 6 outlet, and subplot b) shows the temperature history at the middle of the adsorbent bed during both adsorption and desorption steps. Before conducting the experiments, the columns were activated at 393 K overnight, feeding helium gas at a constant flow rate during the process.

Table 6.11 - Characteristics of the fixed beds.

	Value	Unit
Mass (m)	6.14	g
Internal diameter (d_w)	2.15	cm
Bed length (L)	8.6	cm
Bed porosity (ϵ)	0.66	
Bulk density (ρ_b)	196.7	kg·m ⁻³

Table 6.12 - Experimental conditions of breakthrough experiments with Maxsorb pellets at 303 K and 1.5 bar.

	Type	Adsorbates	Adsorption feed flow rate / SLPM	Desorption gas	Desorption feed flow rate / SLPM	Initial conditions
1	Single	N ₂	0.2	He	0.2	Filled with He
2	Single	CH ₄	0.2	He	0.2	Filled with He
3	Single	CO ₂	0.2	He	0.2	Filled with He
4	Single	Ar	0.2	He	0.2	Filled with He
5	Binary	N ₂ /CH ₄	0.1/0.1	He	0.2	Filled with He

6	Ternary	N ₂ /CH ₄ /CO ₂	0.05/0.05/0.1	CO ₂	0.2	Saturated with CO ₂
7	Ternary	N ₂ /CH ₄ /Ar	0.05/0.05/0.1	Ar	0.2	Saturated with Ar

Table 6.13 - Transport parameter values used in the breakthrough simulations for Maxsorb pellets.

	$D_{ax} \times 10^5$ (m ² ·s ⁻¹)	$k_f \times 10^2$ (m·s ⁻¹)	λ (W·m ⁻¹ ·K ⁻¹)	h_f (W·m ⁻² ·K ⁻¹)	$D_{p,i} \times 10^5$ (m ² ·s ⁻¹)	U (W·m ⁻² ·K ⁻¹)	h_w (W·m ⁻² ·K ⁻¹)
Exp. 1	7.0	4.55	0.37	48.9	N ₂ : 1.86	100	50
Exp. 2	7.0	4.41	0.48	63.1	CH ₄ : 1.93	100	60
Exp. 3	6.8	4.05	0.37	52.6	CO ₂ : 1.53	100	50
Exp. 4	7.1	4.82	0.47	61.1	Ar: 1.85	100	60
Exp. 5	3.0	3.61	0.42	56.0	N ₂ : 1.21 CH ₄ : 1.18	100	60
Exp. 6	3.0	1.42	0.15	23.4	N ₂ : 0.541 CH ₄ : 0.582 CO ₂ : 0.502	100	50
Exp. 7	3.0	1.64	0.17	25.4	N ₂ : 0.638 CH ₄ : 0.687 CO ₂ : 0.634	100	20

Runs 1 to 4, shown in Figure 6.23 to Figure 6.26 correspond to the single-component breakthrough curves for each of the adsorbates used in this work: CH₄, N₂, CO₂, and Ar. These runs were performed with the bed initially filled with an inert gas (helium), and the pure adsorbate fed into the column at a flow rate of 0.2 SLPM until the equilibrium was reached. Once the adsorption step is complete, the desorption starts by feeding helium at the same flow rate. The experiments were all performed at a constant temperature of 303 K and a pressure of 1.5 bar.

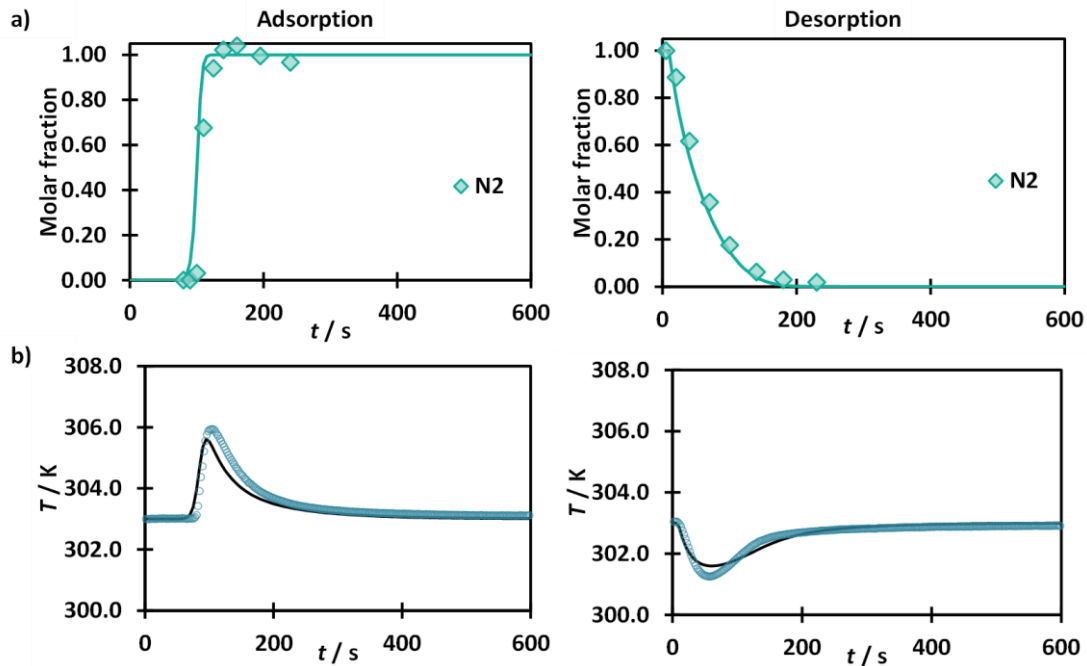


Figure 6.23 - Breakthrough results for single-component adsorption of nitrogen over the pelletized Maxsorb (Run 1): a) molar fraction at the 6th column outlet; b) temperature history in the middle of the 6th column. Lines represent the simulation results.

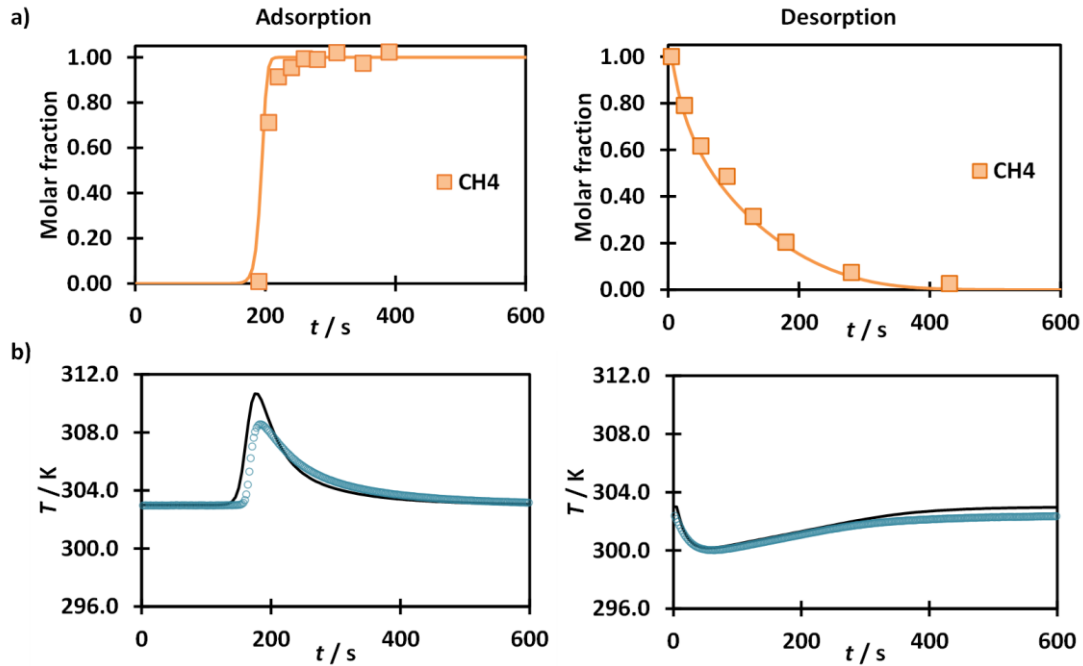


Figure 6.24 - Breakthrough results for single-component adsorption of methane over the pelletized Maxsorb (Run 2): a) molar fraction at the 6th column outlet; b) temperature history in the middle of the 6th column. Lines represent the simulation results.

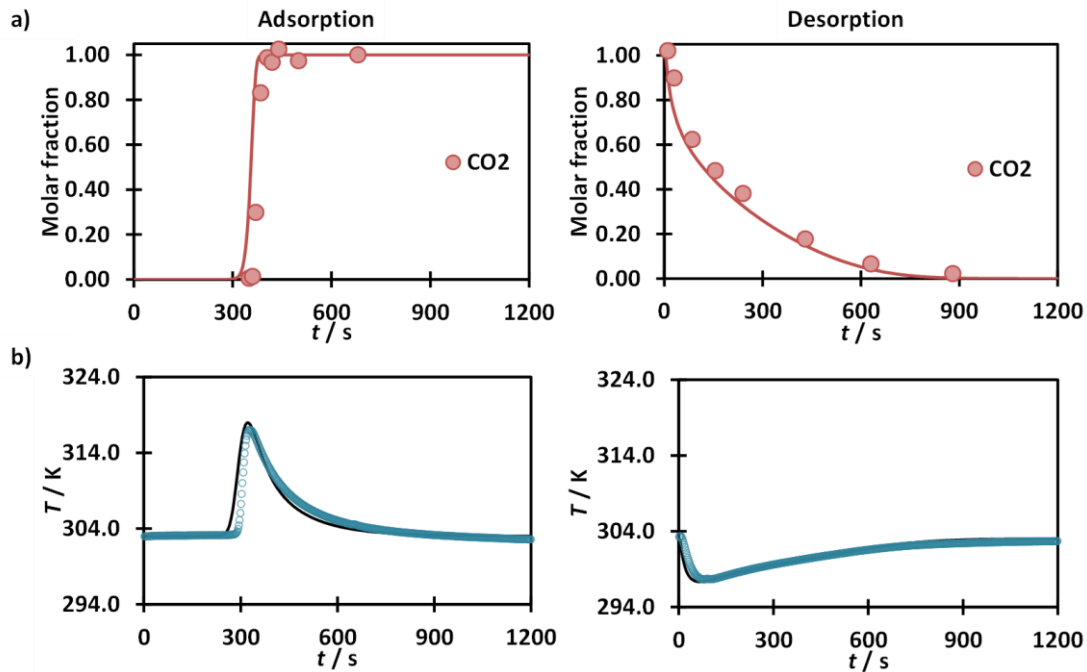


Figure 6.25 - Breakthrough results for single-component adsorption of carbon dioxide over the pelletized Maxsorb (Run 3): a) molar fraction at the 6th column outlet; b) temperature history in the middle of the 6th column. Lines represent the simulation results.

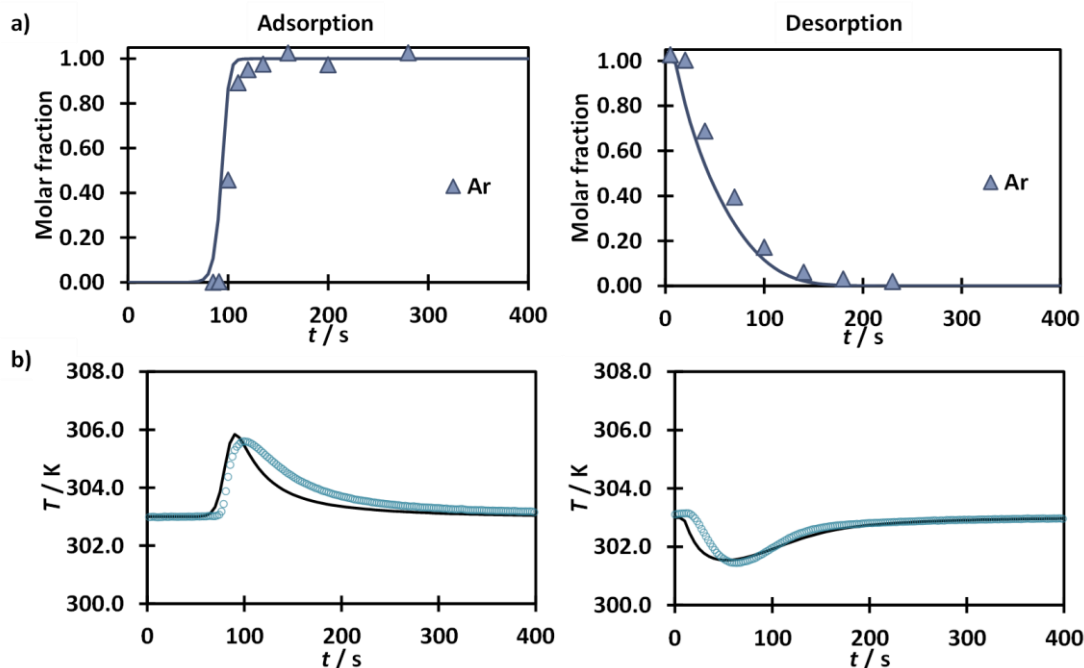


Figure 6.26 - Breakthrough results for single-component adsorption of argon over the pelletized Maxsorb (Run 4): a) molar fraction at the 6th column outlet; b) temperature history in the middle of the 6th column. Lines represent the simulation results.

As expected from the adsorption equilibrium isotherms, argon breaks through the column outlet sooner (at 85 s) than the other components, exhibiting the lowest capacity at the specified operating conditions. For this experiment, the temperature increase as the adsorption process occurs is also the lowest, about 2.9 K. The remaining components' breakthrough times are 90, 180, and 335 s for nitrogen, methane, and carbon dioxide, respectively. The highest thermal peak was observed for the adsorption of CO_2 , with an amplitude of 13.8 K. These results are in accordance with both the adsorption equilibrium data and the heat of adsorption values obtained. Also, the simulation results can predict the adsorption dynamics of the pure adsorbates well.

Run 5 corresponds to the binary adsorption of an equimolar mixture of methane and nitrogen onto the Maxsorb pellets at the same temperature and pressure conditions as the previous runs. To do so, 0.1 SLPM of nitrogen and 0.1 SLPM of methane were fed into the fixed beds, which were previously regenerated with helium. Helium was also used to regenerate the adsorbent during the desorption process. The results of the binary breakthrough experiment are presented in Figure 6.27. The results show that, as nitrogen exhibits a lower adsorption capacity at 0.75 bar when compared to methane, it breaks through sooner, with only nitrogen being detected at the column outlet. As the saturation capacity of methane is reached, it starts to be detected, and the composition of the outlet stream converges to the value of the feed composition until the beds are completely saturated with the mixture. During this process, two thermal peaks can be observed due to the heat released during the adsorption process of both components. The mathematical model is able to describe the multicomponent adsorption behaviour of the mixture well.

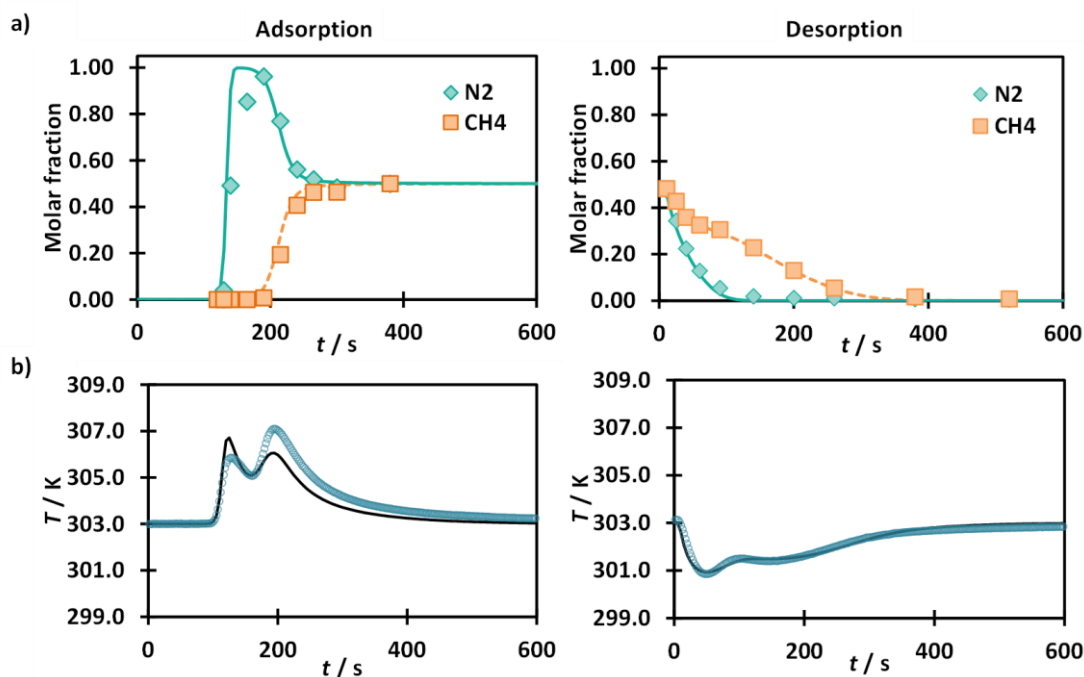


Figure 6.27 - Breakthrough results for the binary adsorption of an equimolar mixture of methane and nitrogen over the pelletized Maxsorb, initially regenerated with helium (Run 5): a) molar fraction of each component at the 6th column outlet; b) temperature history in the middle of the 6th column. Lines represent the simulation results.

For SMB operation, it is also important to investigate the multicomponent adsorption behaviour of the target mixture with the desorbent species. As such, ternary breakthrough experiments with CO_2 and Ar, which were selected as candidates for the role of the desorbent in the process, were also carried out, corresponding to Run 6 and Run 7, respectively. In these cases, the adsorbent bed is saturated with the desorbent before the adsorption step, and this species is then used for the regeneration step (desorption). The feed molar fraction selected for each component for these two assays is close to the average composition found in the separation zone during an SMB cycle to align the breakthrough results with what occurs during the process. As such, a 25% methane, 25% nitrogen, and 50% desorbent mixture with a total flow rate of 0.2 SLPM was used in these runs. These experiments not only aid with the choice of the desorbent gas but also allow the validity of the mathematical model implemented. The results for these two runs can be observed in Figure 6.28 and Figure 6.29.

We can observe that the mixture is capable of displacing the desorbent in the adsorbed phase, while the desorbent itself can also easily regenerate the bed during the desorption step. While this is true for both runs, more dispersive fronts are visible when displacing the carbon dioxide molecules in Run 6 due to the higher strength of adsorption of carbon dioxide when compared with the components present in the mixture, while more compressive fronts are observed during the desorption phase, when pure CO_2 is fed. This is also verified in the temperature histories, as the thermal wave associated with the adsorption process shows two negative peaks as the energy consumed from the CO_2 desorption compensates for the energy released from the adsorption of

the feed mixture and *vice-versa*. Meanwhile, in Run 7, the opposite occurs when argon is used, *i.e.*, the adsorption/desorption step shows compressive/dispersive fronts, respectively, with temperature changes in accordance with the affinity of the involved components. Both experiments are almost isothermal as the temperature variation is lower than 5 K. The mathematical model accurately predicts the ternary fixed-bed results, validating the implemented extended single-site Langmuir method for the multicomponent equilibrium prediction as well as the introduced transport parameters.

The dynamics observed in both steps must be taken into account when choosing a proper desorbent for SMB operation, as the adsorption and desorption happen simultaneously. Since the desorbent competes with the components in the mixture on the adsorbent's surface, its preferential affinity for the adsorption sites may be detrimental to the process. Comparing both graphics, one can conclude that the methane adsorption capacity is increased, which may lead to higher throughputs. This will be further investigated by designing and performing two SMB cycles using each gas as the desorbent.

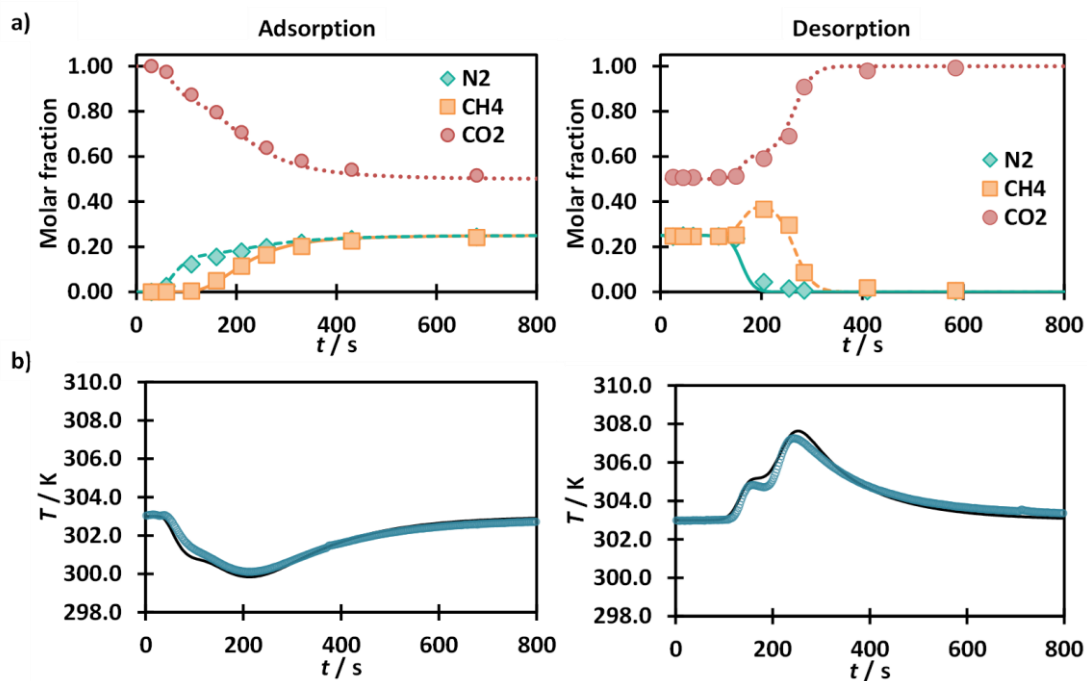


Figure 6.28 - Breakthrough results for the ternary adsorption of a mixture of 25% methane, 25% nitrogen, and 50% carbon dioxide over the pelletised Maxsorb, initially saturated with carbon dioxide (Run 6): a) molar fraction of each component at the 6th column outlet; b) temperature history in the middle of the 6th column. Lines represent the simulation results.

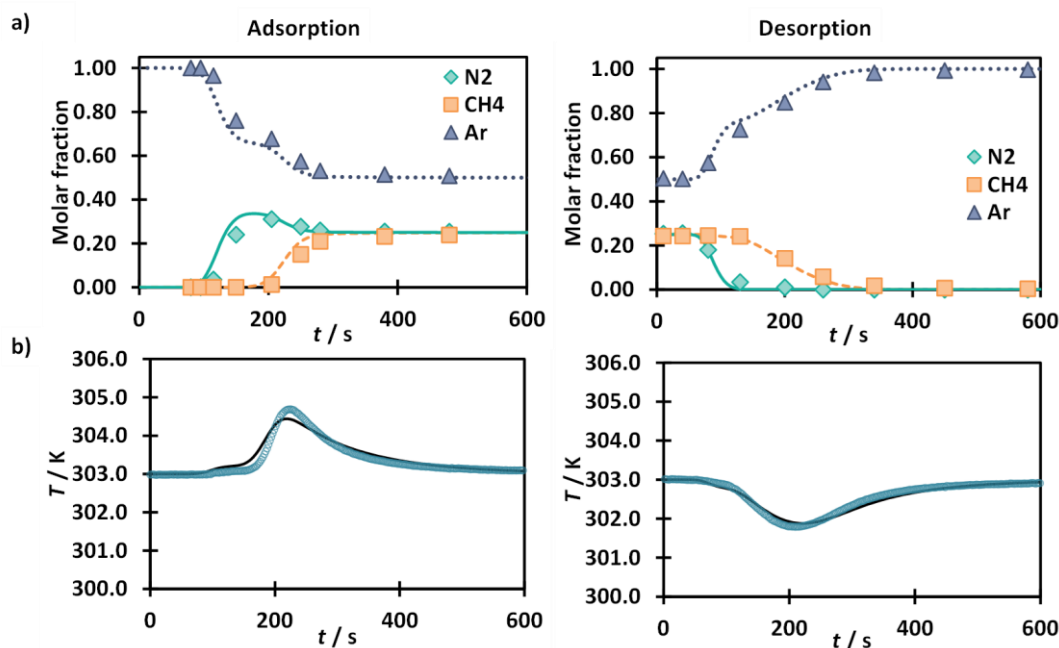


Figure 6.29 - Breakthrough results for the ternary adsorption of a mixture of 25% methane, 25% nitrogen, and 50% argon over the pelletised Maxsorb, initially saturated with argon (Run 7): a) molar fraction of each component at the 6th column outlet; b) temperature history in the middle of the 6th column. Lines represent the simulation results.

6.3.5. SMB Cycles

The SMB cycles for the separation of a mixture of methane and nitrogen were performed using a classical 2-2-2-2 column configuration, operating without the desorbent recycle loop at the end of Zone IV. With this configuration, two columns are designated to each zone of the SMB, *i.e.*, two columns are available in Zone I for adsorbent regeneration, two columns in the methane enrichment and nitrogen enrichment zones (Zone II and III, respectively) and two columns to clean the desorbent in Zone IV. The schematic of the process can be found in Figure 6.30. In Run 1, the desorbent used for the separation was carbon dioxide, while in Run 2, argon was used instead. Both cycles were operated at 303 K and with the backpressure set at 1.5 bar. A switching time of 50 s was used, which was estimated based on the breakthrough results, considering the equilibrium capacity at the defined conditions and flow rates used. The flow rates in each inlet and outlet are given in Table 6.14.

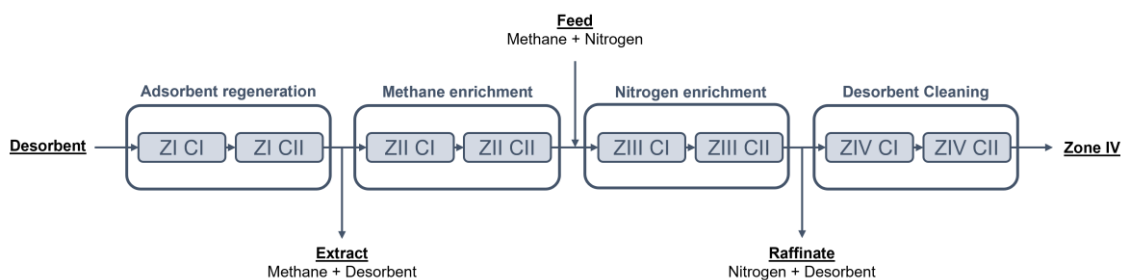


Figure 6.30 - Schematic representation of the gas-phase SMB cycle with a 2-2-2-2 column configuration, in the open-loop operation.

Table 6.14 - Operating conditions for the performed SMB cycles with Maxorb pellets.

Run	T (K)	P (bar)	t_s (s)	Desorbent	Q_D (SLPM)	Q_F (SLPM)	Q_x (SLPM)	Q_R (SLPM)	Q_{IV} (SLPM)
1	303	1.50 - 1.82	50	CO ₂	0.472	0.035 CH ₄ (0.54) 0.030 N ₂ (0.46)	0.182	0.264	0.091
2	303	1.50 - 2.00	50	Ar	0.720	0.066 CH ₄ (0.51) 0.060 N ₂ (0.49)	0.584	0.197	0.065

The composition profiles along the beds, presented in Figure 6.31 and Figure 6.33, were obtained at 50% of the switching time once the system reached a cyclic steady state, taken after 15 cycles had elapsed. Also, the molar fraction histories at the outlet of each column for both runs are presented in Figure 6.32 and Figure 6.34 to analyse how the concentration front travels during each step. The performance of each cycle is then evaluated in terms of purity (desorbent-free basis), recovery, productivity, and desorbent consumption. The equations utilised to calculate the performance parameters are available in Section 3.7.2. The values obtained for each of the performance parameters are presented in Table 6.15.

As can be seen, in both cycles, the molar fraction of the most retained species, CH₄, increases in section II, enriching the extract stream obtained at the end of section I. In section III, the least retained species, N₂, travels with the fluid phase toward the raffinate port at the end of section III, with its content increasing. In section I, the desorbent displaces the adsorbed phase, regenerating the solid material. In zone IV, the desorbent is cleaned, allowing the stream to be recycled into section I without contamination. Further analysis of both sections, section I and section IV, indicate that both SMB cycles can be optimised by not only decreasing the desorbent flow rate but also increasing the zone IV outlet stream to make better use of the second column in each section. The unit should also be operated in closed loop to decrease the desorbent consumption. Also, after separation of the downstreams, which is a necessary step in an SMB process to obtain pure CH₄ and N₂, the desorbent can be recovered and reintroduced into the process.

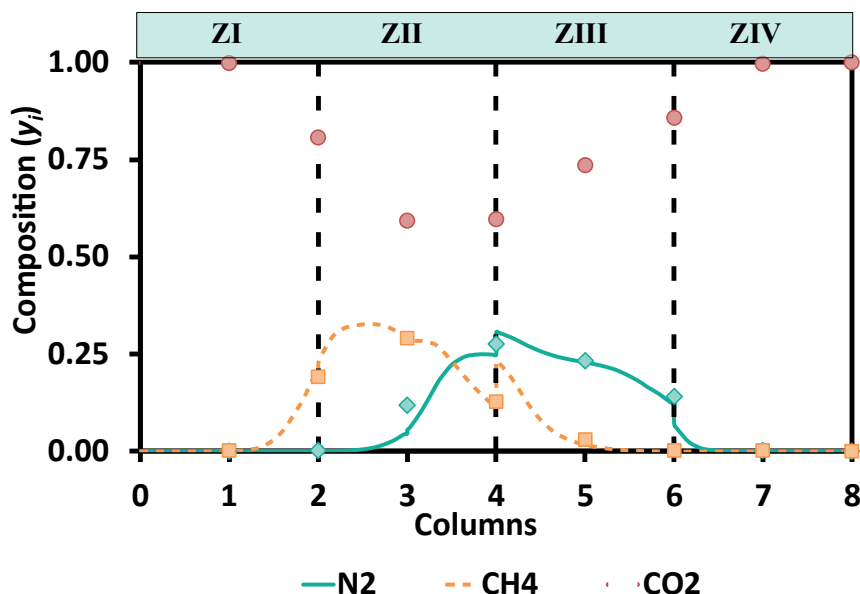


Figure 6.31 - Internal profile at 50% of the switching time for Run 1 of SMB operation with Maxsorb pellets, where carbon dioxide is used as the desorbent. Points represent experimental data, and lines represent the model predictions.

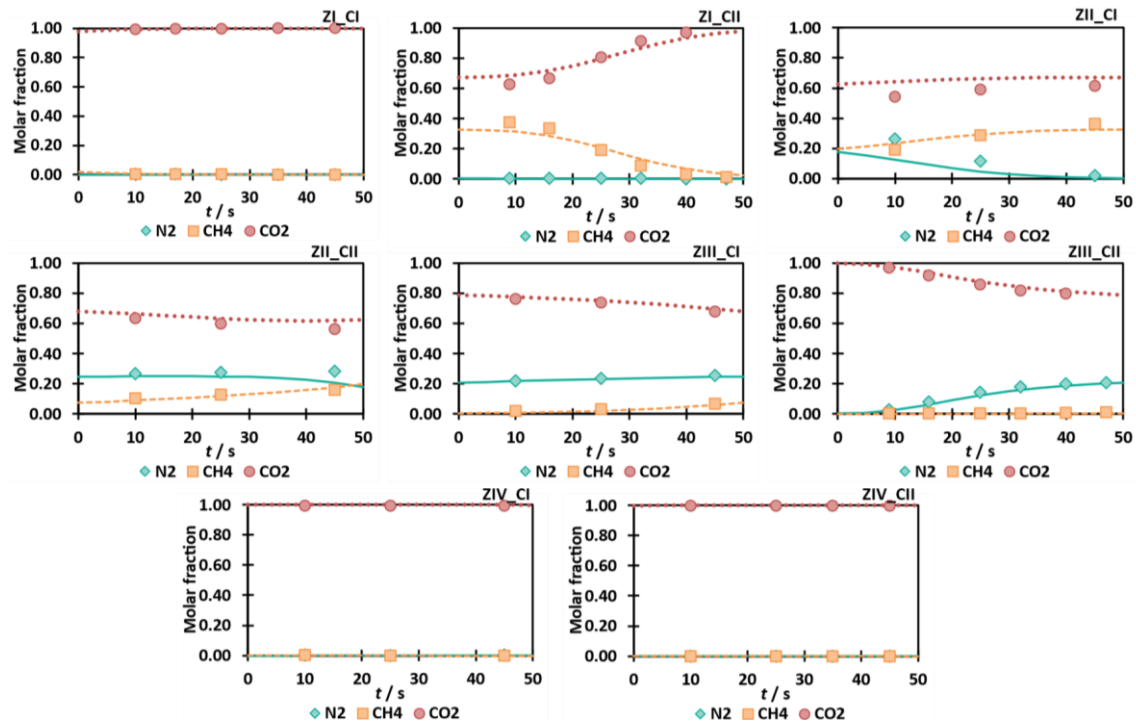


Figure 6.32 - Composition history at each column outlet for Run 1 of SMB operation with Maxsorb pellets. Points correspond to experimental data and lines to simulation data.

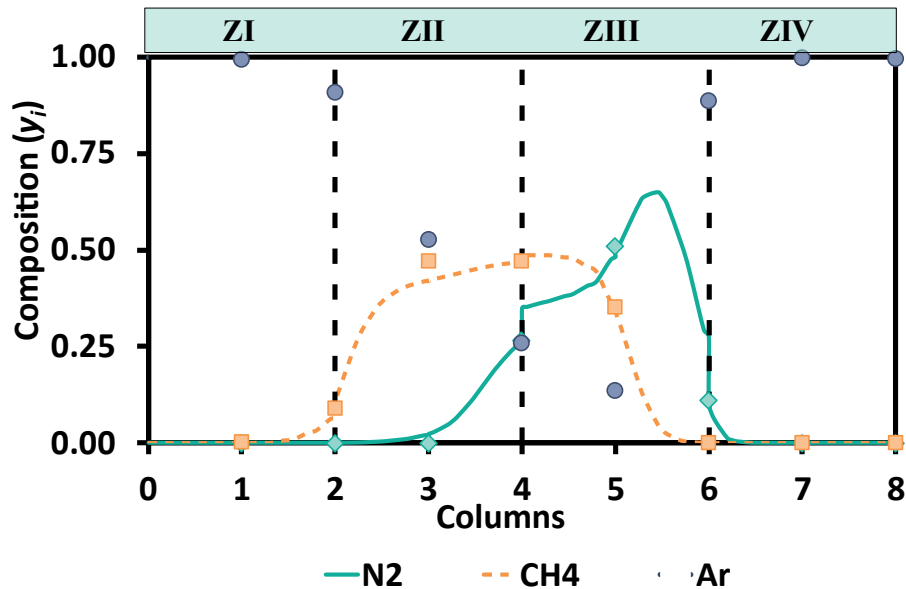


Figure 6.33 - Internal profile at 50% of the switching time for Run 2 of SMB operation with Maxsorb pellets, where argon is used as the desorbent. Points represent experimental data, and lines represent the model predictions.

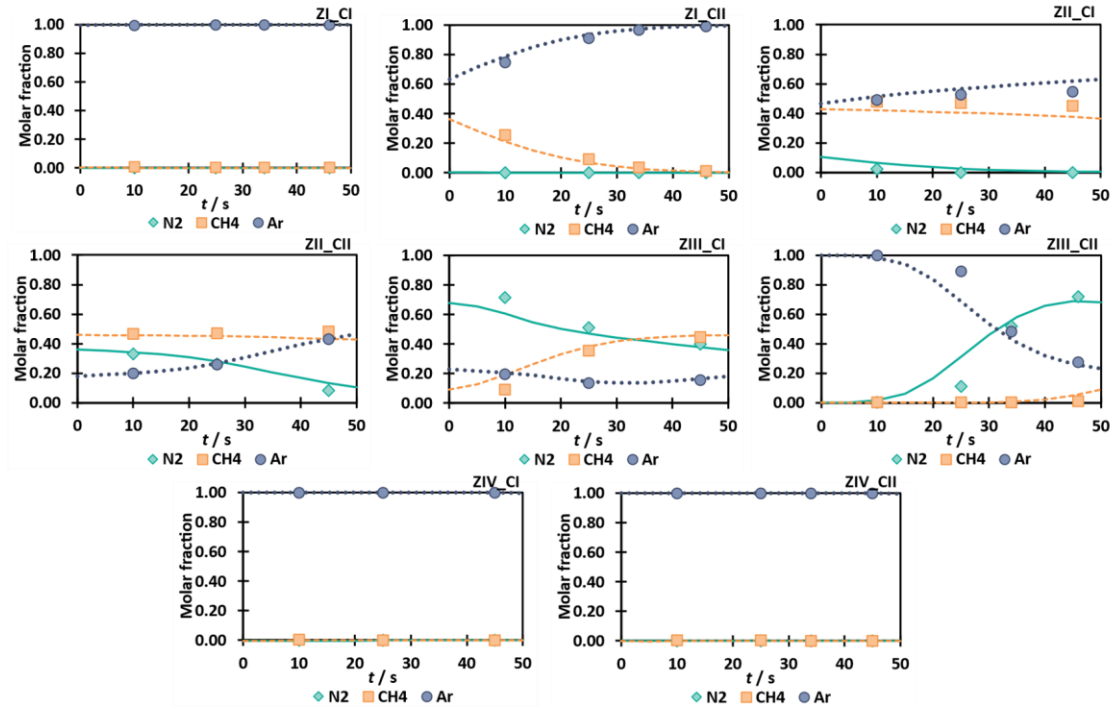


Figure 6.34 - Composition history at each column outlet for Run 2 of SMB operation with Maxsorb pellets. Points correspond to experimental data and lines to simulation data.

Table 6.15 - Performance parameters for both SMB cycles with Maxsorb pellets.

	Run 1 – CO ₂		Run 2 - Ar	
	Extract	Raffinate	Extract	Raffinate
Purity (%)	99.3	97.0	100.0	98.8
Recovery (%)	97.2	99.2	99.0	100.0
Productivity (kg·m⁻³_{ads}·h⁻¹)	17.8	26.7	35.1	55.8
Desorbent Consumption (m³_{STP,desorbent}·kg⁻¹)	18.9		15.3	

The pressure and temperature variation during the cycle, for each run, can be observed in Figure 6.35 to Figure 6.38. The more noticeable pressure drop between section I and section IV can be explained by the difference in fluid velocity. If operating in closed-loop, a vacuum pump is necessary to recompress the desorbent to be fed in section I. Otherwise, the pressure differential set by the pressure of the inlet gases and the backpressure is sufficient to maintain gas flow without requiring additional compression. The temperature variation during a cycle is about 10 K for Run 1 and 7 K for Run 2. In Run 1, because of the higher affinity of CO₂ relative to the mixture components, a temperature increase is observed in section I while the temperature decreases inside the separation zone (sections II and III). In Run 2, the higher heat of adsorption of CH₄ and N₂ when compared to Ar leads to the opposite behaviour of the temperature fronts inside the columns.

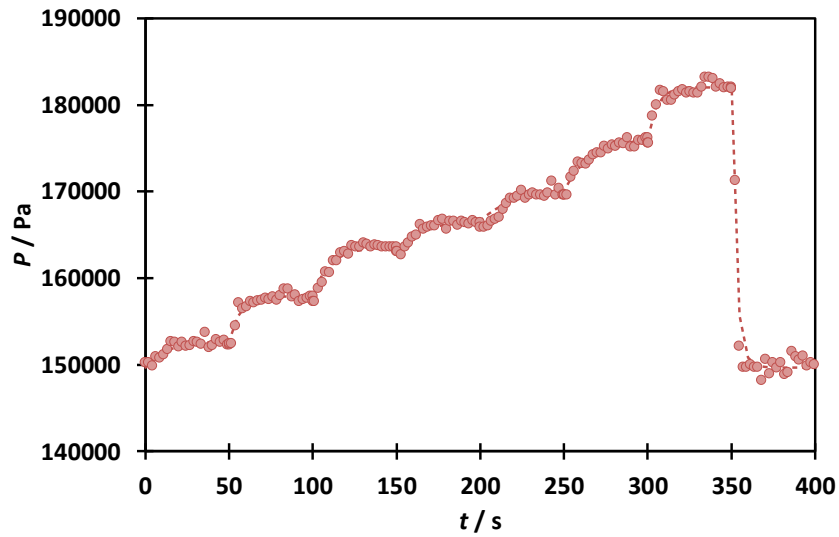


Figure 6.35 - Pressure history at the column outlet during an SMB cycle with Maxsorb pellets for Run 1.

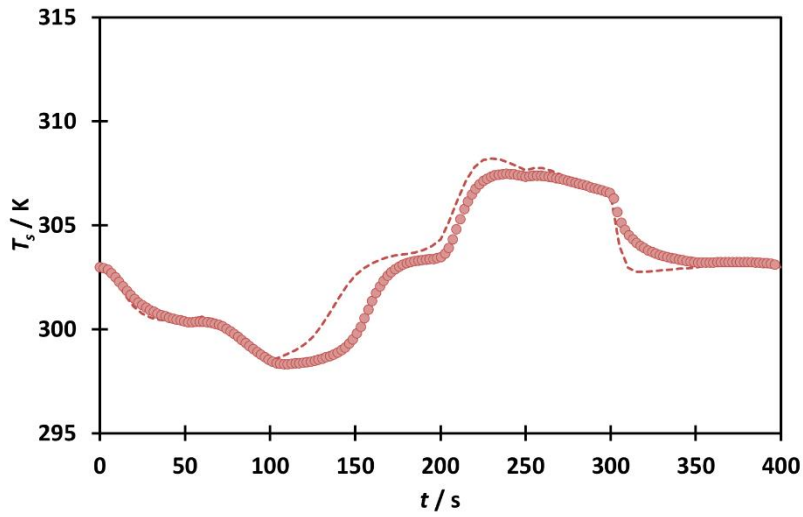


Figure 6.36 - Temperature history at the solid surface, measured in the middle of C6, during an SMB cycle with Maxsorb pellets for Run 1.

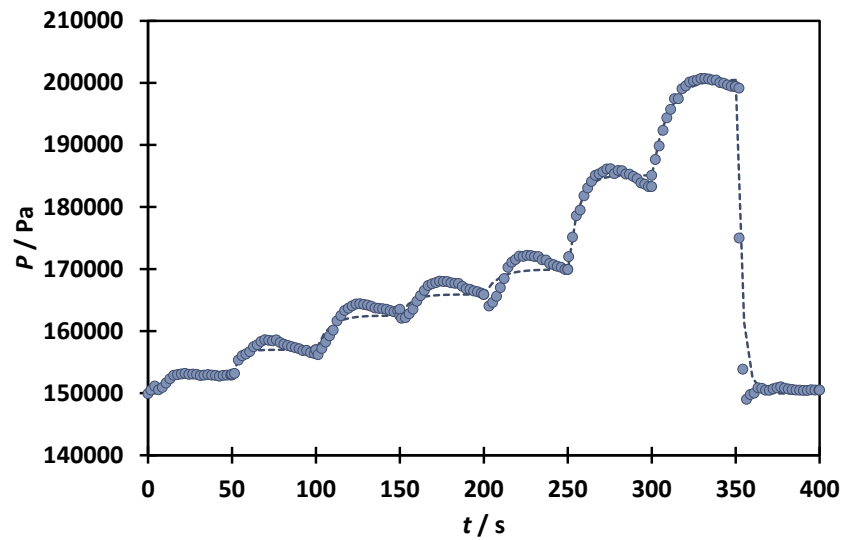


Figure 6.37 - Pressure history at the column outlet during an SMB cycle with Maxsorb pellets for Run 2.

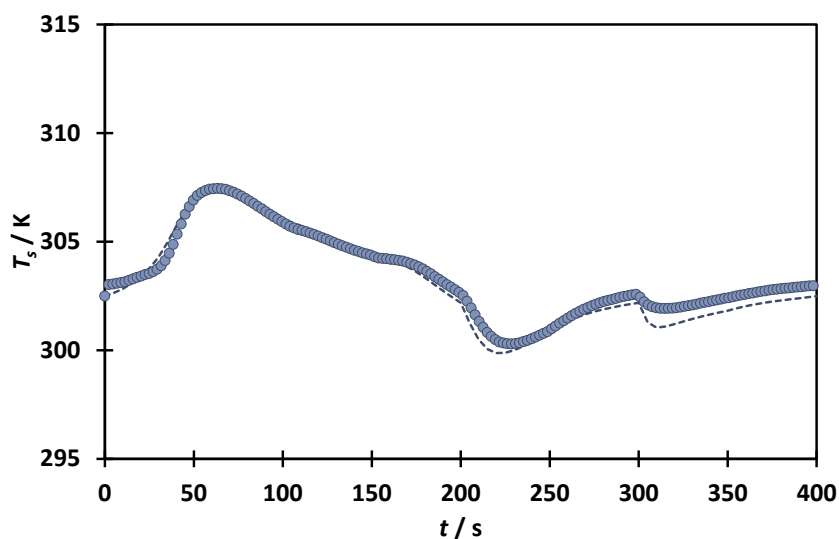


Figure 6.38 - Temperature history at the solid surface, measured in the middle of C6, during an SMB cycle with Maxsorb pellets for Run 2.

Figure 6.39 shows the computed separation regions for the design of the SMB process with both CO_2 and Ar as the desorbent species. The temperature, pressure, switching time, and feed molar fractions for each of the runs were used as inputs for the simulation. The purity specifications for the product streams were 97% and 99% for the methane and nitrogen streams, respectively. The flow rates in each section are given by the balance to the nodes (Section 3.7). The observed shape of each separation region is reflected by the nature of the desorbent used in the process, as described by Mazotti and co-workers [5]. Both operation points lie within the respective separation region. Run 1 lies on the vertex of the triangle, which indicates that the productivity is maximised for the designed process. For Run 2, a maximum of 0.155 SLPM of feed mixture can be treated to enhance the productivity of the process, *i.e.*, by operating in the separation region vertex. This way, the extract productivity value increases to $40.2 \text{ kg}_{\text{CH}_4} \cdot \text{m}^{-3}_{\text{ads}} \cdot \text{h}^{-1}$.

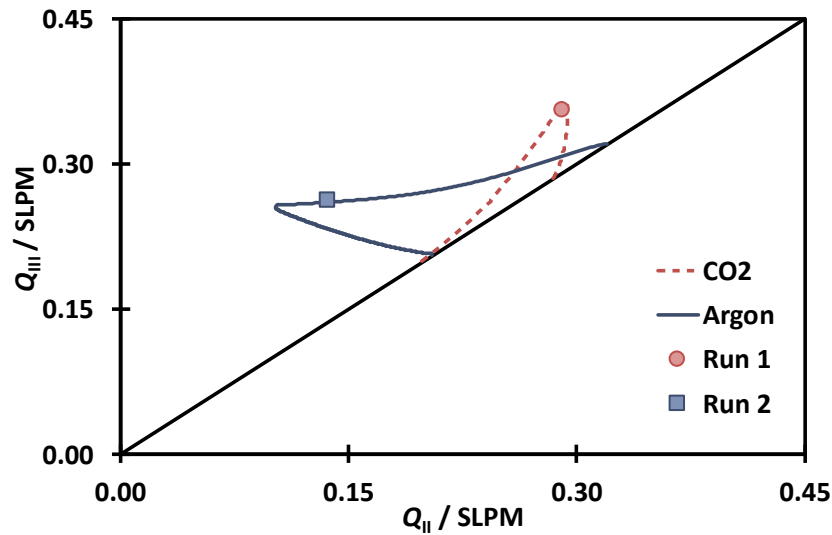


Figure 6.39 - Separation region for CH_4/N_2 separation in Maxsorb pellets determined with the complete model, with a 2-2-2-2 configuration, switching time of 50 s, temperature of 303 K, and extract and raffinate purity of 97 and 99 %, respectively, using argon (full line) and carbon dioxide (dashed line) as the desorbent gas. Points correspond to the operating conditions for Run 1 and Run 2.

Study of the Column Configuration

As discussed above, with the selected operating conditions for the two runs, only one column is necessary for both Sections I and IV of the SMB process. This way, a parametric study was conducted, focusing on the number of columns in the separation zone (sections II and III). Three different column configurations from the classical 2-2-2-2 configuration were tested to evaluate potential enhancements in the performance of the process: 1-3-3-1, 1-4-2-1, and 1-2-4-1.

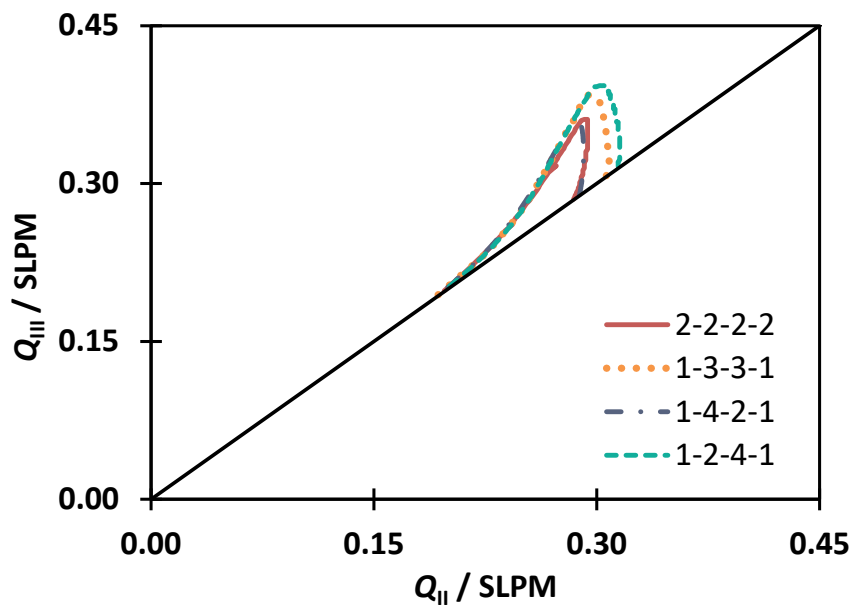


Figure 6.40 - Effect of the different column configurations in the separation region of an SMB process with Maxsorb pellets and using CO_2 as the desorbent gas.

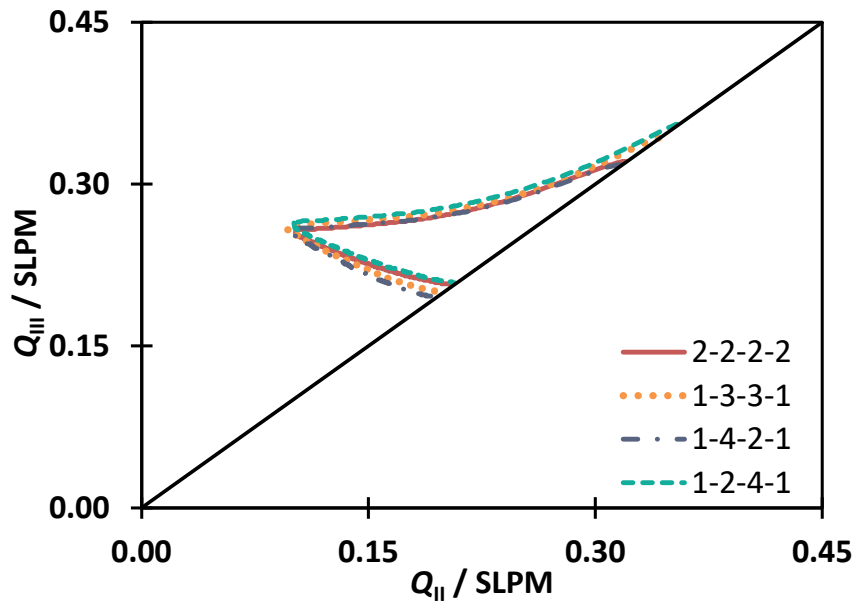


Figure 6.41 - Effect of the different column configurations in the separation region of an SMB process with Maxsorb pellets and using Ar as the desorbent gas.

The respective separation regions were computed for the three new configurations, considering both desorbents, and are compared to the traditional configuration in Figure 6.40 and Figure 6.41. The maximum productivity values were calculated for each case and can be observed in Table 6.16. The internal profiles at 90% of the switching time at cyclic steady state were also obtained for the operating conditions at maximum productivity for each case and are presented in Figure 6.42 to Figure 6.49.

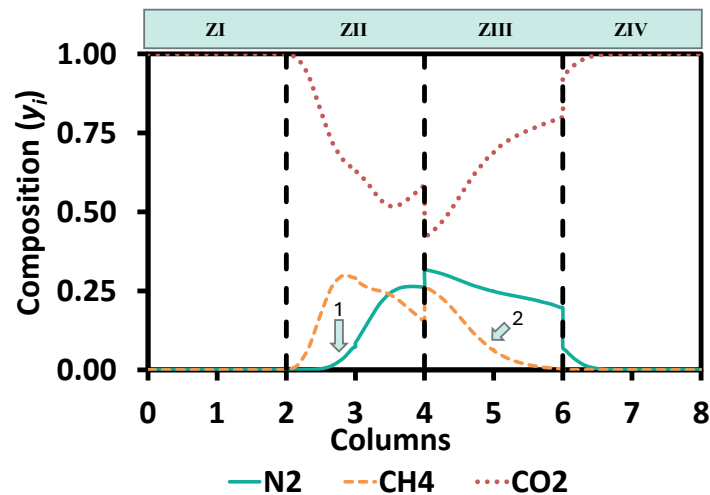


Figure 6.42 - Internal profile at 90% of the switching time for a 2-2-2-2 SMB column configuration using Maxsorb pellets and CO₂ as the desorbent at maximum productivity conditions.

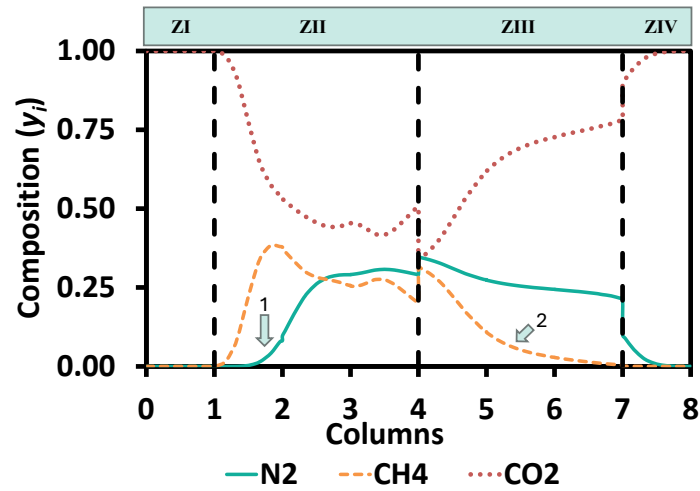


Figure 6.43 - Internal profile at 90% of the switching time for a 1-3-3-1 SMB column configuration using Maxsorb pellets and CO₂ as the desorbent at maximum productivity conditions.

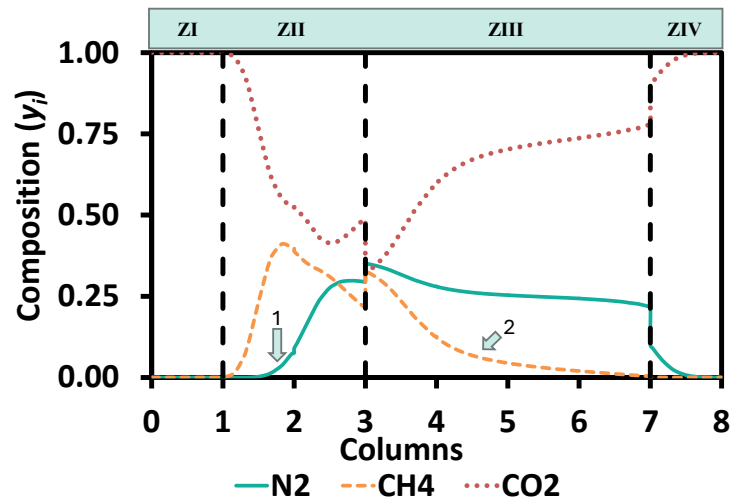


Figure 6.44 - Internal profile at 90% of the switching time for a 1-2-4-1 column configuration and CO₂ as the desorbent at maximum productivity conditions.

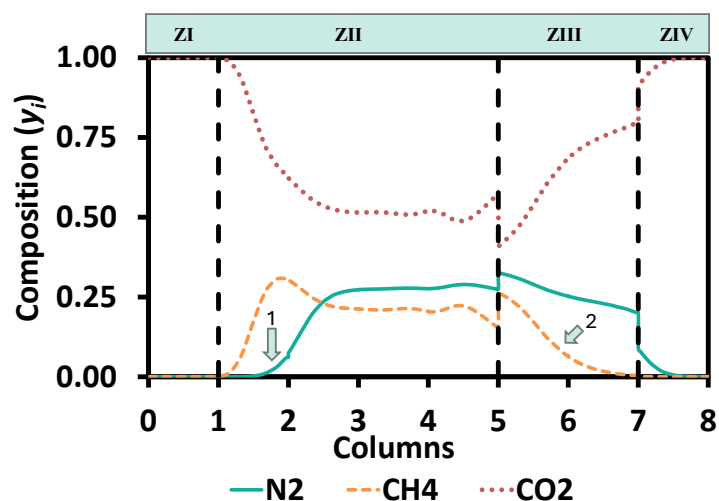


Figure 6.45 - Internal profile at 90% of the switching time for a 1-4-2-1 SMB column configuration using Maxsorb pellets and CO_2 as the desorbent at maximum productivity conditions.

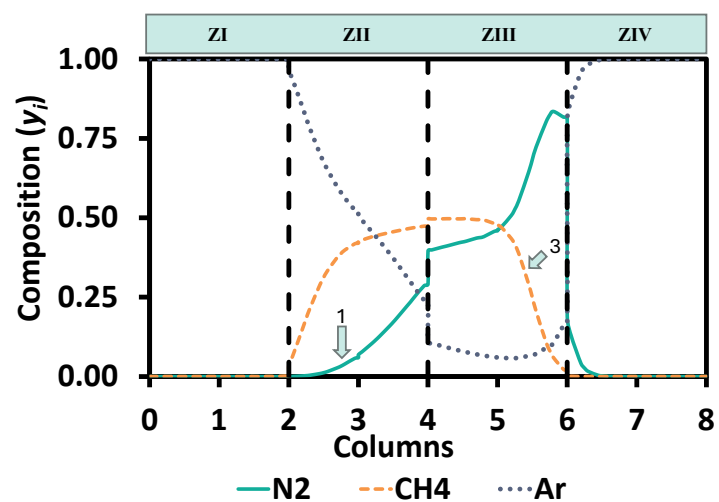


Figure 6.46 - Internal profile at 90% of the switching time for a 2-2-2-2 SMB column configuration using Maxsorb pellets and Ar as the desorbent at maximum productivity conditions.

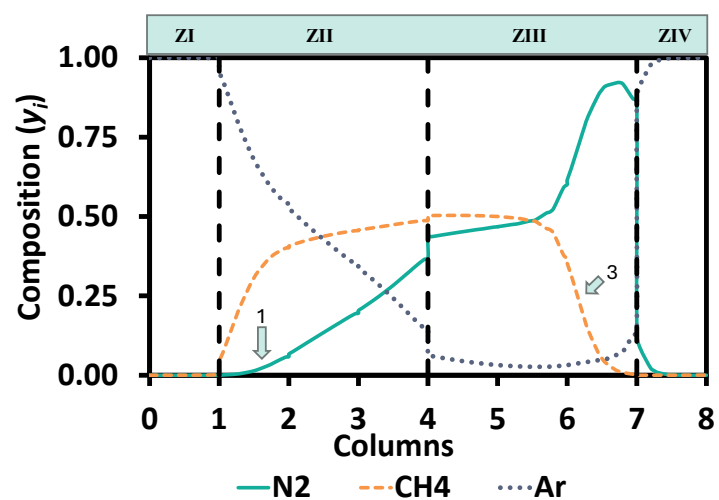


Figure 6.47 - Internal profile at 90% of the switching time for a 1-3-3-1 SMB column configuration using Maxsorb pellets and Ar as the desorbent at maximum productivity conditions.

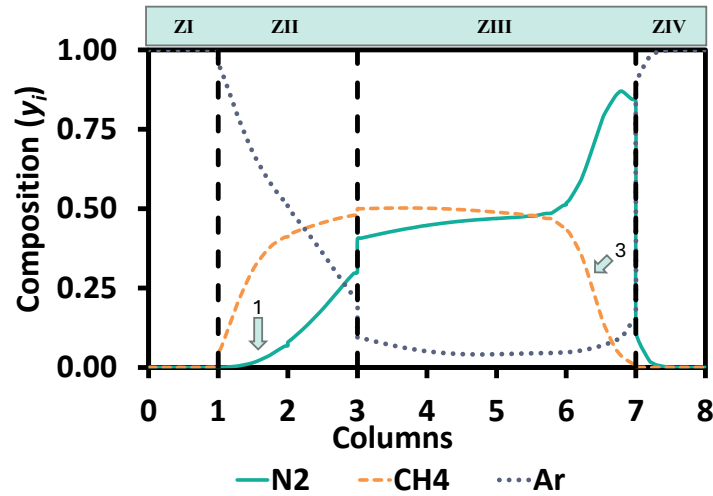


Figure 6.48 - Internal profile at 90% of the switching time for a 1-2-4-1 SMB column configuration using Maxsorb pellets and Ar as the desorbent at maximum productivity conditions.

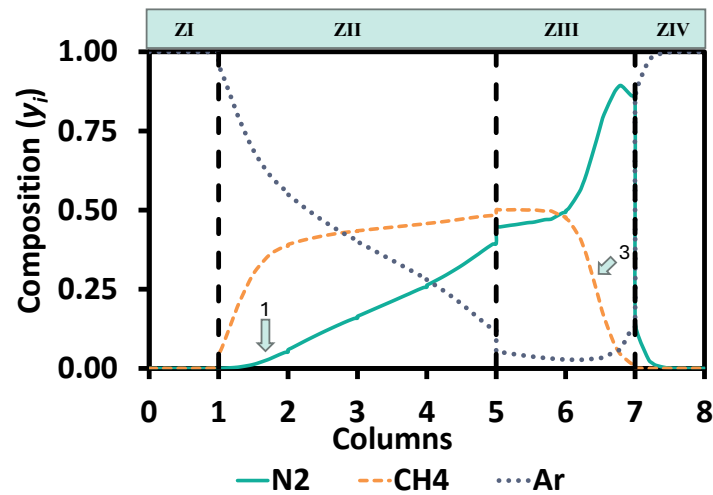


Figure 6.49 - Internal profile at 90% of the switching time for a 1-4-2-1 SMB column configuration using Maxsorb pellets and Ar as the desorbent at maximum productivity conditions.

When using CO_2 as the desorbent gas, increasing the number of columns in section II, i.e., where displacement of the mixture occurs, has no effect on the separation region. On the contrary, adding columns in Section III, i.e., the adsorption zone, originates a larger separation zone, with the maximum productivity also increasing with the number of columns allocated. Observing the regions obtained when Ar is used as the desorbent gas, increasing the number of columns in either section does not seem to impact the size of the separation region significantly, with the maximum productivity remaining approximately the same despite the number of columns. For both desorbents, when the concentration approaches zero inside the displacement zone, the mass transfer zone will travel at the same velocity, and the concentration front will always travel a fixed distance. This behaviour can be verified by comparing the fronts in the first column of Section II

(arrow 1) in Figure 6.42 to Figure 6.49. This way, increasing the number of columns in Section II will not significantly affect the separation conditions. The different behaviour observed by introducing more columns in Section III can be attributed to the difference in desorbent strength. In the case of a strong desorbent, like CO₂, the adsorption front is dispersive (arrow 2 in Figure 6.42 to Figure 6.45), so adding columns to Section III will favour the adsorption and allow higher feed flow rates to be purified. When a weak desorbent is used, which is the case of Ar, the adsorption curves are steep (arrow 3 in Figure 6.46 to Figure 6.49), and the concentration front will always be contained in the last column of the section, independently of the number of columns.

Table 6.16 - Maximum methane productivity obtained for each column configuration and desorbent using Maxsorb pellets.

	CO ₂	Ar
Column Configuration	Maximum productivity / kg _{CH₄} · m ⁻³ _{ads} · h ⁻¹ .	Maximum productivity / kg _{CH₄} · m ⁻³ _{ads} · h ⁻¹ .
2-2-2-2	17.6	40.2
1-3-3-1	23.6	42.0
1-4-2-1	18.5	40.8
1-2-4-1	25.8	42.2

This way, to improve the productivity values, the unused columns in Sections I and IV can be allocated to Section III when using CO₂ as the desorbent, increasing the methane productivity up to 25.8 kg · m⁻³_{ads} · h⁻¹.

6.4. Maxsorb activated carbon monoliths

6.4.1. Pure component adsorption equilibrium data

To verify if the adsorptive capabilities of each of the printed monoliths were similar, one of the monoliths was fragmented, and the adsorption equilibrium of each adsorbate was measured using the volumetric method described in Section 5.5.1. Pure component CH_4 , N_2 , CO_2 and Ar isotherms were collected at 303, 323, and 343 K at a pressure of up to 2.5 bar, after activation under vacuum at 383 K, overnight. The obtained equilibrium data is shown in Figure 6.50. The obtained results were then compared with the already measured equilibrium data, through a gravimetric method, by Pereira *et al.* [11].

In Figure 6.51, the comparison between the isotherms of two different monolith fragments for the four adsorbates is reported. The similarity observed between the adsorption capacities of both monoliths proves the uniformity of the 3D-printed materials. Thus, the packed beds are assumed to be homogeneous, allowing the use of the previously obtained isotherm parameters to describe the adsorption equilibrium inside the columns in the simulations. The DSL model parameters can be seen in Table 6.17, which were taken from the referenced work [11]. Regarding the desorbent strength, it is expected that, in the SMB process, CO_2 will behave as a strong desorbent while Ar will behave as a weak desorbent.

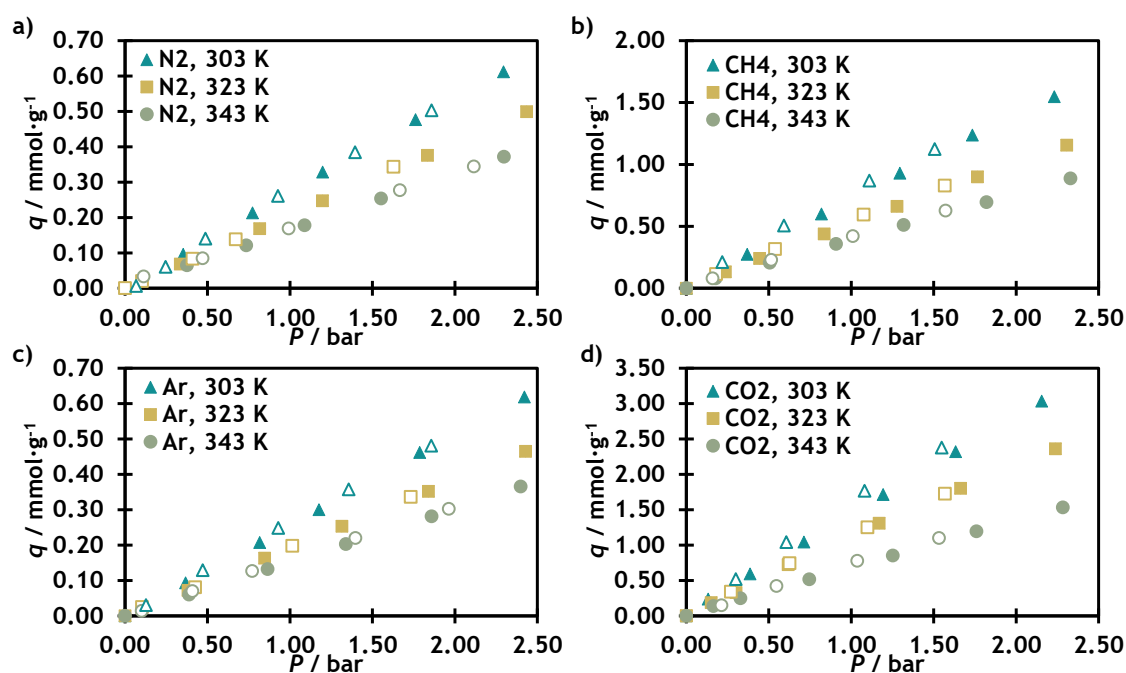


Figure 6.50 - Adsorption isotherms of a) N_2 , b) CH_4 , c) Ar and d) CO_2 over the 3D-printed Maxsorb activated carbon monoliths at 303 ($\blacktriangle$), 323 ($\blacksquare$), and 343 K ($\bullet$). Closed and open symbols represent adsorption and desorption points, respectively.

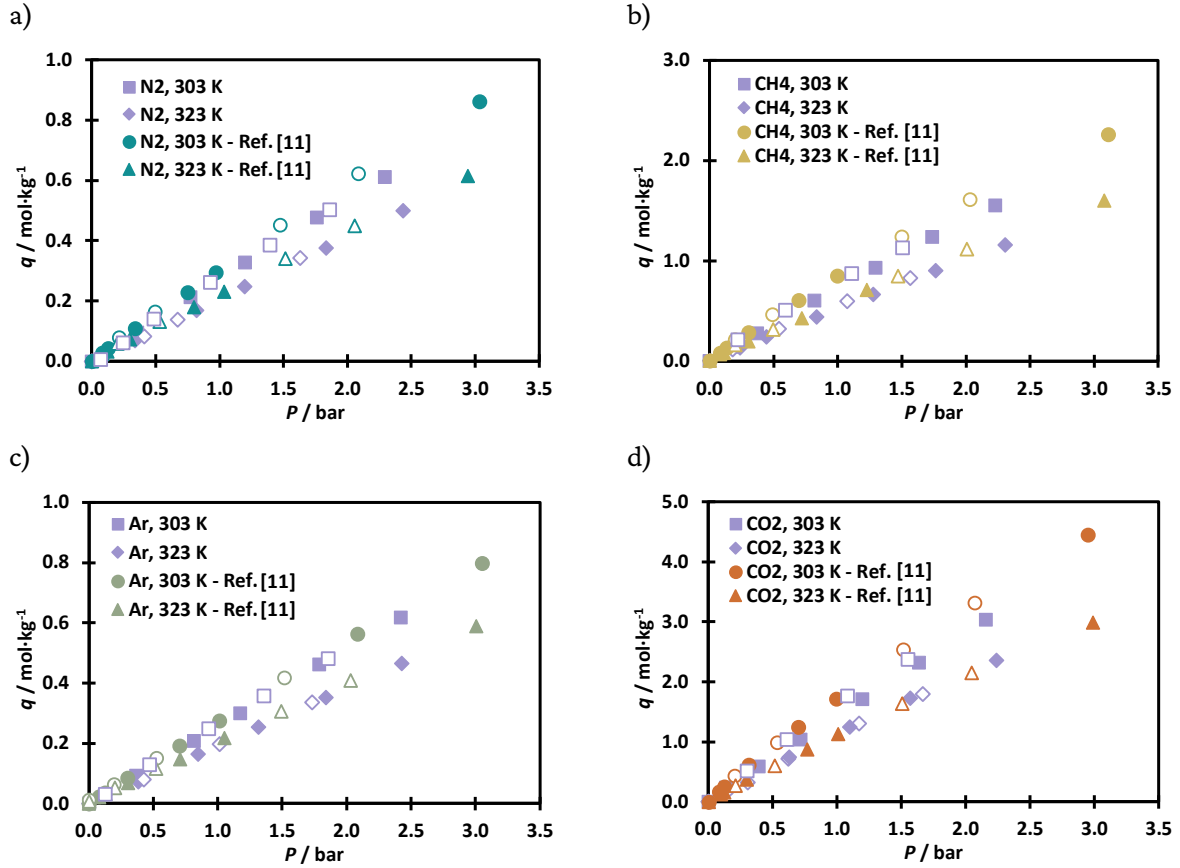


Figure 6.51 - Comparison of the adsorption equilibrium isotherms of pure a) N_2 , b) CH_4 , c) Ar , and d) CO_2 over two different printed Maxsorb monoliths at 303 and 323 K. Squares and diamonds represent the experimental points measured in this work at 303 and 323 K, respectively. Circles and triangles represent the experimental data collected from Pereira *et al.* [11] at the same temperatures. Closed and open symbols correspond to the adsorption and desorption branches, respectively.

Table 6.17 – DSL model parameters for printed Maxsorb monoliths, taken from Pereira *et al.* [11].

Species	$q_{m,1}$ mol·kg ⁻¹	$q_{m,2}$ mol·kg ⁻¹	$b_{0,1} \times 10^4$ bar ⁻¹	$b_{0,2} \times 10^4$ bar ⁻¹	$-\Delta H_1$ kJ·mol ⁻¹	$-\Delta H_2$ kJ·mol ⁻¹
N_2	4.68	3.05	1.16	2.74	14.6	13.0
CH_4	4.97	5.15	2.37	0.663	14.9	18.4
CO_2	9.32	9.49	0.185	0.716	21.9	18.3
Ar	3.81	4.24	1.91	2.04	13.2	13.3

6.4.2. Fixed Bed Experiments

To evaluate the performance of the monoliths for the target separation, breakthrough experiments were conducted at 303 K and a pressure of 1.5 bar. For this purpose, two sequential columns of the SMB unit were used, each packed with eight monoliths with $2.7 \times 2.7 \times 1.0 \text{ cm}^3$ dimensions and an average mass of 13.3 g. The characteristics of the fixed beds and of the monolith are presented in Table 6.18. An approximate total flow rate of 0.19 SLPM was used in these adsorption tests. To activate the adsorbent beds, the columns were heated overnight inside the SMB oven at 393 K

under helium. The outlet composition was analysed by gas chromatography (GC), as detailed in Section 5.6.

To assess the pure component adsorption dynamics, single breakthrough experiments were performed for the four gases (N_2 , CH_4 , Ar, and CO_2). As observed in Table 6.19, the experiment begins with the beds filled with helium, with the adsorption step starting by feeding the respective gas (Runs 1 to 4). To evaluate the competitive adsorption behaviour, binary and ternary tests were carried out. The operating conditions for these assays are also presented in Table 6.19 (Runs 5 to 7). Through these experiments, it is possible to validate the mathematical model proposed in Section 3.6.

Table 6.18 - Fixed-bed, and monolith properties.

Properties	Value
Bed Length / m	0.081
Bed Internal Width / m	0.027
Column Wall Width / m	0.001
Bed Mass / g	13.3
Bed Voidage Fraction (ϵ_b)	0.385
Bed Density (ρ_b) / $\text{kg} \cdot \text{m}^3$	220.8
Solid Density / $\text{kg} \cdot \text{m}^3$	2076
Wall Specific Heat Capacity ($\tilde{c}_{pw}$) / $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	500
Column wall density (ρ_w) / $\text{kg} \cdot \text{m}^3$	8238

Table 6.19 - Operating and initial conditions for the fixed-bed experiments with printed Maxsorb monoliths performed at 303 K and 1.5 bar.

Run	1	2	3	4	5	6	7
Initial Conditions	He	He	He	He	He	Ar	CO_2
Flow rate / SLPM	0.196	0.190	0.183	0.192	0.189	0.179	0.191
Adsorption Step	N_2	CH_4	Ar	CO_2	50% CH_4 + 50% N_2	25% CH_4 + 25% N_2 + 50% Ar	25% CH_4 + 25% N_2 + 50% CO_2
Regeneration Conditions	He	He	He	He	He	Ar	CO_2

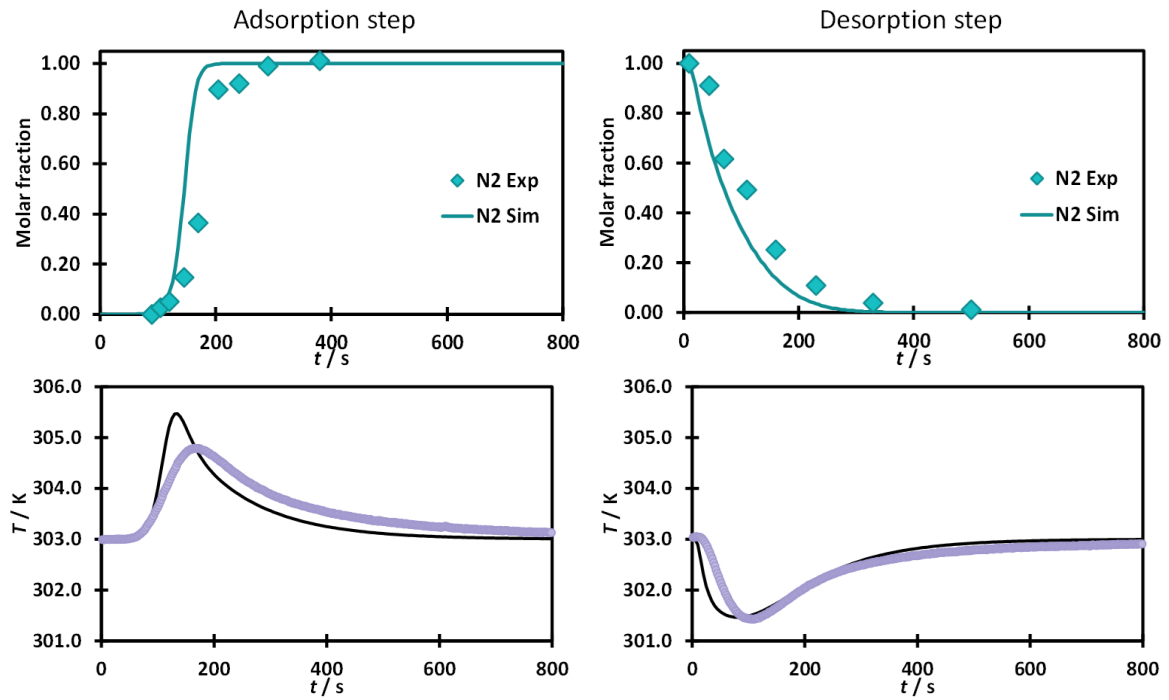
The single component, binary and ternary breakthrough tests, performed at 303 K and 1.5 bar, are presented in Figure 6.52. The temperature histories at the middle of the second column for each assay are also presented in this figure. All experimental data is also compared with the respective dynamic simulation. The transport parameters used in the simulations are presented in Table 6.20.

Table 6.20 - Transport parameters used in the breakthrough simulations using printed Maxsorb monoliths.

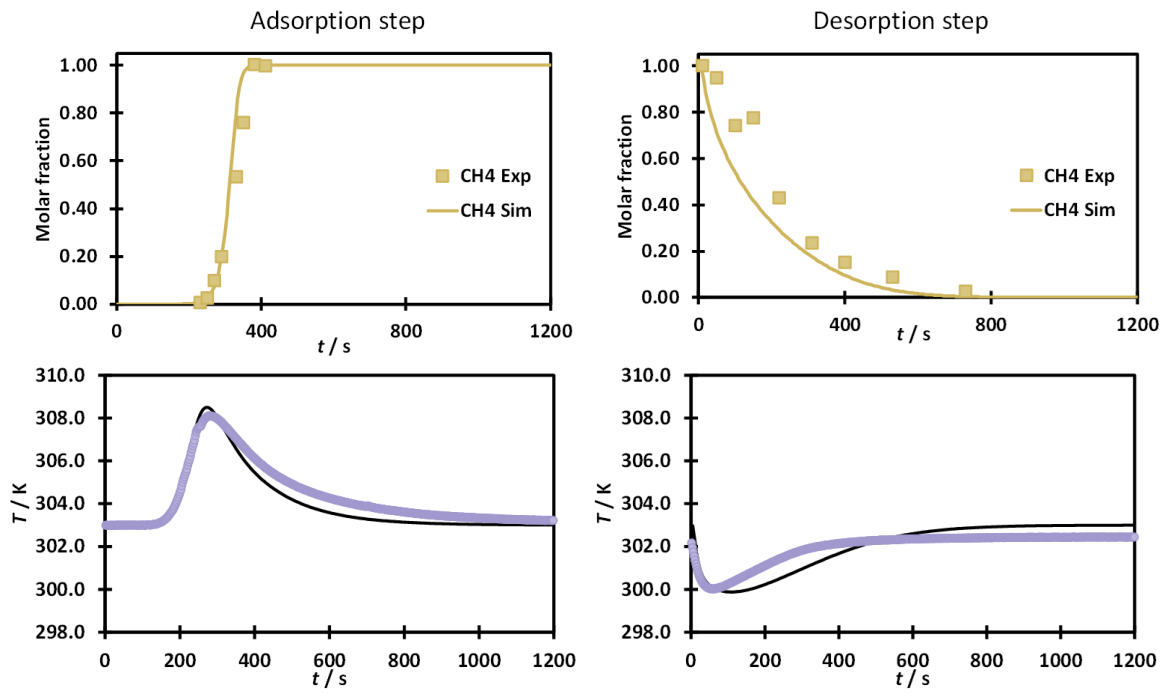
	D_{ax} $\times 10^5$ ($m^2 \cdot s^{-1}$)	k_f $\times 10^2$ ($m \cdot s^{-1}$)	λ ($W \cdot m^{-1} \cdot K^{-1}$)	h_f ($W \cdot m^{-2} \cdot K^{-1}$)	$k_{macro,i}$ (s^{-1})	$k_{micro,i}$ (s^{-1})	U ($W \cdot m^{-2} \cdot K^{-1}$)	h_w ($W \cdot m^{-2} \cdot K^{-1}$)
Run 1	5.4	3.98	0.36	42.4	1	1	50	100
Run 2	5.34	3.86	0.47	55	1	1	50	100
Run 3	5.51	4.21	0.46	53.4	1	1	50	100
Run 4	5.08	3.49	0.36	44.9	1	0.1	50	30
Run 5	5	3.14	0.42	48.6	N ₂ : 1 CH ₄ : 1	N ₂ : 1 CH ₄ : 1	50	100
Run 6	3	1.37	0.16	21.1	N ₂ : 1 CH ₄ : 1 Ar: 1	N ₂ : 1 CH ₄ : 1 Ar: 1	50	20
Run 7	5	1.17	0.14	19.1	N ₂ : 1 CH ₄ : 1 CO ₂ : 1	N ₂ : 1 CH ₄ : 1 CO ₂ : 0.1	50	40

Figure 6.52a) to Figure 6.52d) show the single breakthrough curves for each of the four pure adsorbates. For these tests, the columns are initially filled with helium. The adsorption step starts by feeding approximately 0.19 SLPM of the pure gas. Initially, only helium exits the column at the outlet while the mass transfer zone propagates through the column. When the breakthrough occurs, the molar fraction of the adsorbate increases sharply until the bed is saturated, reaching the molar composition of the feed stream. This way, the breakthrough times for N₂, CH₄, Ar, and CO₂ are approximately 120, 260, 110, and 440 s, respectively, which is in agreement with the adsorption equilibrium results. Moreover, the sharp increase observed in the single-component BT curves near the expected stoichiometry time confirms the absence of mass dispersion and does not indicate any bypass through the monolith channels. The simulation results were able to predict the experimental data accurately.

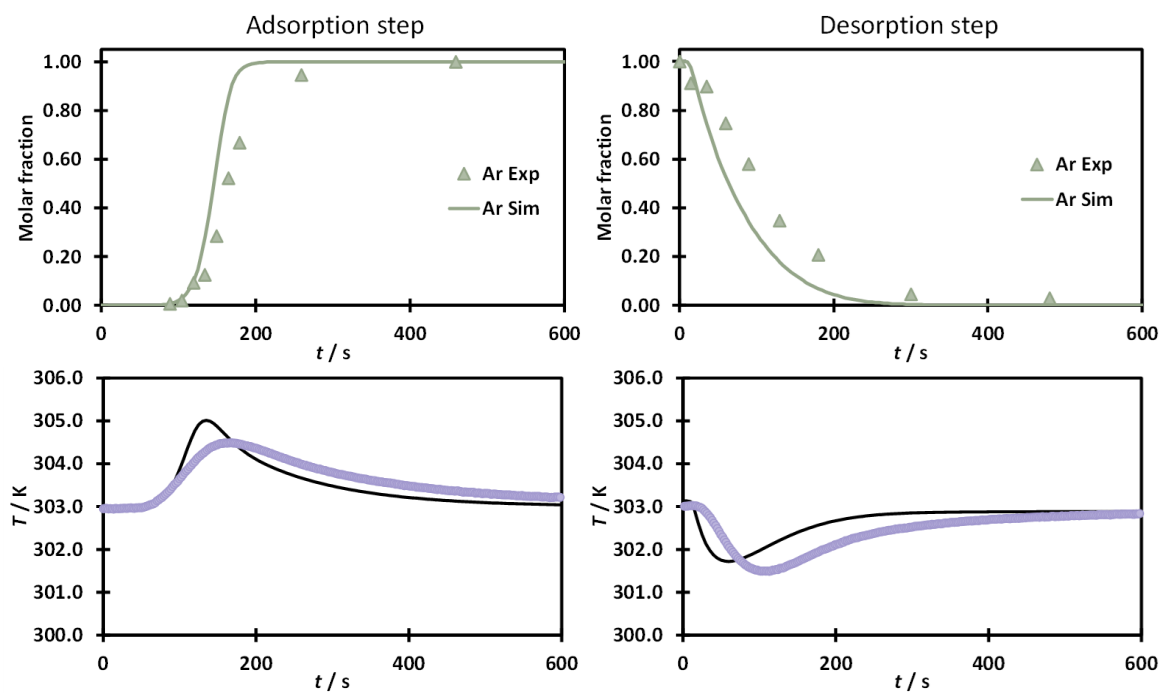
a)



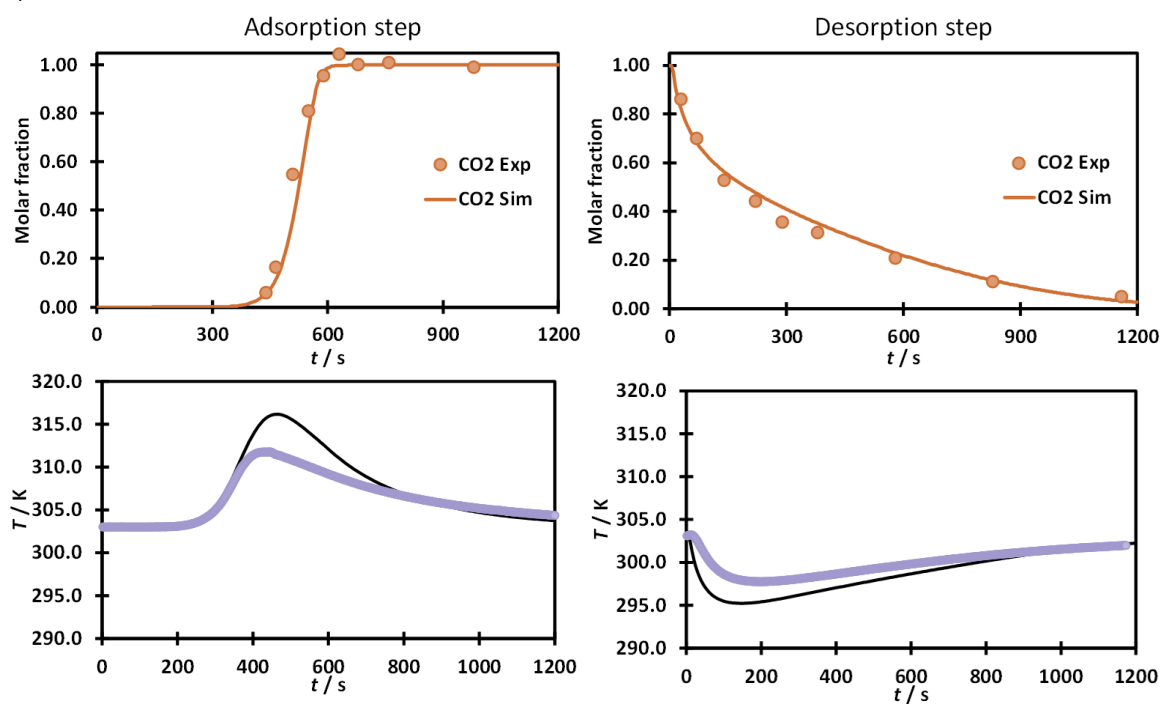
b)



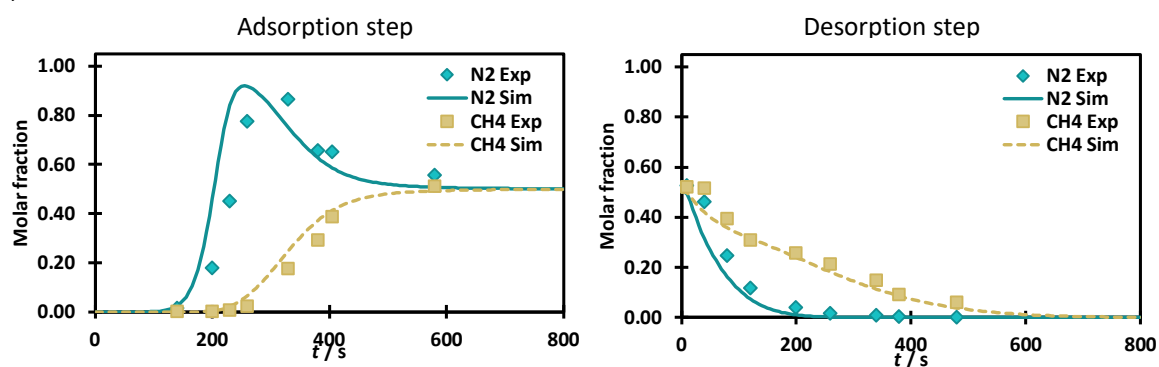
c)

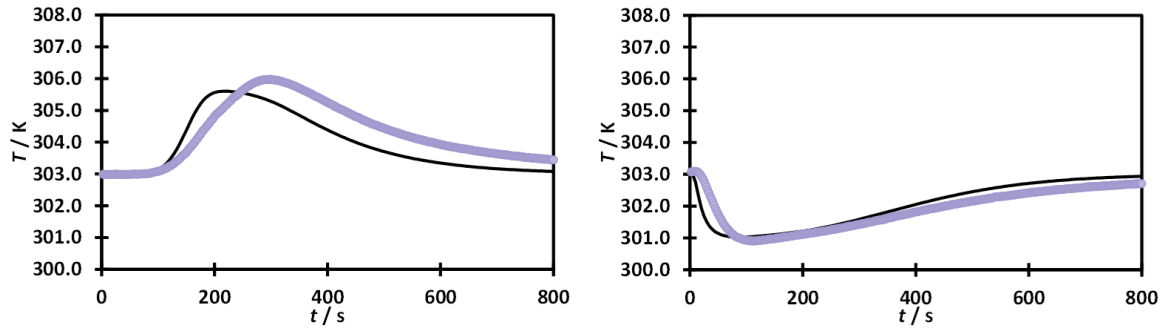


d)

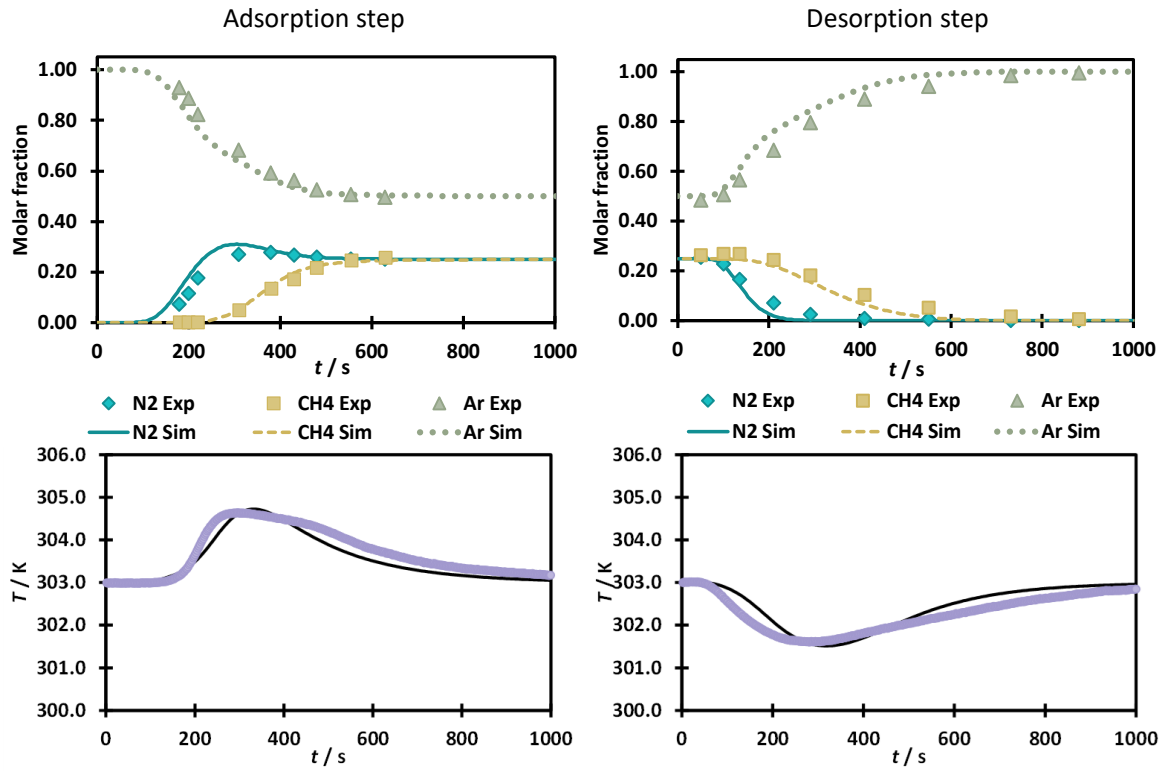


e)





f)



g)

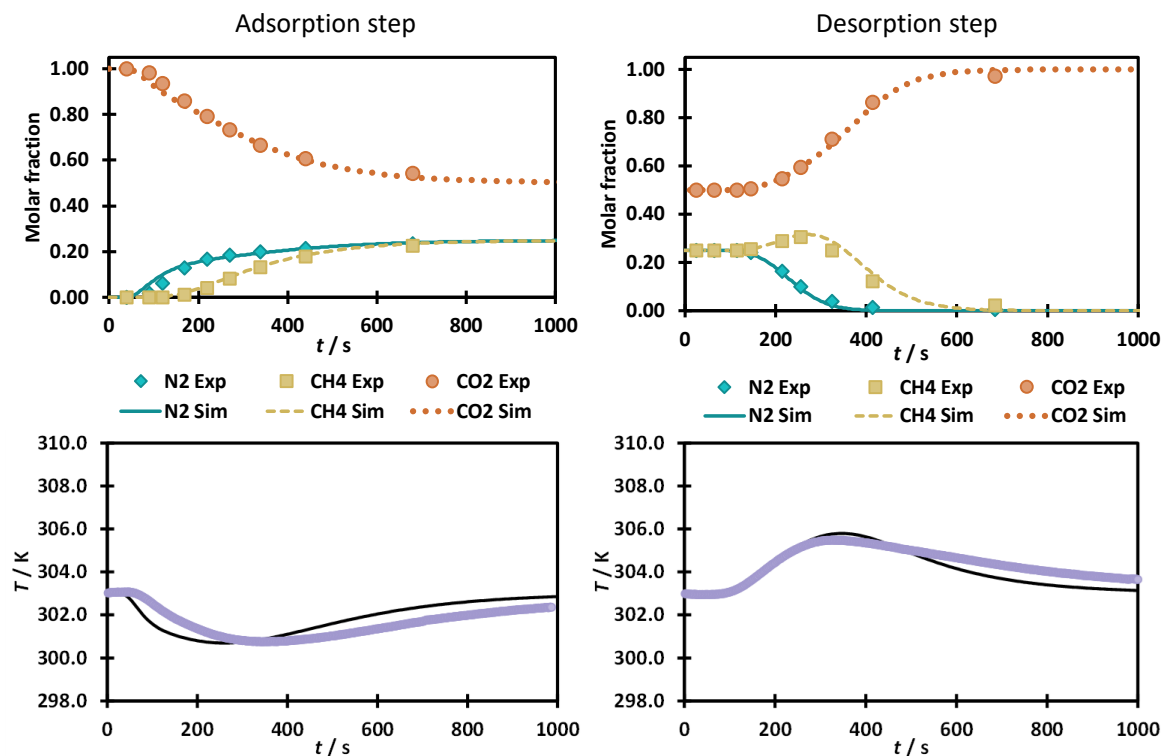


Figure 6.52 – Breakthrough curves with printed Maxsorb monoliths performed at 303 K and 1.5 bar for both adsorption and desorption steps. Figures a) to d) correspond to the single component fixed-bed experiments (Runs 1 to 4). Figure e) corresponds to the binary experiment (Run 5). Figures f) and g) correspond to the ternary experiments (Runs 6 and 7). Points correspond to experimental data, and lines represent the simulation results.

The results of the binary breakthrough test are shown in Figure 6.52e). An equimolar mixture of CH_4 and N_2 was fed into the columns, which were previously filled with helium, at a total flow rate of around 0.19 SLPM. The N_2 breakthrough occurred at approximately 150 s, with its content rapidly increasing at the column outlet. As the methane breaks through the column at 265 s, the N_2 molar fraction decreases until it reaches the feed composition. Given that the breakdown of methane occurs significantly later than that of nitrogen, it substantiates its higher affinity to the adsorbent surface.

Lastly, two ternary fixed-bed experiments were conducted to assess the adsorption behaviour of the mixture when in the presence of the desorbent. Figure 6.52f) and Figure 6.52g) show the results obtained for the test using argon and carbon dioxide, respectively. The experiment started with the beds saturated with the respective desorbent. Afterwards, a 50% desorbent, 25% methane and 25% nitrogen mixture were fed into the columns at a flow rate of approximately 0.19 SLPM. In both experiments, the mixture demonstrated the capacity to replace the desorbent, and *vice versa*. As expected, during the adsorption step, the CO_2 mass transfer front is dispersive, while for argon, the front is compressive. In the regeneration step, the contrary behaviour is noted. This indicates that the relative strength of the desorbent, when compared to the components of the target mixture, is higher for CO_2 than for Ar. This restates that CO_2 will act as a strong desorbent, while

argon will act as a weak desorbent when integrated into an SMB cycle. The performance of each of the desorbents will be further compared through the SMB runs presented in Section 6.4.3.

6.4.3. SMB Cycles

To minimise the effort of printing the adsorbent monoliths to pack the columns, the cycles were simulated beforehand using the mathematical model presented in Section 3.6 and the adsorption equilibrium isotherms presented by Pereira *et al.* [11]. With this, it was possible to define the number of columns and how to distribute them in each section to obtain complete separation of the target mixture. To reach a desorbent-free purity of 97% in the extract stream and 99% in the raffinate stream, a total of six columns are necessary, with a column configuration of 1-2-2-1. An illustration scheme of the process is presented in Figure 6.53.

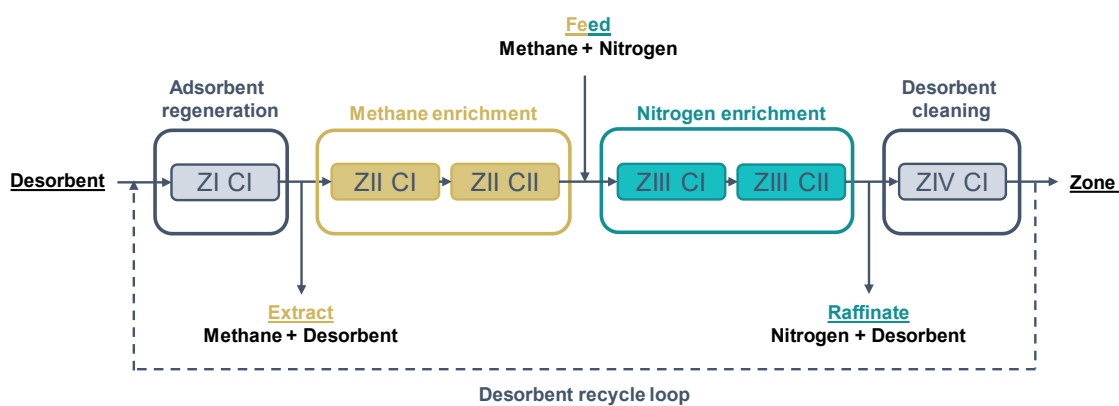


Figure 6.53 - Schematic representation of the SMB process with a column configuration of 1-2-2-1. The desorbent recycle loop is only used when in closed loop operation.

In addition, with these simulations, the separation regions for both desorbents were drawn to estimate possible conditions for SMB operation. Notably, this separation region is only used to obtain a preliminary starting point, and the conditions are tuned during each experiment until the mixture is effectively separated. The protocol used to obtain the separation regions can be found in Section 3.7.3.

This way, three SMB cycles were designed and performed, with a switching time of 110 s. The first two cycles were operated in open loop, with argon and carbon dioxide as desorbents, since it is easier to maintain the stability and to control the cyclic operation in this mode, as it eliminates the need for desorbent recycling. Then, a third cycle, in closed-loop operation, with argon as the desorbent, was conducted as proof of concept. Figure 6.54 to Figure 6.56 show the internal composition profile along the columns at half of the switching time for Case 1, Case 2, and Case 3, respectively. Throughout the experiments, composition histories at the column outlet were acquired to assess the variation of the gas molar fraction during a time step. These histories can also be found in Figure 6.54 to Figure 6.56. Table 6.21 shows the operating flow rates of each of the conducted experiments, where P is the system pressure, and Q_D , Q_F , Q_X , Q_R , and Q_{IV} are the desorbent, feed, extract, raffinate, and zone IV flowrates, respectively.

Table 6.21 – Operating conditions in each SMB case using printed Maxsorb monoliths.

Case	Mode	P / kPa	Desorbent	Q_D / SLPM	Q_F / SLPM	Q_x / SLPM	Q_R / SLPM	Q_{IV} / SLPM
1	Open-loop	149-192	CO ₂	0.591	0.020 CH ₄ + 0.020 N ₂	0.285	0.227	0.119
2	Open-loop	150-196	Ar	0.730	0.040 CH ₄ + 0.040 N ₂	0.532	0.238	0.040
3	Closed-loop	190-233	Ar	0.590	0.040 CH ₄ + 0.040 N ₂	0.515	0.138	0.159

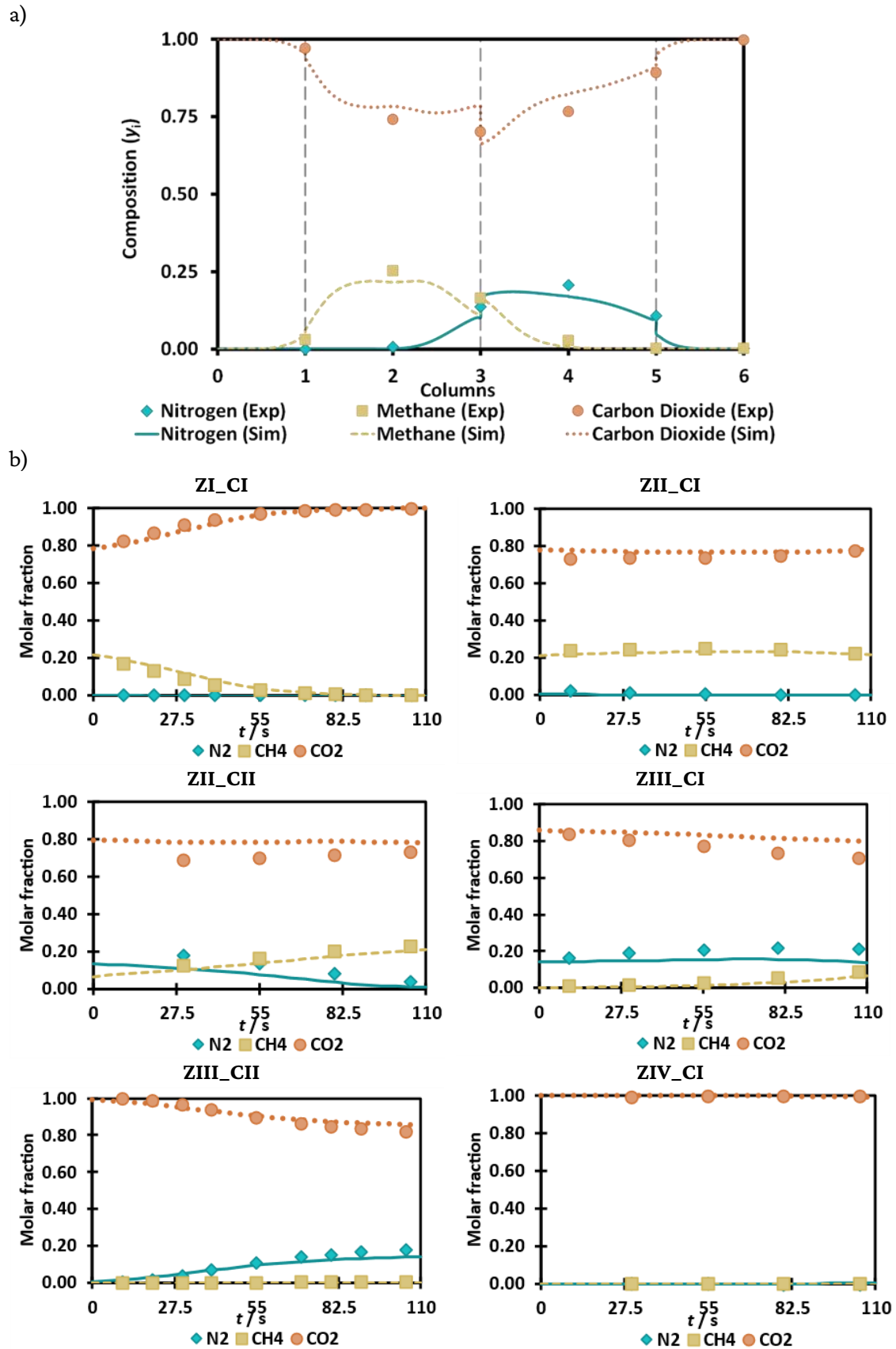
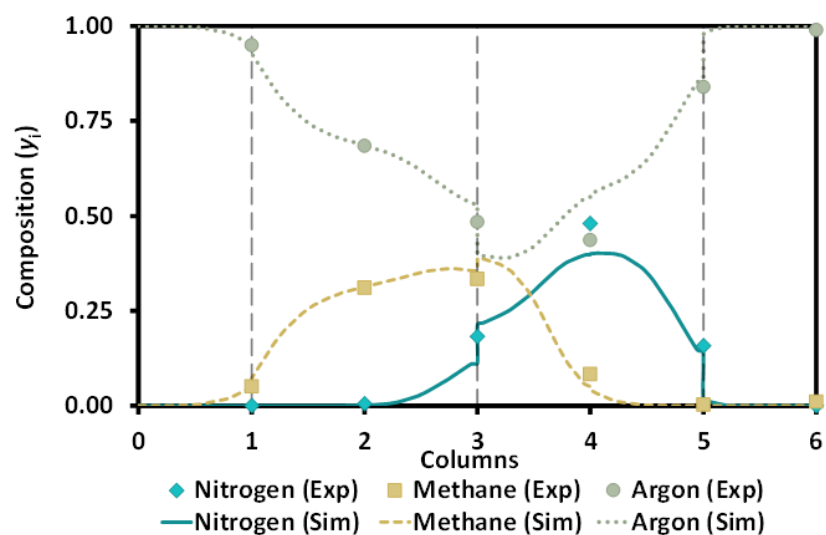


Figure 6.54 – Internal profile at 50% of the switching time for Case 1 of SMB operation using printed Maxsorb monoliths and CO_2 as desorbent. Points correspond to experimental data, and lines represent the simulation results.

a)



b)

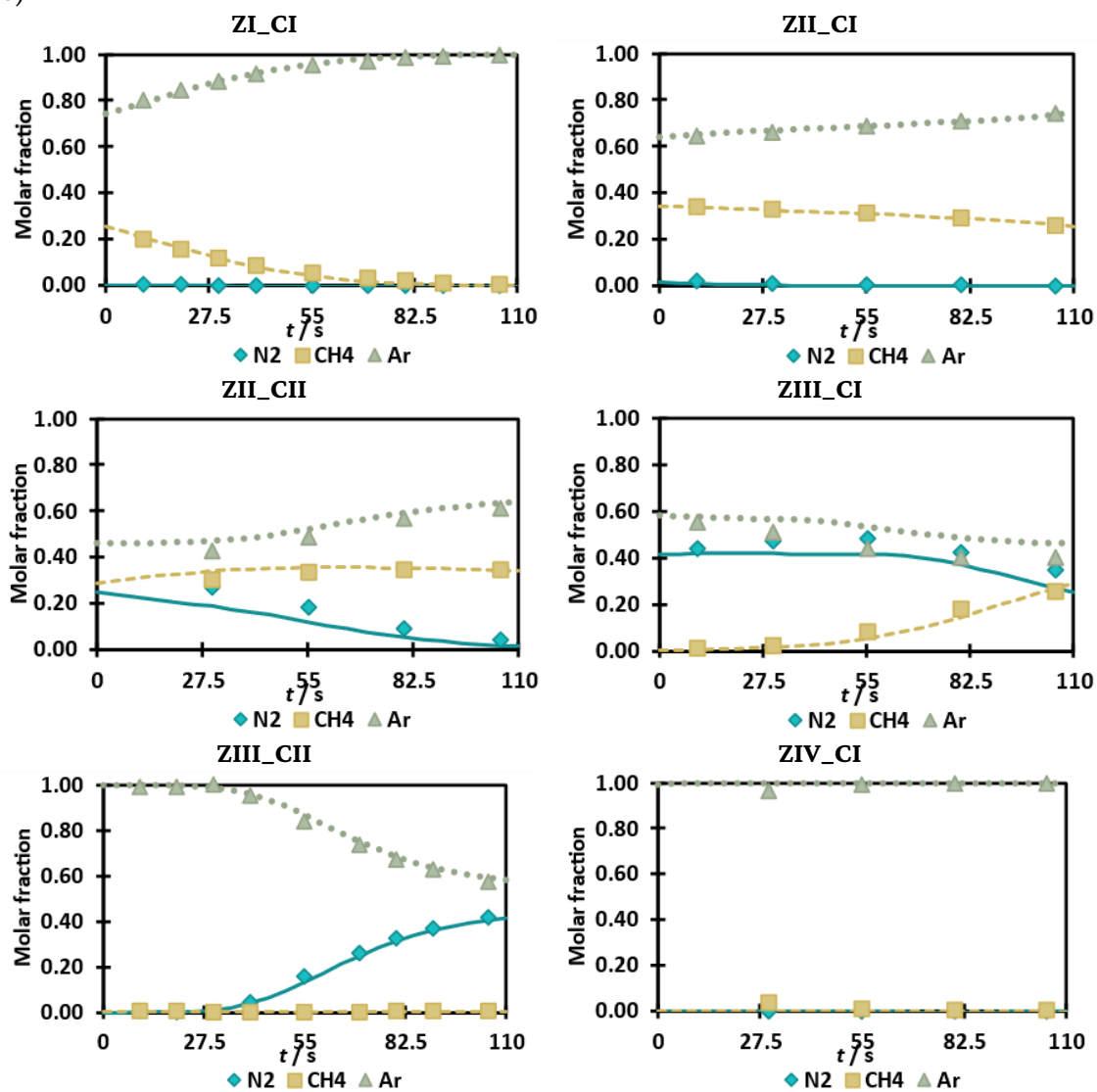
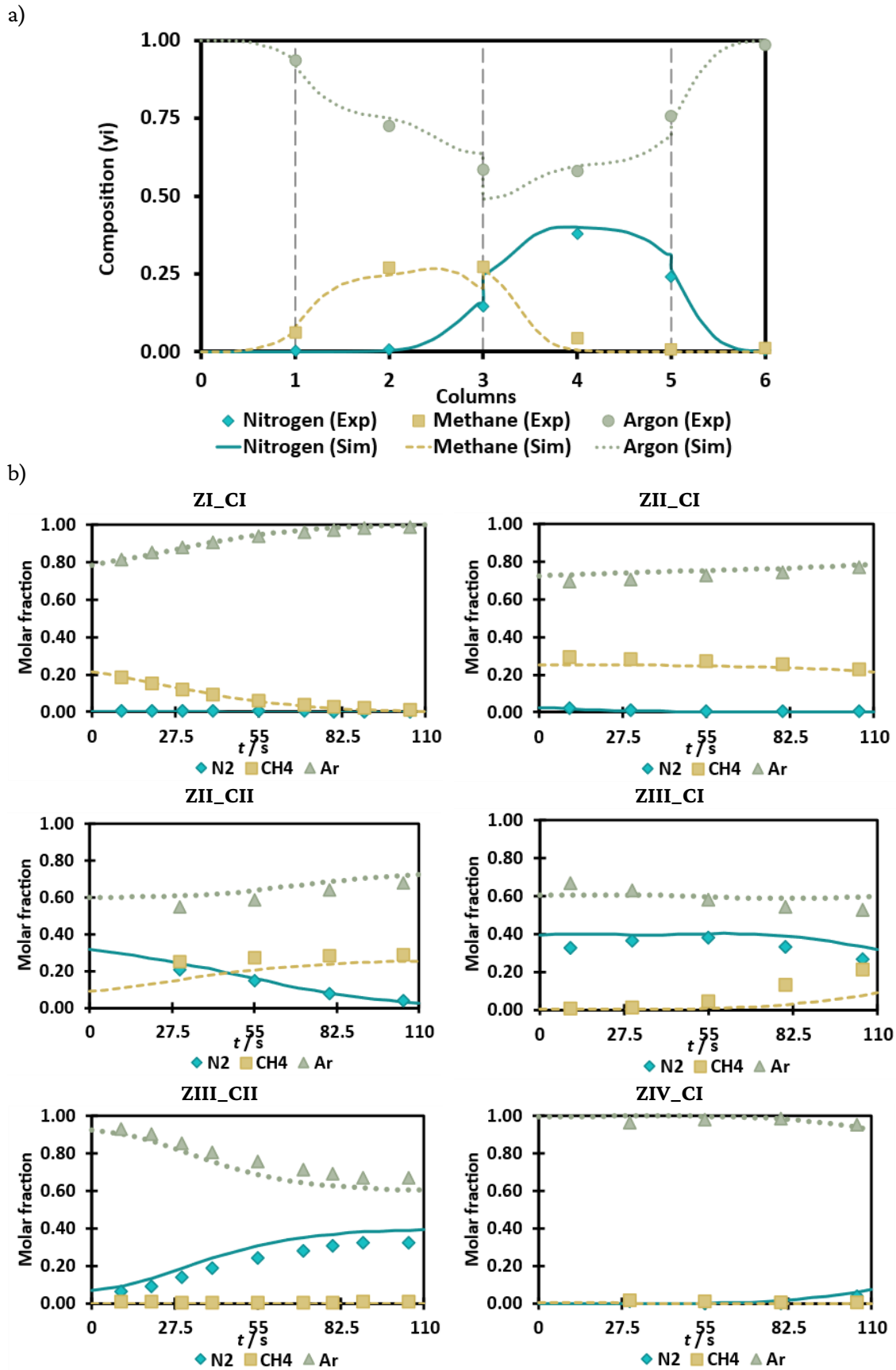


Figure 6.55 – Internal profile at 50% of the switching time for Case 2 SMB operation using printed Maxsorb monoliths and Ar as desorbent. Points correspond to experimental data, and lines represent the simulation results.



In zone I, which corresponds to column 1, the desorbent is able to regenerate the bed, decreasing the content of the most retained species, CH_4 , until the adsorbent is completely clean before the switch. The mixture is fed at the beginning of column 4. Since CH_4 is the most adsorbed component, it travels with the solid phase in zone II (columns 2 and 3), enriching the extract stream, located at the end of column 1. N_2 , being the less retained species, moves with the direction of the fluid flow in section III (columns 4 and 5) to the raffinate port, located at the end of column 5. In zone IV, the desorbent is cleaned in order to be recycled, if the SMB is operated in closed loop.

Analysing Figure 6.54 to Figure 6.56, it can be inferred that the mixture can be successfully separated. In Table 6.22, the SMB performance parameters were calculated to evaluate the efficiency of the process, according to the expressions provided in Section 3.7.2. Figure 6.57 shows the computed separation regions for the SMB processes where either CO_2 or Ar are used as desorbent. Note that the difference between the separation regions for open and closed-loop operation is a result of the pressure difference between assays. Otherwise, no distinction between the separation regions would be observable. The pressure used to compute the region when using CO_2 as the desorbent, in closed-loop operation, was estimated based on the pressure difference of the argon experiments. This separation region is presented in Figure 6.57 as Case 4. The pressure histories at the column outlet and the temperature history at the middle of column 2 during a cycle can be observed in Figure 6.58 and Figure 6.59, respectively. The specified extract and raffinate purities were 97% and 99%, respectively. Figure 6.57 also shows the operating points for each of the assays.

Table 6.22 - Performance parameters obtained for the SMB cycles.

	Case 1		Case 2		Case 3	
	Extract	Raffinate	Extract	Raffinate	Extract	Raffinate
Average N_2 molar fraction	0.001	0.096	0.001	0.176	0.007	0.217
Average CH_4 molar fraction	0.059	0.002	0.078	0.002	0.080	0.003
Purity (%)	98.5	98.3	99.2	99.0	96.6	97.0
Recovery (%)	96.3	98.0	97.2	99.2	93.2	89.2
Productivity ($\text{kg} \cdot \text{m}^{-3}_{\text{ads}} \cdot \text{h}^{-1}$)	2.7	6.1	6.5	11.6	6.5	8.3
Desorbent Consumption ($\text{m}^3_{\text{STP,desorbent}} \cdot \text{kg}^{-1}_{\text{CH}_4}$)	50.6		24.8		14.7	

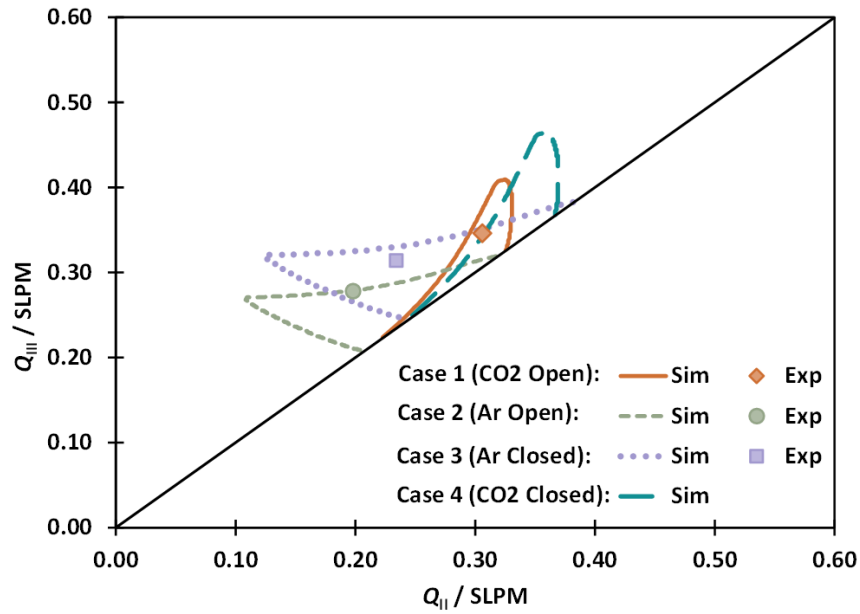


Figure 6.57 - Separation regions obtained with the complete mathematical model using printed Maxsorb monoliths and CO₂ or Ar as possible desorbents, considering a CH₄ extract purity of 97% and N₂ raffinate purity of 99%, in both open and closed loop operation. The symbols correspond to the operating points for each of the studied cases.

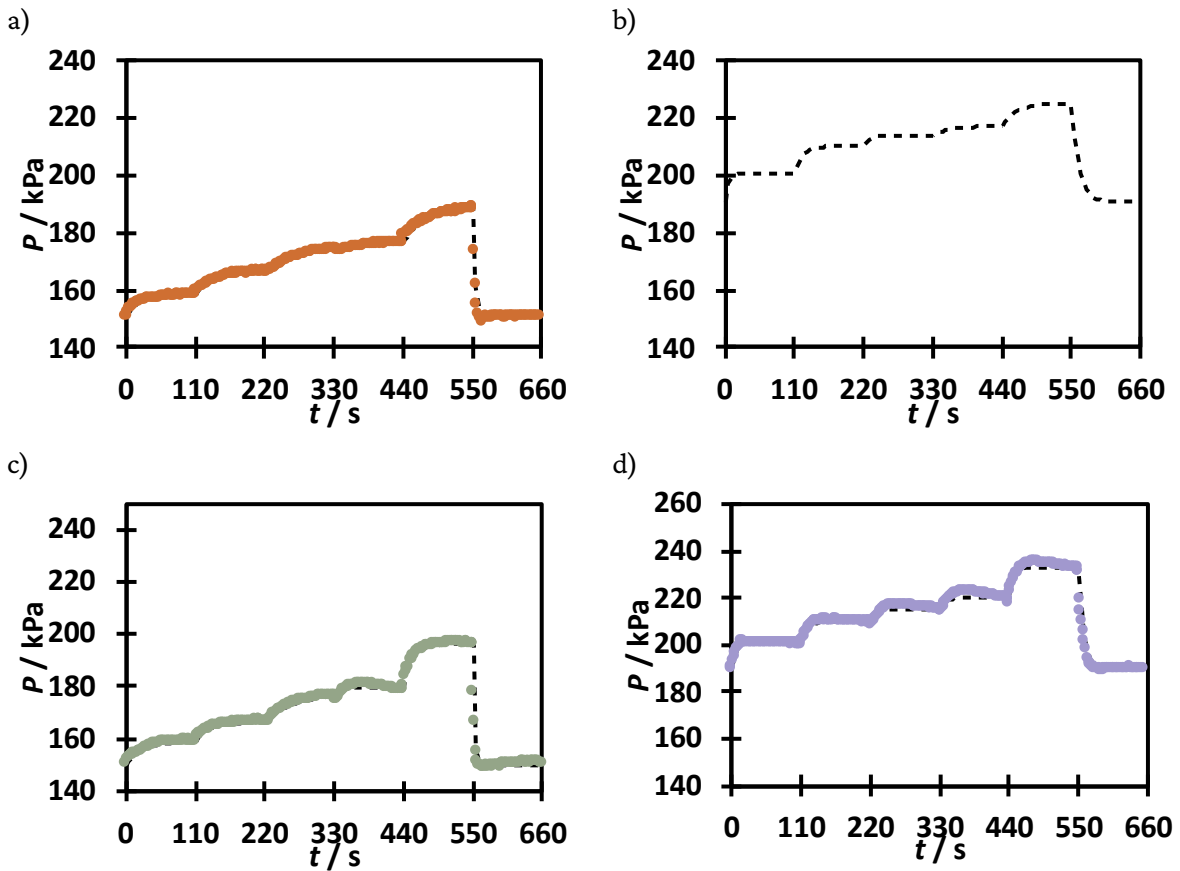


Figure 6.58 - Pressure histories at the column outlet during a cycle: a) experiment using CO₂ as a desorbent, in open-loop operation; b) experiment using CO₂ as a desorbent, in closed-loop operation; c) experiment using Ar as a desorbent, in open-loop operation; d) experiment using Ar as a desorbent, in closed-loop operation.

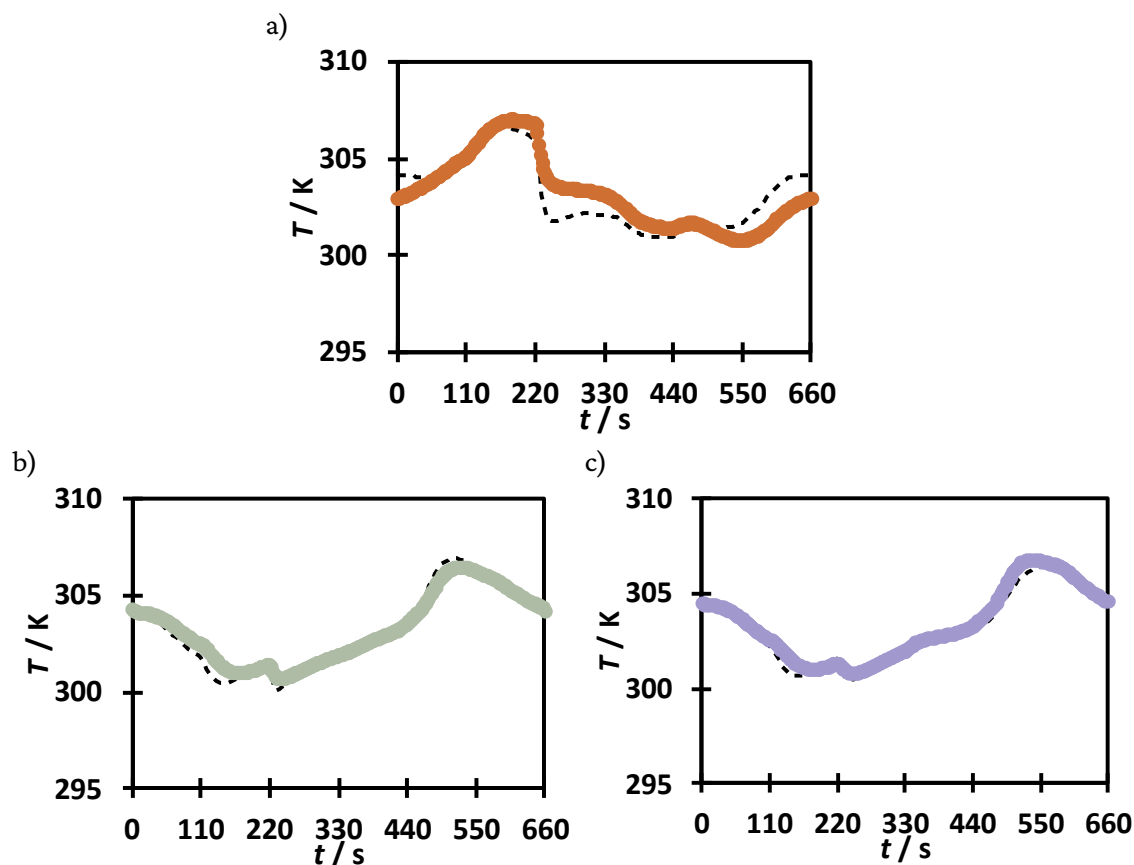


Figure 6.59 - Temperature histories at the middle of the column during a cycle: a) experiment using CO_2 as a desorbent, in open-loop operation; b) experiment using Ar as a desorbent, in open-loop operation; c) experiment using Ar as a desorbent, in closed-loop operation.

When comparing the recovery values for the three cases, it is possible to observe that for Case 3, where the SMB was operated in closed-loop, a lower value for both the extract and raffinate stream was obtained. This can be explained by the high velocity in section IV, which led to the breakthrough of the N_2 at the end of the switching time, which also accounts for the lower purity of the extract stream. To improve this value, a lower recycle flow rate should be used.

As observed when comparing Figure 6.55 and Figure 6.56, the internal profiles are similar, indicating that the introduction of a desorbent recycle loop, while maintaining the internal flow rates in zones II and III, does not affect the concentration fronts. Therefore, if the unit were operated in closed-loop mode with CO_2 as the desorbent under the same conditions, a similar internal profile to that shown in Figure 6.54 would be expected.

Figure 6.57 shows that the operating points are located inside the respective separation region, indicating that the mixture is completely separated. However, the conditions used in each experiment can be optimised to obtain the maximum productivity with this setup (vertex of the separation zone). This way, when considering these optimal conditions, the production yields and the desorbent consumption were calculated and are summarised in Table 6.23.

Table 6.23 - Productivity and desorbent consumption when operating at the optimal conditions for each case SMB operation using printed Maxsorb monoliths.

	Case 1		Case 2		Case 3	
	Extract	Raffinate	Extract	Raffinate	Extract	Raffinate
Productivity ($\text{kg} \cdot \text{m}^{-3}_{\text{ads}} \cdot \text{h}^{-1}$)	6.7	11.6	12.4	21.5	15.2	26.0
Desorbent Consumption ($\text{m}^3_{\text{STP,desorbent}} \cdot \text{kg}^{-1}_{\text{CH}_4}$)	17.8		12.1		10.7	

Comparing the maximum productivity for Case 1 and Case 2, using Ar leads to better results, highlighting that using a weak desorbent is better for achieving higher throughputs, as observed for the previous materials.

6.5. Conclusions

In this chapter, the performance of a commercial activated carbon, BPL, in-house extruded Maxsorb pellets and Maxsorb activated carbon monoliths manufactured via 3D-printing were explored for the separation of CH_4/N_2 mixtures by gas-phase SMB.

Adsorption equilibrium isotherms for each pure adsorbate were measured at 303, 323, and 343 K, in a pressure range up to 2.5 bar, using a volumetric method, over the three materials. Regardless of the material, the collected results indicate preferential adsorption of CO_2 over the entire temperature and pressure range, with Ar weakly adsorbing to the adsorbent's surface. Comparing the uptakes at 303 K and 1.5 bar, the pelletised Maxsorb exhibits a higher capacity for all measured adsorbates.

Fixed-bed experiments were performed in the gas-phase SMB unit to investigate the multicomponent dynamic behaviour and validate the proposed mathematical model, which is a necessary step for designing the SMB cycles and computing the separation regions for each adsorbent/desorbent pair. The adsorption capacity observed in the single-component breakthrough tests agrees with the equilibrium results. Results show that the proposed model equations can predict the breakthrough curves accurately for the single and multi-component tests for the tested materials. The ternary dynamic tests shown that the mixture can be displaced by both desorbents and can displace both desorbent from the adsorbed phase, which is very important for SMB operation.

For each of the materials, two SMB cycles for separating a CH_4/N_2 stream with an equimolar feed composition, at 303 K, were performed with two different desorbents, Ar and CO_2 . The performance of each cycle was evaluated in terms of purity, recovery, productivity, and desorbent consumption for both product streams. All cycles were able to produce a methane stream with a high desorbent-free purity (above 96.2%) and high methane recovery (>92.7%). With the drawn separation regions, the maximum productivity, determined at the vertex of the separation region, was obtained for all adsorbent/desorbent sets. Table 6.24 shows the maximum productivity values per mass of adsorbent and per volume of column.

Table 6.24 - Maximum productivities obtained for each adsorbent/desorbent pair at the inputted conditions.

Adsorbent	Desorbent	Prod_x ($\text{g}_{\text{CH}_4} \cdot \text{kg}_{\text{ads}}^{-1} \cdot \text{h}^{-1}$)	Prod_x ($\text{kg}_{\text{CH}_4} \cdot \text{m}^{-3} \cdot \text{col} \cdot \text{h}^{-1}$)
BPL	CO ₂	18.4	7.3
	Ar	59.1	23.5
Maxsorb Pellets	CO ₂	32.3	6.4
	Ar	69.0	13.6
Maxsorb Monoliths	CO ₂	18.7	4.1
	Ar	34.5	7.6

When analysing the obtained maximum productivities in terms of adsorbent mass, higher throughputs were observed when using the pelletised Maxsorb activated carbon as the adsorbent, for both desorbent gases. However, from a unit design standpoint, productivity per column volume is a more reliable metric. In this regard, choosing BPL as the stationary phase leads to better performance overall. It is important to note, however, that the operating conditions were not optimized for each material, meaning that these values could be further improved with optimization. Additionally, the longer switching time used for the monolith experiments, compared to the other two materials, resulted in lower feed and section flow rates, ultimately leading to reduced productivity values.

Table 6.25 and Table 6.26 show the calculated values for the SPI presented in Section 4, for each adsorbent/desorbent pair.

Table 6.25 - SPI calculation for the three tested materials with CO₂ used as the desorbent.

Adsorbent	$\alpha_{\text{CH}_4/\text{N}_2}$	q_{CH_4} ($\text{mol} \cdot \text{kg}^{-1}$)	ΔH_{N_2} ($\text{J} \cdot \text{mol}^{-1}$)	ΔH_{CH_4} ($\text{J} \cdot \text{mol}^{-1}$)	SPI
BPL AC	3.293	0.223	12068	17647	0.239
Maxsorb pellets	2.815	0.382	12049	13897	0.475
Maxsorb monoliths	3.017	0.363	13885	16735	0.479

Table 6.26 - SPI calculation for the three tested materials with Ar used as the desorbent.

Adsorbent	$\alpha_{\text{CH}_4/\text{N}_2}$	q_{CH_4} ($\text{mol} \cdot \text{kg}^{-1}$)	ΔH_{N_2} ($\text{J} \cdot \text{mol}^{-1}$)	ΔH_{CH_4} ($\text{J} \cdot \text{mol}^{-1}$)	SPI
BPL AC	3.721	0.344	12068	17647	0.644
Maxsorb pellets	2.827	0.470	12049	13897	0.721
Maxsorb monoliths	2.948	0.401	13885	16735	0.573

Analysing the SPI values, if the desorbent used in the process is CO₂, both shaped Maxsorb materials were expected to perform similarly, while when using Ar, the pelletised Maxsorb was expected to be the best choice for the stationary phase. It is important to note that the SPI metric was developed without considering the specific characteristics of the adsorbents, meaning that

the same adsorbent mass was assumed regardless of the material. As such, the SPI can effectively predict the best adsorbent choice for the separation at hand using either desorbent gas when the maximum productivity is expressed per unit of adsorbent mass.

Comparing the results obtained for both desorbents, argon presented better results overall. However, one must not forget that separation and purification of the eluent is necessary *a posteriori* for SMB processes. To recover the CH₄ and N₂ from the downstream products, as well as the desorbent to be reused, a PSA process can be utilised, using an adsorbent with high selectivity between product and desorbent. N₂/Ar separation would be the most difficult to achieve out of the four pairs. In this case, an air separation adsorbent such as the 5A molecular sieve can be used [12]. Zeolites 13X and LiX have also shown good performance for this specific separation [13, 14]. As an alternative to argon, helium could be utilised as desorbent, although its use may not be economically viable for industrial purposes [15]. For both CO₂/CH₄ and CO₂/N₂ mixtures, two *in silico* studies have shown that a commercial silicalite, HiSiv3000, could be an effective choice for both separations [16, 17]. These downstream separations are much easier to be achieved and the desorbent gas is also cheaper. As such, the use of CO₂ for the separation of CH₄/N₂ streams by gas-phase SMB might be preferable. Also, according to Storti *et al.*, when the desired component is recovered in the extract stream, a strong eluent is more appropriate from an operation standpoint since the system is less sensitive to disturbances in the section flow rates [18].

In summary, this study demonstrates that a weakly adsorbed desorbent gas is preferable to a strongly adsorbed one, resulting in a more efficient separation and higher productivity values. Additionally, the validated mathematical model allowed to successfully predict the experimental results, providing proof of concept and enabling the design of industrial-scale gas-phase SMB processes.

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CHAPTER 7 – SMB/PSA HYBRID PROCESS

7.1. Introduction

As observed in the previous chapter, the conventional gas-phase SMB process is a promising alternative to the cryogenic distillation for the rejection of nitrogen from methane streams. However, one of its biggest disadvantages is the need to separate the downstream products, in this case, methane and nitrogen, from the desorbent species that is used in the process to regenerate the adsorbent. To overcome this, one can use a combination of pressure swing adsorption steps and displacement chromatography to remove the adsorbed phase from the solid material. This way, the desorbent gas can be effectively removed from the process. This process was described in detail in Section 3.8. The process is illustrated in Figure 7.1.

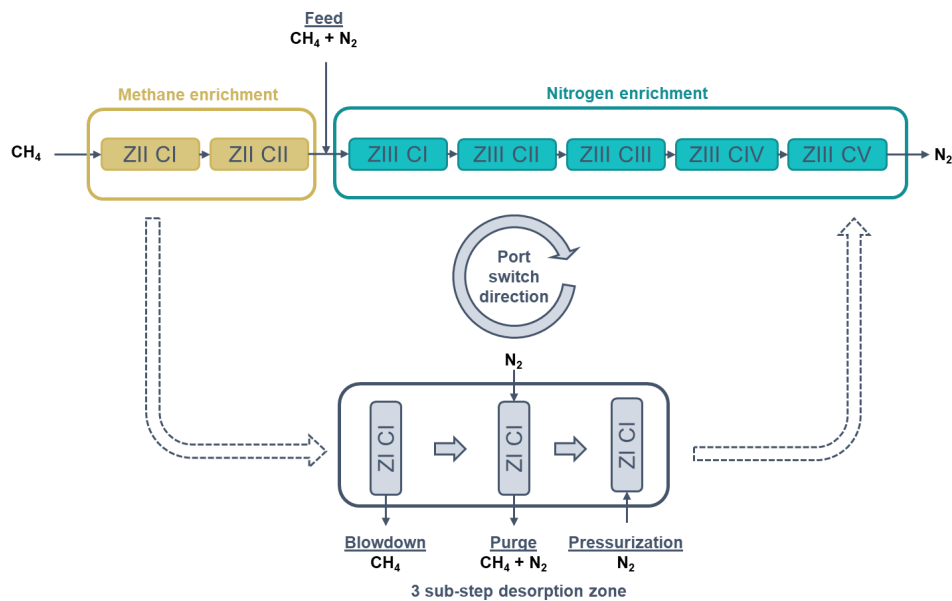


Figure 7.1 - Schematic of a hybrid SMB/PSA unit.

Briefly, in the hybrid SMB/PSA unit, one column is decoupled from the system and undergoes a PSA sequence comprised of three sub-steps – blowdown (where the heavy component, CH_4 , is produced), purge and pressurization. Meanwhile, the remaining columns are interconnected in series, where in Section II (displacement section), the bed is enriched in the more retained species by displacement chromatography with a portion of the heavy product, while in Section III (adsorption section) the CH_4/N_2 mixture is separated based on the adsorption affinity. The light product (N_2) is produced at the end of this section. After a step, the inlets and outlets of the system shift to simulate the movement of the solid, promoting the mass transfer between the solid and gas phases. In the following step, the first column in Section II becomes the column undergoing the PSA sub-steps, while the column that ended the PSA sequence becomes the last column in Section III.

This chapter presents an *in-silico* study of such hybrid SMB/PSA process. A parametric study was also conducted to observe the effect of different operating conditions on the performance and improve the process.

7.2. Results

For the simulations, the BPL activated carbon was selected as the stationary phase, as from a process design perspective, it showed a higher productivity per column volume when compared to the other two materials tested. This way, the DSL model parameters for CH₄ and N₂, determined in Section 6.2.2, were used to describe the pure component adsorption equilibria. For the multicomponent adsorption equilibrium prediction, the extended DSL model was utilised. Also, the characteristics of the adsorption bed considered for this study are presented in Table 7.1. The transport parameters required for performing the simulations were obtained according to the equations presented in Chapter 3 and can be found in Table 7.2.

Table 7.1 – Characteristics of the adsorption bed.

	Value	Unit
Mass (m)	36.0	g
Internal diameter (d_w)	2.15	cm
Bed length (L)	25.0	cm
Bed porosity (ϵ)	0.41	
Bulk density (ρ_b)	396.6	kg·m ⁻³

Table 7.2 - Transport parameter values used in the simulations for the hybrid process.

Parameter	Value
$D_{ax} \times 10^4 / \text{m}^2 \cdot \text{s}^{-1}$	2.0
$k_f \times 10^2 / \text{m} \cdot \text{s}^{-1}$	1.41
$\lambda / \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	0.16
$h_f / \text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$	24.9
$D_{p,i} \times 10^6 / \text{m}^2 \cdot \text{s}^{-1}$	N ₂ : 5.43 CH ₄ : 5.52
$U / \text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$	40.4
$h_w / \text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$	126.3

The initial simulation conditions are presented in Table 7.3. For all the simulations presented in this Chapter, cyclic steady state was considered achieved when the product purities remained constant between consecutive cycles, while ensuring mass conservation for both components. This way, cyclic steady state was reached in approximately 35 cycles. The separation region obtained for this set of operating conditions can be observed in Figure 7.2. The procedure employed to determine the boundaries of the region is analogous to that described for the SMB

process in Section 3.7.3, with the modification that the displacement gas flow rate, F_{Disp} , is changed instead of the desorbent flow rate. Also, in addition to the purity specifications (97 % for the methane-rich stream and 99 % for the nitrogen-rich stream), two restrictions for the productivity were also considered to ensure positive values for both products. To derive the equations that define the boundaries of separation region in terms of productivity, a range of Q_{II} and Q_{III} pairs was scanned, and the performance parameters were evaluated. These restrictions can also be found in Figure 7.2.

Table 7.3 – Initial set of operating conditions (Case 1).

Operating conditions	Value
P / bar	1.52-2.15
T / K	298
P_{high} / bar	1.52
P_{low} / bar	0.10
t^* / s	200
t_{blow} / s	100
t_{pg} / s	60
t_{press} / s	40
Q_{pg} / SLPM	0.1

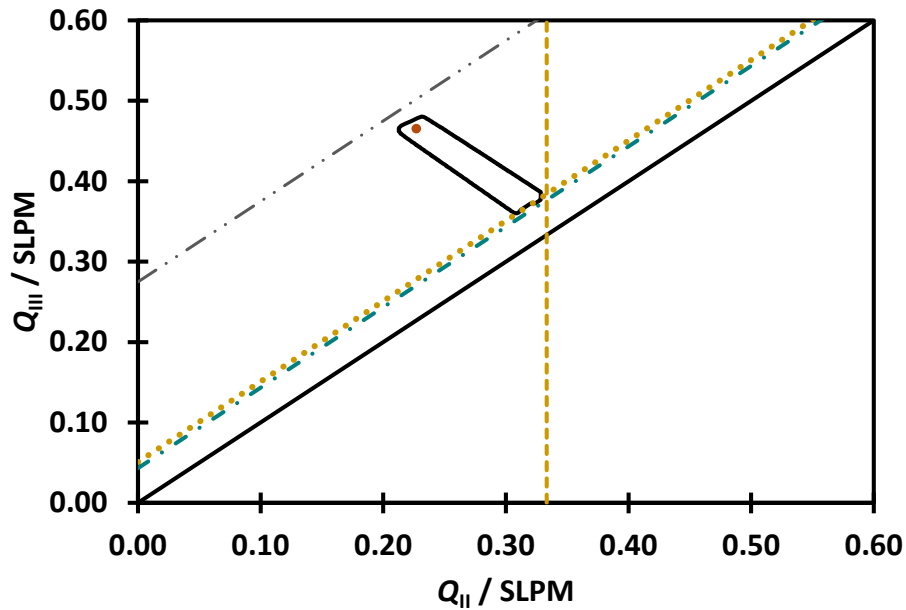


Figure 7.2 – Hybrid process separation region for CH_4/N_2 separation using BPL determined with the complete model, with a 1-2-5 configuration, for the initial set of operating conditions presented in Table 7.3, and heavy and light component purities of 97 and 99 %, respectively (full black line). The yellow lines represent the displacement gas (---) and feed flow rate (···) restrictions for positive CH_4 productivity. The teal line represents the feed flow rate restriction for positive N_2 productivity (— · —). The slanted grey line represents the maximum feed flow rate constraint obtained through the equilibrium theory (— · · —). The point (•) represents the operating conditions for Case 4.

Based on the analysis of Figure 7.2, to prevent negative productivity values in the heavy component stream, the amount of methane used to displace the adsorbed phase in zone II during a step cannot exceed the amount of methane produced during the blowdown sub-step. This is translated by Equation (7.1) and defines the yellow vertical dashed line (---) in Figure 7.2.

Additionally, negative methane productivities are also obtained if the amount of methane removed at the column outlet during the purge sub-step exceeds the amount of methane fed to the system. This results in Equation (7.2) and describes the yellow slanted dotted line (···) in Figure 7.2.

This way, the following constraints can be established:

$$F_{\text{Disp}} t^* < \Delta n_{\text{blow,CH}_4}, \quad \Delta n_{\text{blow,CH}_4} = \frac{\Delta P_{\text{blow}} \varepsilon_t V}{R_g T_{\text{blow}}} + \Delta q_{\text{blow,CH}_4} m \quad (7.1)$$

$$F_F y_{F,\text{CH}_4} t^* > n_{\text{pg,out,CH}_4} \quad (7.2)$$

where $\Delta n_{\text{blow,CH}_4}$ is the amount of methane produced during the blowdown sub-step, ΔP_{blow} is the pressure difference between the start and end of the blowdown sub-step, ε_t is the total porosity, $\Delta q_{\text{blow,CH}_4}$ is the adsorbed concentration change observed during the blowdown sub-step, m is the adsorbent mass, and $n_{\text{pg,out,CH}_4}$ is the amount of methane exiting the column during the purge sub-step.

To estimate $n_{\text{pg,out,CH}_4}$, the total moles of CH_4 remaining in the column after the blowdown sub-step are calculated. This estimation accounts for the CH_4 present in both the bed and particle voids, as well as the adsorbed phase, all evaluated at P_{low} .

To prevent negative productivities for the nitrogen stream, a feed flow rate restriction can be found:

$$F_F y_{F,\text{N}_2} t^* > F_{\text{pg,in,N}_2} t_{\text{pg}} \quad (7.3)$$

where $F_{\text{pg,in,N}_2}$ is the purge molar flow rate of nitrogen, which is an approximation to the nitrogen purged during the purge sub-step, $F_{\text{pg,out,N}_2}$. This equation defines the teal slanted line in Figure 7.2 (— · —).

In addition to the productivity restrictions presented above, another feed limitation can be found through the equilibrium theory. As such, the maximum feed flow rate limit, also presented in Figure 7.2 (— · · —), was estimated based on the equilibrium theory for non-linear and diluted systems described by a Langmuir isotherm as proposed by Mazzotti *et al* [1].

To do so, the N_2 and CH_4 adsorption equilibrium data was fitted with the Langmuir model. The obtained parameters are presented in Table 7.4.

Table 7.4 – Fitting parameters for the Langmuir isotherm for the calculation of the $Q_{F,\max}$.

Species	$q_{m,i}$ mol·m ⁻³	$b_{0,i} \times 10^6$ m ³ mol ⁻¹	$-\Delta H_i$ J·mol ⁻¹
CH ₄ , <i>A</i>	2201.2	7.10	17232.4
N ₂ , <i>B</i>	3783.9	8.91	11959.9

With these values, the $Q_{F,\max}$ was estimated by solving the equation presented below:

$$Q_{F,\max} = \left(\frac{\omega_G[\omega_F(\lambda_A - \lambda_B) + \lambda_B(\lambda_B - \omega_F)]}{\lambda_B(\lambda_A - \omega_F)} - \frac{\lambda_B \omega_G}{\lambda_A} \right) \cdot \frac{(1 - \varepsilon)LA}{t^*}, \lambda_i = q_{m,i} b_i \quad (7.4)$$

$\omega_G > \omega_F > 0$ are given by the roots of the quadratic equation:

$$(1 + b_A C_A^F + b_B C_B^F) \omega^2 - [\lambda_B(1 + b_A C_A^F) + \lambda_A(1 + b_B C_B^F)] \omega + \lambda_A \lambda_B = 0 \quad (7.5)$$

Where C_i^F is the feed concentration of each component.

The obtained value for $Q_{F,\max}$, in m³·s⁻¹, can then be converted to SLPM. However, this value can serve only as an approximation, as it neglects the mass transfer resistance effects and assumes a diluted system, whereas this process involves a non-diluted system where gas velocity variations occur.

After establishing the productivity constraints, the feasible separation region is determined based on the specified operating conditions and purity requirements. Defining these boundaries in advance reduces the computational effort involved in determining the optimal flow rate conditions, as they provide both the maximum displacement gas flow rate and the minimum viable feed flow rate for the process. These boundaries define the starting point for the search of the separation region.

In Figure 7.3, the different regions of the Q_{II}/Q_{III} plane regarding the purity of the outlet streams are defined. If a low displacement gas flow rate is used, then the nitrogen is not sufficiently displaced from the column, contaminating the methane stream produced during the blowdown sub-step above the 3 % limit. On the other hand, if the flow rate in zone III is too high, then methane is carried with the fluid and the light product is contaminated. A combination of the two leads to impure heavy and light products.

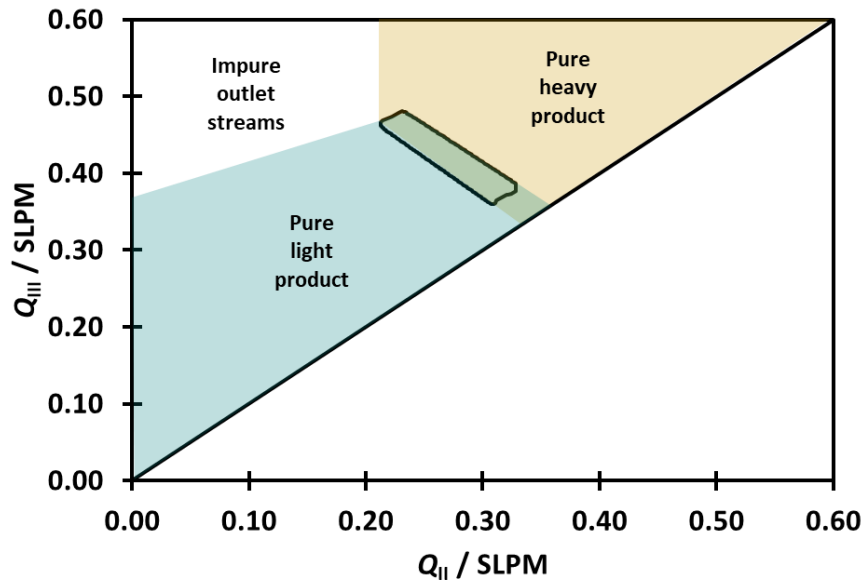
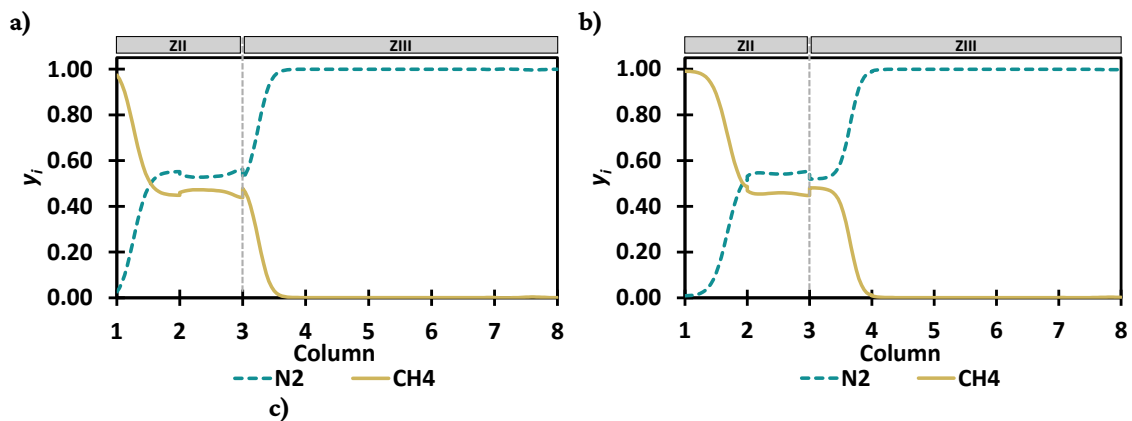


Figure 7.3 – Regions of the Q_{II}/Q_{III} plane in terms of purity of the outlet streams.

Once the separation region is obtained, the concentration fronts inside the hybrid system were analysed to understand the multicomponent adsorption dynamics at cyclic steady state. For the columns in Zone II and III (SMB component of the hybrid unit), the internal molar composition profile at 10 %, 50 %, and 90 % of the switching time was determined. For the column under PSA operation, the concentration profiles were obtained at the beginning and end of each sub-step, to account for the pressure changes imposed during the sequence. To do so, an operation point inside the separation region was selected, corresponding to a Q_{Disp} of 0.227 SLPM and a Q_F of 0.238 SLPM (Case 4). Figure 7.4 and Figure 7.5 show the obtained concentration profiles.



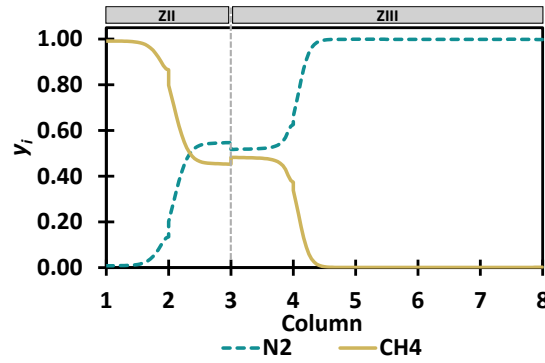


Figure 7.4 – Internal profiles at a) 10%, b) 50%, and c) 90% of the switching time for the columns in Zone II and III, operating in SMB mode, obtained at cyclic steady state at the defined operating conditions.

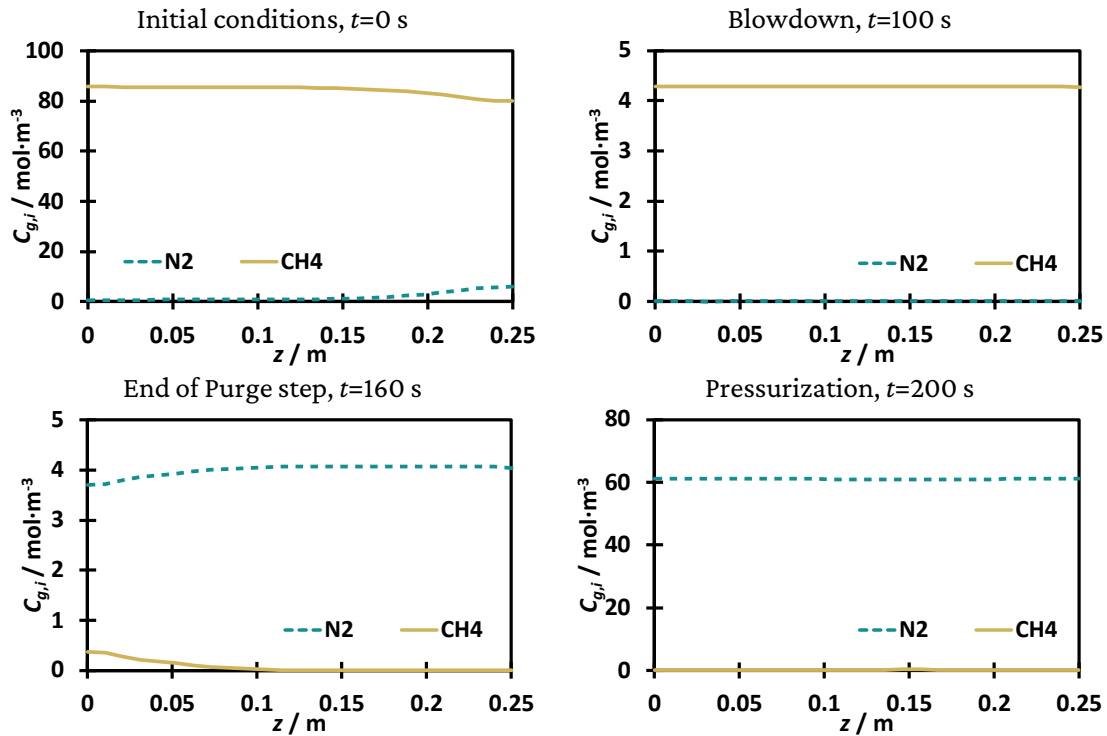


Figure 7.5 – Concentration profiles at the end of each sub-step of the PSA sequence, obtained at cyclic steady state.

It can be noted, in Figure 7.4, that the defined CH₄ displacement gas flow rate is sufficient to ensure that the first column becomes saturated with methane, preparing it for the PSA sequence in the next step. Additionally, in Zone II, the methane content increases, moving with the solid phase, while in Zone III, nitrogen travels with the fluid phase, leading to an increase in the N₂ molar fraction within these columns. During a step, the concentration fronts move in the direction of the fluid flow within the SMB component of the unit, from one column to another, until the switching occurs. The internal concentration profiles suggest that a higher flow rate in Zone III could be used, allowing an increase in the process feed flow rate, which is supported by the defined separation region.

Analysing Figure 7.5, the heavy product gas is obtained by desorbing the full methane column from the displacement zone (corresponding to column I of Zone II, before the switch), during the blowdown sub-step. Also, the defined purge flow rate is enough to ensure that most of the methane is removed from the column, ensuring the 99 % constraint for the light product purity. The pressurization step then increases the pressure back to the high pressure employed at the end of Section III.

As previously mentioned, in the SMB/PSA hybrid process, the heavy product is produced during the blowdown, while the light product gas corresponds to the outlet stream at the end of the adsorption zone (corresponding to column V of Zone III). In Figure 7.6, the concentration histories for both product streams are presented.

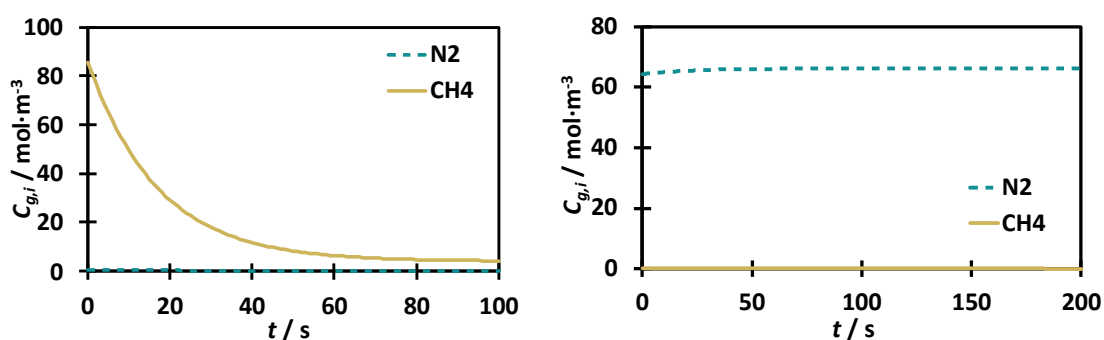


Figure 7.6 – Concentration histories obtained for the heavy product gas, CH₄ (left) and light product gas, N₂ (right).

The concentration histories show that high purity streams are obtained for both products, with an average molar fraction of 99% methane for the CH₄-rich stream and 99% nitrogen for the N₂-rich stream.

7.3. Parametric study

A parametric study is essential for understanding how key operating variables affect the performance of the hybrid SMB/PSA process. Parameters such as switching time, duration of the PSA sub-steps, purge gas flow rate, and the pressure reached during the desorption steps (P_{low}) directly impact the separation region, purity, recovery, productivity and power consumption. By analysing these factors, it is possible to identify optimal operating conditions, improve the process efficiency, and expand the feasible separation region. This study provides insights into how each parameter affects the overall performance of the hybrid system. In each subsection, the operating conditions for each case are summarised in Table 7.5, Table 7.6, and Table 7.8. For all cases, a temperature of 298 K was used and a pressure profile inside the columns of the SMB component of the unit between 1.52 – 2.15 bar.

7.3.1. Switching time

The effect of the switching time on the hybrid process was investigated. To do so, the separation regions were computed for two additional switching times, 100 s and 300 s, while maintaining the

initial time percentage of the switching time for each of the sub-steps of the PSA sequence (50 % for the blowdown, 30 % for the purge and 20 % for the pressurization sub-step) and adjusting the purge flow rate accordingly. The operating conditions for each case are shown in Table 7.5. Case 1 refers to the initial set of operating conditions used for the determination of the separation region presented in Section 7.2. In Case 2 and Case 3, only the switching time and consequently, the sub-step durations and purge flow rate were altered. Once again, the values of Q_{Disp} and Q_F were varied to define the limits of the separation region.

Table 7.5 - Operating conditions defined for each case studied in the study of the effect of the switching time in the hybrid process.

Operating conditions	Case 1	Case 2	Case 3
$P_{\text{high}} / \text{bar}$	1.52	1.52	1.52
$P_{\text{low}} / \text{bar}$	0.10	0.10	0.10
t^* / s	200	100	300
$t_{\text{blow}} / \text{s}$	100	50	150
t_{pg} / s	60	30	90
$t_{\text{press}} / \text{s}$	40	20	60
$Q_{\text{pg}} / \text{SLPM}$	0.1	0.2	0.067

The obtained separation regions are presented in Figure 7.7. As observed, changing the switching time shifts the operating window, affecting the flow rate ratios in the different zones of the unit. Increasing the switching time shifts the operating conditions toward lower flow rates in zones II and III. On the contrary, reducing the switching time requires higher flow rates in these zones to achieve complete separation of the feed mixture. Also, a higher switching time results in a smaller separation region, which may hinder the feasibility of the separation. Reducing the switching time results in a larger separation region, however, it may lead to mass transfer limitations which compromises the separation efficiency. The effects observed can also be observed for a conventional SMB process [2].

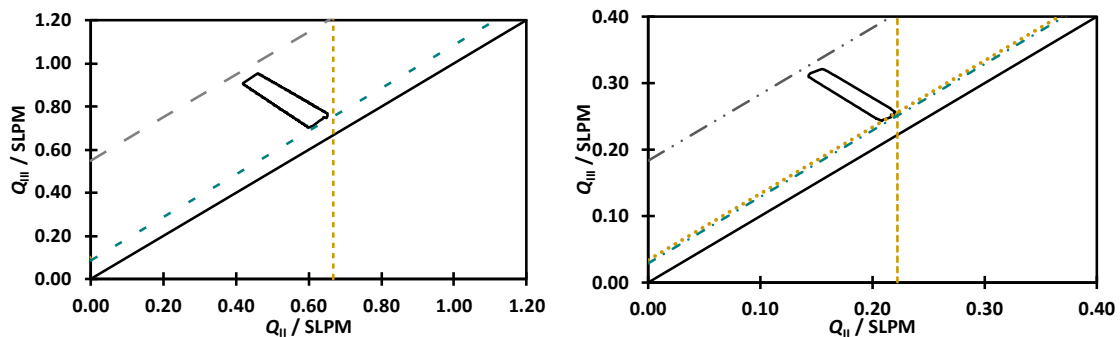


Figure 7.7 - Hybrid process separation region for CH_4/N_2 separation using BPL determined with the complete model, with a 1-2-5 column configuration, for a switching time of 100 s (left) and 300 s (right), and heavy and light component purities of 97 and 99 %, respectively (full black line). The yellow lines represent the displacement gas (---) and feed flow rate (· · ·) restrictions for positive CH_4 productivity. The teal line represents the feed flow rate restriction for positive N_2

productivity ($-\cdot-$). The slanted grey line represents the maximum feed flow rate constraint obtained through the equilibrium theory ($-\cdot-\cdot-$).

To verify if there is an equivalence to the conventional SMB, for each separation region, the section flow rates were converted into the dimensionless ratio of the interstitial fluid and solid velocities, γ_j and the γ_{II}/γ_{III} plots were compared. This comparison can be found in Figure 7.8.

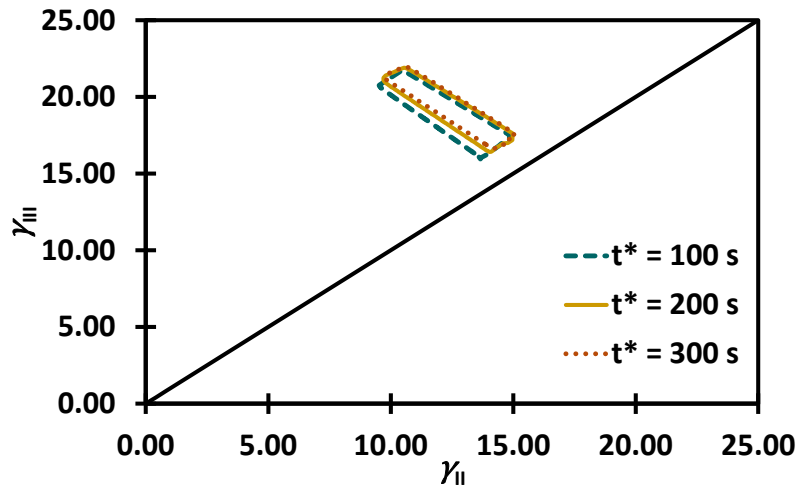


Figure 7.8 – Comparison of the separation regions computed for a switching time of 100, 200 and 300 s in terms of γ_j .

As observed, the separation regions overlap one another, indicating that the values of γ_j are the same regardless of the switching time. This is important from a design perspective, as with this equivalence, we can predict the operating flow rates when changing the switching time of the process.

7.3.2. PSA sub-step time and purge flow rate

To assess the impact of the duration of each sub-step of the PSA sequence, the percentage of the switching time allocated to each of the sub-steps (blowdown/purge/pressurization) was modified. In addition to Case 4 (50 %/30 %/20 %), which corresponds to the operating conditions used for the analysis of the concentration fronts inside the hybrid unit in Section 7.2, two cases were examined: 25 %/50 %/25 % (Case 5) and 10 %/80 %/10 % (Case 6). The operating conditions used in each case are presented in Table 7.6. The methane purity, recovery and productivity were obtained with and without the recovery of the methane during the purge sub-step and the power consumption per kilogram of methane produced was determined. The simulation results are summarised in Table 7.7.

Table 7.6 - Operating conditions defined for each case studied in the study of the influence of the sub-step duration and purge flow rate in the hybrid process performance.

Operating conditions	Case 4	Case 5	Case 6
$P_{\text{high}} / \text{bar}$	1.52	1.52	1.52

$P_{\text{low}} / \text{bar}$	0.10	0.1	0.1
t^* / s	200	200	200
$t_{\text{blow}} / \text{s}$	100	50	20
t_{pg} / s	60	100	160
$t_{\text{press}} / \text{s}$	40	50	20
$Q_{\text{disp}} / \text{SLPM}$	0.227	0.227	0.227
$Q_{\text{F}} / \text{SLPM}$	0.238	0.238	0.238
$Q_{\text{pg}} / \text{SLPM}$	0.1	0.1	0.1
$Q_{\text{pg, min}} / \text{SLPM}$	0.06	0.035	0.022

Analysing the product stream purities confirms that the purity requirements were met for both components in all simulated cases. This was expected, since the selected operation point lies within the computed separation region.

In terms of recovery of each product, discarding the purge outlet stream leads to a low methane and nitrogen recovery, with recovery values below 76.3 % and 81.1 % for the heavy and light products, respectively. However, if a portion of the purge outlet stream is recovered as methane product (while the methane purity specification is kept above 97 %), both recovery and productivity can be significantly improved, reaching up to 97.3 % and $11.5 \text{ kg} \cdot \text{m}^{-3}_{\text{ads}} \cdot \text{h}^{-1}$, respectively, for the main product.

The results also show that the N_2 recovery is significantly impacted when increasing the duration of the purge sub-step, without minimising the purge flow rate. This results in excessive nitrogen consumption, halving the productivity of the light product for the longest purge sub-step.

To improve the recovery and productivity of the light component stream, the nitrogen purge flow rate was tuned for each case. To do so, the purge flow rate was decreased until the nitrogen stream purity was compromised, indicating that the desorption of the adsorbed methane in the purge sub-step was inefficient. The minimum Q_{pg} obtained for each case is presented in Table 7.7, as well as the performance parameters achieved for each run.

Table 7.7 – Performance parameters obtained for each run performed with different sub-step times, at a purge flow rate of 0.1 SLPM and minimum purge flow rate.

	Case 4		Case 5		Case 6	
$Q_{\text{pg}} / \text{SLPM}$	0.1	0.06	0.1	0.035	0.1	0.022
$Pu_{\text{CH}_4} / \%$	99.2	99.2	99.2	99.2	99.1	99.2
$Pu_{\text{N}_2} / \%$	99.8	99.0	100.0	99.0	100.0	99.0
$Rec_{\text{CH}_4} / \%$	76.3	76.6	75.9	76.3	72.9	73.4
$Rec_{\text{N}_2} / \%$	81.1	90.7	64.5	91.2	39.3	91.3
$Rec_{\text{CH}_4} \text{ with purge} / \%$	96.2	97.2	95.9	97.3	95.0	97.3

$Prod_{CH_4} / \text{kg} \cdot \text{m}^{-3}_{\text{ads}} \cdot \text{h}^{-1}$	9.0	9.0	8.9	9.0	8.6	8.7
$Prod_{N_2} / \text{kg} \cdot \text{m}^{-3}_{\text{ads}} \cdot \text{h}^{-1}$	16.7	18.7	13.3	18.8	8.1	18.8
$Prod_{CH_4} \text{ with purge} / \text{kg} \cdot \text{m}^{-3}_{\text{ads}} \cdot \text{h}^{-1}$	11.3	11.5	11.3	11.5	11.2	11.5
Power consumption / $\text{W} \cdot \text{h} \cdot \text{kg}^{-1}_{CH_4}$	503.0	476.0	555.7	491.3	648.3	525.8

By minimising the purge flow rate for each case, both nitrogen recovery and productivity values increased, reaching a maximum value of 91.3 % and $18.8 \text{ kg} \cdot \text{m}^{-3}_{\text{ads}} \cdot \text{h}^{-1}$ for the defined conditions. Also, if the purge flow rate is minimized to account for the increase in the duration of the purge sub-step, most of the methane that would be lost during the purge sub-step can be recovered. This way, the maximum methane recovery and productivity of 97.3 % and $11.5 \text{ kg} \cdot \text{m}^{-3}_{\text{ads}} \cdot \text{h}^{-1}$, respectively, can be achieved.

In terms of power consumption, the blowdown sub-step exhibits the highest influence on the energy requirements. A decrease in the blowdown duration results in increased power consumption to maintain the performance parameters achieved for the CH_4 stream. As such, for the shortest blowdown duration of 20 s, the power consumption reached $525.8 \text{ W} \cdot \text{h} \cdot \text{kg}^{-1}_{CH_4}$. Nevertheless, the power consumption values across the three examined cases remain within the same order of magnitude.

This way, the percentage of the switching time allocated to each of the PSA sub-steps seems to not have an impact on the efficiency of the process, as long as the purge flow rate is minimised according to the duration of the purge sub-step. Also, part of the purge outlet stream can be recovered to not waste the non-desorbed methane that remains inside the column after the blowdown sub-step occurs, maximising the methane recovery.

7.3.3. Low Pressure

The low pressure defined during the desorption steps in the PSA sequence greatly affects the overall power consumption, particularly due to the multiple vacuum stages required to reduce the pressure down to 0.1 bar. If a desorption pressure above 0.2 bar can be employed without compromising the process performance, energy efficiency can be improved. To test this possibility, two different values of P_{low} were tested - 0.2 (Case 7) and 0.3 bar (Case 8) - and their impact on the performance parameters was assessed. The operating conditions for each case are presented in Table 7.8. The corresponding results are summarized in Table 7.9.

Table 7.8 - Operating conditions defined for each case in the study investigating the effect of P_{low} on the performance of the hybrid process.

Operating conditions	Case 4	Case 7	Case 8
$P_{\text{high}} / \text{bar}$	1.52	1.52	1.52
$P_{\text{low}} / \text{bar}$	0.10	0.20	0.30

t^* / s	200	200	200
t_{blow} / s	100	100	100
t_{pg} / s	60	60	60
t_{press} / s	40	40	40
$Q_{\text{disp}} / \text{SLPM}$	0.227	0.227	0.227
Q_F / SLPM	0.238	0.238	0.238
$Q_{\text{pg}} / \text{SLPM}$	0.1	0.20	0.30

Table 7.9 – Influence of the value of P_{low} in the performance parameters of the hybrid process.

	Case 4	Case 7	Case 8
$P_{\text{low}} / \text{bar}$	0.1	0.2	0.3
$Q_{\text{pg}} / \text{SLPM}$	0.1	0.2	0.3
$Pu_{\text{CH}_4} / \%$	99.2	99.1	99.0
$Pu_{\text{N}_2} / \%$	99.8	99.7	99.7
$Rec_{\text{CH}_4} / \%$	76.3	57.0	37.6
$Rec_{\text{N}_2} / \%$	81.1	63.1	45.1
$Rec_{\text{CH}_4} \text{ with purge} / \%$	96.2	86.0	74.3
$Prod_{\text{CH}_4} / \text{mol} \cdot \text{m}^{-3}_{\text{ads}} \cdot \text{h}^{-1}$	9.0	6.7	4.4
$Prod_{\text{N}_2} / \text{mol} \cdot \text{m}^{-3}_{\text{ads}} \cdot \text{h}^{-1}$	16.7	13.0	9.3
$Prod_{\text{CH}_4} \text{ with purge} / \text{mol} \cdot \text{m}^{-3}_{\text{ads}} \cdot \text{h}^{-1}$	11.3	10.1	8.8
Power consumption / $\text{W} \cdot \text{h} \cdot \text{kg}^{-1}_{\text{CH}_4}$	503.0	482.0	452.1

As observed, increasing the value of P_{low} leads to incomplete desorption of the methane, which negatively impacts the methane recovery. Also, to compensate for the poor methane desorption during the blowdown sub-step, a higher purge flow rate was required, which led to process inefficiency. As expected, the use of a very low pressure (0.10 bar) for regeneration has a high negative impact on the energy consumption, with the power consumption improving when higher pressures are used during the desorption sub-steps.

This indicates that, to optimize the CH_4/N_2 separation by an SMB/PSA hybrid process, the value of P_{low} needs to be set to very low values to ensure effective methane desorption and maximize product recovery and productivity.

7.4. Conclusions

In this chapter, an SMB/PSA hybrid process for the separation of CH_4/N_2 mixtures was developed, and the influence of key parameters was assessed. This novel technique was able to produce high purity methane and nitrogen streams, meeting the 97 % and 99 % purity requirements specified

for each component. By partially recovering the purge outlet stream as heavy product gas, the methane recovery and productivity can be increased up to 97.3 % and $11.5 \text{ kg} \cdot \text{m}^{-3}_{\text{ads}} \cdot \text{h}^{-1}$, respectively. Optimising the purge flow rate utilised during this sub-step allows the recovery of the light product to be kept above 90 %.

Also, increasing the value of P_{low} is inefficient in terms of process performance, as it reflects in a lower recovery of methane and, consequently, lower productivity. This way, to obtain a high purity and high recovery methane stream, the pressure during the desorption sub-steps in the PSA sequence needs to be set to very low values (0.1 bar), leading to a power consumption of $503.0 \text{ W} \cdot \text{h} \cdot \text{kg}^{-1}_{\text{CH}_4}$.

The presented results show that this advanced hybrid process can be a competitive alternative to the state-of-the-art nitrogen removal technologies, allowing the production of purified methane with high throughputs.

7.5. References

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2. Rodrigues, A. E., Pereira, C., Minceva, M., Pais, L. S., Ribeiro, A. M., Ribeiro, A., Silva, M., Graça, N., and Santos, J. C., *Simulated moving bed technology: principles, design and process applications*. 2015, Oxford: Butterworth-Heinemann.

CHAPTER 8 – CONCLUSIONS AND FUTURE WORK

8.1. Main conclusions

The main objective of this thesis was to develop a new and advanced adsorption process for the separation of nitrogen from methane based on the gas-phase SMB technology. To achieve this goal, it was essential to select suitable adsorbent and desorbent gas, and to investigate their adsorption equilibria and multicomponent adsorption behaviour. This would provide the necessary basis for developing an accurate mathematical model that is able to describe the system and design an effective process. As such, a comprehensive literature review was first carried out to assess the performance of various adsorbents for CH₄/N₂ separation. With the obtained database, an SMB-specific performance metric was created to easily identify the most effective adsorbent/desorbent combination for a specific application. Experimental studies, including adsorption isotherm measurements and fixed-bed tests, were conducted for the selected materials, followed by the design and evaluation of gas-phase SMB processes for each pair. Finally, a simulation study was undertaken to conceptualize a hybrid SMB/PSA system which would remove the need for a desorbent gas and, thus, enhance the efficiency of the process. Below, the main conclusions presented in this thesis are summarised.

First, an SMB Performance Indicator was developed to discriminate between several adsorbent/desorbent pairs for a specific separation by SMB. This metric was validated for the CH₄/N₂ separation using CO₂ as the desorbent gas. However, its success was also shown for different desorbents, with varying adsorption strengths when compared to the target mixture. Its validity was demonstrated for another binary gas separation application (ethane/ethylene). For the screening process, the pure component isotherms must be gathered, and a preliminary pressure, temperature, and feed compositions must be defined in advance for the calculations. The indicator can then be calculated using multicomponent adsorption data at the specified pressure and temperature conditions (selectivity and uptake), and the heat of adsorption of both components of the gas mixture. This removes the necessity of experiments or simulations for selecting the adsorbent/desorbent pair, which can be time-consuming, allowing for a much easier screening process.

Then, the separation performance of a commercial activated carbon (BPL), in-house extruded Maxsorb pellets, and 3D-printed Maxsorb AC monoliths was evaluated for CH₄/N₂ mixtures using the conventional gas-phase SMB. The performance of the adsorbents for the target separation was assessed through adsorption equilibrium measurements, model fitting of the obtained equilibria, dynamic tests and modelling of the fixed-bed experiments, and both experimental and modelling of SMB cycles.

Commercial BPL activated carbon was tested for the upgrade of nitrogen-contaminated methane streams. Adsorption equilibrium isotherms for each pure adsorbate were measured at 303, 323, and 343 K, in a pressure range up to 2.5 bar, using a volumetric method, over the BPL material. The

experimental data was successfully fitted with the DSL model and the isosteric heat of adsorption for each adsorbate was determined. Analysis of the collected results indicated preferential adsorption of CO₂ over the entire temperature and pressure range, with Ar weakly adsorbing to the surface of the material. Then, fixed-bed experiments were performed in the gas-phase SMB unit to investigate the multicomponent dynamic behaviour and validate the proposed mathematical model, which was necessary for designing the SMB cycles and computing the separation regions for each eluent. The adsorption capacity obtained through the single-component breakthrough tests was in agreement with the equilibrium results. Results showed that the model equations were able predict the breakthrough curves accurately for the single and multi-component tests. Two SMB cycles for separating a CH₄/N₂ stream with a 0.50/0.50 feed composition, at 303 K, in an open-loop mode were performed using the BPL activated carbon and two different desorbents, Ar and CO₂, to evaluate the impact of the desorbent strength on the SMB performance. A classic four-zone 2-3-2-1 configuration was utilized, with a switching time of 50 s. The performance of each cycle was evaluated in terms of purity, recovery, productivity, and desorbent consumption for both product streams. Complete separation was achieved with both desorbent gases. The cycle performed with argon showed better results overall, producing 13.9 kg·m⁻³_{ads}·h⁻¹ of a methane stream with 96.2% purity and 97.4% recovery and 30.8 kg·m⁻³_{ads}·h⁻¹ of a nitrogen stream with 97.4% purity and a recovery of 93.4%. Regarding the desorbent consumption, a value of 15.3 and 6.9 m³_{STP,Ar}·kg⁻¹ was obtained for the extract and raffinate stream, respectively.

Maxsorb powder was extruded into pellets with 10% binder (CMC) content. The material was characterised, and its adsorptive capabilities were evaluated for its application in an SMB process for the separation of methane and nitrogen mixtures. The adsorption equilibrium isotherms were assessed for N₂, CH₄, CO₂, and Ar at 303, 323, and 343 K, up to a pressure of 2.5 bar. The Langmuir equation was able to fit the experimental points, and the model parameters necessary for the design of the SMB process were acquired. Carbon dioxide exhibited the highest uptake among the measured adsorbates, followed by CH₄, N₂ and Ar. The dynamic behaviour of single and multicomponent adsorption over the pelletised Maxsorb was evaluated through breakthrough experiments, and the acquired data was predicted with a mathematical model. The breakthrough results allowed the validation of the adsorption equilibrium data measured as well as the transport parameters and model equations used in the simulations. No prominent mass transfer limitations were observed in the performed experiments. Then, two SMB runs were designed for the separation of a CH₄/N₂ stream at 303 K and 1.5 bar in open-loop mode. The experiments were conducted using two desorbents, CO₂ and Ar. Both runs were able to separate the compounds from each other. The cycle using argon as the desorbent has shown better results when compared with the carbon dioxide run. Regarding the methane-rich stream, a purity of 99.3% and a 97.2% recovery was obtained, with a productivity of 17.8 kg·m⁻³_{ads}·h⁻¹ for the CO₂ cycle, while a purity of 100.0% and a 98.9% recovery was obtained, with a productivity of 35.1 kg·m⁻³_{ads}·h⁻¹ was achieved

with argon as the desorbent gas. Also, a parametric study on the number of columns in each section was also conducted, which showed that introducing more columns in section III when using a strong desorbent allowed the treatment of a higher feed flow rate, improving the methane productivity by 31.4%.

Activated carbon-based monoliths for separating CH₄ and N₂ gases were 3D-printed. Then, equilibrium data of CH₄, N₂, Ar, and CO₂ and breakthrough experiments involving these components were performed. The similarity between the measured isotherms in different printed monoliths ensured that the equilibrium data could be used to predict the dynamic behaviour of the system. The mathematical model was sufficiently robust to predict the breakthrough results for the single, binary and ternary experiments. Thus, this model was implemented to design and simulate the SMB cyclic experiments. A total of three SMB experiments were performed, with purities above 96.6 % and 97 % for both extract and raffinate, respectively. The SMB configuration consisted of six columns in a 1-2-2-1 arrangement, and a switch time interval of 110 s was utilised. Regarding the methane-rich stream, the productivities attained were 2.7 and 6.5 kg·m⁻³_{ads}·h⁻¹ for the CO₂ and Argon experiments, respectively. By operating in closed loop, *i.e.*, with desorbent recycling, the desorbent consumption was reduced by 40.7%.

The separation region for each material was determined with the validated mathematical model and the maximum productivity for each case (at the vertex of the region) was obtained per mass of adsorbent and per volume of column. As predicted by the SPI, the pelletised Maxsorb AC presented a higher productivity per mass of adsorbent, when compared with the other two materials, for both desorbents. In terms of maximum productivity per volume of column, the BPL AC exhibited the best performance, making it more appealing from a design perspective.

Finally, a hybrid SMB/PSA process was developed using BPL as the adsorbent media, and a parametric study was conducted to observe the influence of the key operating conditions on the performance of the process. The SMB simulation code was adapted to model the hybrid process. The simulation results show that this process can successfully produce high-purity methane and nitrogen streams, meeting the target purities of 97% and 99%, respectively. The partial recovery of the purge outlet stream as CH₄ product allowed an improvement in both CH₄ recovery and productivity, up to 97.3 % and 11.5 kg·m⁻³_{ads}·h⁻¹, respectively. Optimizing the purge flow rate is needed to prevent a significant decrease in N₂ recovery and productivity. This way, N₂ recovery can go up to 91.3%, with a productivity of 18.8 kg·m⁻³_{ads}·h⁻¹. Additionally, increasing the lower pressure during desorption was found to be detrimental, leading to reduced CH₄ recovery and lower productivity. Therefore, achieving both high purity and high recovery requires maintaining very low desorption pressures, around 0.1 bar, which results in a specific energy consumption of 503.0 W·h·kg⁻¹_{CH₄}.

8.2. Future Work

In future work, incorporating kinetics into the calculation of the SMB performance indicator could be investigated to assess whether the metric still reliably predicts material performance in the SMB process.

Future work should also focus on the separation and purification of the downstream products obtained from the SMB cycles, aiming to recover the target components and regenerate the desorbent to be reused within the SMB process. Conducting an economic analysis of the global process would further add value to the study by assessing the competitiveness of this technology relatively to the current state-of-the-art technologies.

Additionally, the exploration of new materials, such as MOFs, could further enhance SMB process efficiency. Recently, several MOFs have emerged with high methane uptake and high adsorption selectivities which can significantly improve equilibrium-based separation processes.

Regarding the SMB/PSA hybrid process, instead of partially recovering the purge outlet stream as methane product, another approach could be to recycle the purge flow rate to the feed inlet of the SMB/PSA unit, which could improve both methane/nitrogen recovery and productivity.

Additionally, I propose the modification of the existing gas-phase SMB unit to integrate an SMB/PSA hybrid system, followed by experimental validation using the pilot-scale unit to demonstrate proof-of-concept and assess its feasibility for industrial application.

APPENDIX A

Table A.1 - Adsorption equilibrium isotherm parameters of N₂ over the screened adsorbent materials.

Adsorbent	T (K)	Isotherm	q_1 (mmol·g ⁻¹)	$b_1 \times 10^5$ (Pa ⁻¹)	q_2 (mmol·g ⁻¹)	$b_2 \times 10^5$ (Pa ⁻¹)	n	t	Max. P (kPa)	Method	Ref.
Carbon-based materials											
2GA-H2J	303	Sips	4.099	0.764	-	-	1.091	-	≈1000	V	[17]
AC	303	Sips	9.35	0.19	-	-	1.095	-	≈3500	G	[16]
AC Beads	303	Sips	5.52	0.466	-	-	1.09	-	≈5000	G	[15]
BPL	303	Langmuir	1.687	2.065	-	-	-	-	≈300	BT	[14]
CMS 3A	303	Sips	3.97	0.46	-	-	1.22	-	≈1500	V	[13]
CMS 3K	303	DSL	0.476	8.472	8.817	0.128	-	-	≈2000	G	[12]
DARCO	298	DSL	6.118	0.201	0.543	2.594	-	-	≈1000	G	[11]
Degussa F30-470	303	Toth	5.123	0.745	-	-	-	0.826	≈5000	V	[10]
Norit R1 Extra	298	Sips	6.442	0.409	-	-	1.124	-	≈6000	G	[9]
Norit R2030	303	Sips	2.29	1.268	-	-	1.064	-	≈700	G	[8]
Norit RB3	303	Toth	8.45	0.385	-	-	-	0.54	≈5000	V	[6, 7]
Maxsorb	298	Langmuir	13.7	0.34	-	-	-	-	≈4000	V	[5]
PCB	303	Sips	1.423	1.577	-	-	1.097	-	≈1500	V	[4]
WV1050	303	Langmuir	6.801	0.255	-	-	-	-	≈3700	G	[3]
Xtrusorb A754	303	Sips	4.967	0.553	-	-	1.124	-	≈1000	G	[1, 2]
Activated aluminas / Silica Gel											
AA-300	303	Sips	0.679	0.247	-	-	0.914	-	≈1000	G	[1, 2]

Table A.1 (cont.)- Adsorption equilibrium isotherm parameters of N₂ over the screened adsorbent materials.

Adsorbent	T (K)	Isotherm	q_i (mmol·g ⁻¹)	$b_1 \times 10_6$ (Pa ⁻¹)	q_2 (mmol·g ⁻¹)	$b_2 \times 10^5$ (Pa ⁻¹)	n	t	Max. P (kPa)	Method	Ref.
Zeolites											
4A (Binderless)	303	DSL	3.24	0.991	0	0	-	-	≈900	G	[18]
5A	303	Sips	2.937	0.908	-	-	1.276	-	≈1000	G	[1, 2]
5A	303	Toth	6.365	0.54	-	-	-	0.744	≈5900	G	[19]
13X	303	Toth	3.37	1.189	-	-	-	1	≈500	G	[20]
13X	303	Sips	3.268	0.875	-	-	1.028	-	≈1000	V	[21]
CaX	303	Sips	4.506	0.444	-	-	1.908	-	≈1000	G	[1, 2]
Chabazite	303	Toth	3.24	2.923	-	-	-	0.56	≈3000	V	[22]
Clinoptilolite (Raw)	303	Toth	1.178	11.685	-	-	-	0.474	≈800	G	[23]
Si ²⁺ Clinoptilolite	303	Toth	1.368	60.192	-	-	-	0.398	≈800	G	[23]
Cs ⁺ Clinoptilolite	303	Toth	0.575	1.984	-	-	-	0.604	≈800	G	[23]
Fe ³⁺ Clinoptilolite	303	Toth	1.076	1.628	-	-	-	0.607	≈800	G	[23]
DD3R	303	DSL	1.56	0.878	3.84	0.002	-	-	≈7000	G	[24]
H-β	303	Langmuir	4.39	0.591	-	-	-	-	≈410	BT	[25]
HiSiv3000	303	Sips	1.85	0.73	-	-	1.098	-	≈1000	G	[26]
LiX	303	Sips	3.26	1.535	-	-	1.332	-	≈1000	V	[17]
H-Mordenite	303	Toth	2.44	0.786	-	-	-	0.886	≈2000	V	[27]
NaY	303	Toth	5.233	0.302	-	-	-	1.014	≈1000	V	[28]
ZSM-5	302	Sips	1.7	1.6	-	-	0.971	-	≈3000	G	[29]

Table A.1 (cont.) - Adsorption equilibrium isotherm parameters of N₂ over the screened adsorbent materials.

Adsorbent	T (K)	Isotherm	q_1 (mmol.g ⁻¹)	$b_1 \times 10^6$ (Pa ⁻¹)	q_2 (mmol.g ⁻¹)	$b_2 \times 10^5$ (Pa ⁻¹)	n	t	Max. P (kPa)	Method	Ref.
Metal-Organic Frameworks											
CAU-1	303	Toth	3.955	0.32	-	-	-	1.189	≈6000	G	[19]
CuBTC	303	Langmuir	7.45	0.386	-	-	-	-	≈700	G	[42]
Cu-MOF	303	Langmuir	0.58	2.7	-	-	-	-	≈120	V	[41]
MIL-53(Al)	303	Sips	5.931	1.706	-	-	1.207	-	≈3300	G	[39, 40]
MIL-100(Al)	303	Toth	6.422	0.19	-	-	-	1.033	≈5000	G	[19]
MIL-100(Fe)	303	Toth	7.432	0.35	-	-	-	0.887	≈5000	G	[19]
MIL-101(Cr)	303	Langmuir	12.248	0.069	-	-	-	-	≈800	V	[38]
MIL-125(Ti)	303	Toth	6.198	0.29	-	-	-	0.97	≈5000	G	[19]
MIL-125(Ti)-NH ₂	303	Langmuir	5.377	0.292	-	-	-	-	≈700	G	[37]
MIL-127(Fe)	303	Toth	5.186	0.44	-	-	-	1.094	≈5000	G	[19]
MOF-508b	303	Langmuir	18.34	0.277	-	-	-	-	≈450	BT	[36]
Ni-MOF-74	298	DSL	4.453	2.3	0.094	10.48	-	-	≈1000	G	[11]
Co-MOF-74	298	DSL	10.533	0.24	1.907	0.786	-	-	≈1000	G	[11]
Mg-MOF-74	298	DSL	12.712	0.296	1.287	2.68	-	-	≈1000	G	[11]
MOF Al-Fumarate	303	Langmuir	2.74	0.801	-	-	-	-	≈800	G	[35]
UiO-66(Zr)	303	Toth	3.181	0	-	-	-	1.124	≈4700	G	[19]
UiO-66(Zr)-NH ₂	303	Toth	4.771	0	-	-	-	0.768	≈4100	G	[19]
UiO-66(Zr)-(COOH) ₂	303	DSL	1.417	0.494	0.18	0.18	-	-	≈6000	G	[34]
UTSA-16	303	DSL	1.326	0.644	1.773	0.028	-	-	≈4000	V	[33]
ZIF-8	298	DSL	8.287	0.071	4.087	0.007	-	-	≈1000	V	[32]
ZIF-94	298	Langmuir	3.11	1.05	-	-	-	-	≈120	V	[30, 31]

Table A.2 - Adsorption equilibrium isotherm parameters of CH₄ over the screened adsorbent materials.

Adsorbent	T (K)	Isotherm	q_1 (mmol·g ⁻¹)	$b_1 \times 10^6$ (Pa ⁻¹)	q_2 (mmol·g ⁻¹)	$b_2 \times 10^5$ (Pa ⁻¹)	n	t	Max. P (kPa)	Method	Ref.
Carbon-based materials											
2GA-H2J	303	Sips	5.798	1.426	-	-	1.236	-	≈1000	V	[17]
AC	303	Sips	11.607	0.327	-	-	1.203	-	≈3500	G	[16]
AC Beads	303	Sips	6.79	1.277	-	-	1.23	-	≈5000	G	[15]
BPL	303	Langmuir	2.731	5.019	-	-	-	-	≈300	BT	[14]
CMS 3A	303	Sips	4.11	1.164	-	-	1.45	-	≈1500	V	[13]
CMS 3K	303	DSL	1.114	16.858	3.296	0.855	-	-	≈2000	G	[12]
DARCO	298	DSL	5.699	0.513	0.924	8.408	-	-	≈1000	G	[11]
Degussa F30-470	303	Toth	7.249	2.436	-	-	-	0.665	≈5000	V	[10]
Norit R1 Extra	298	Sips	9.402	0.713	-	-	1.277	-	≈6000	G	[9]
Norit R2030	303	Sips	3.738	2.638	-	-	1.174	-	≈700	G	[8]
Norit RB3	303	Toth	11.06	1.443	-	-	-	0.45	≈5000	V	[6, 7]
Maxsorb	298	Langmuir	17.91	0.443	-	-	-	-	≈4000	V	[5]
PCB	303	Sips	6.828	1.573	-	-	1.255	-	≈1500	V	[4]
WV1050	303	Langmuir	8.774	0.571	-	-	-	-	≈3700	G	[3]
Xtrusorb A754	303	Sips	7.873	0.957	-	-	1.307	-	≈1000	G	[1, 2]
Activated aluminas / Silica Gel											
AA-300	303	Sips	1.141	0.355	-	-	0.932	-	≈1000	G	[1, 2]

Table A.2 (cont.)- Adsorption equilibrium isotherm parameters of CH₄ over the screened adsorbent materials.

Adsorbent	T (K)	Isotherm	q_1 (mmol.g ⁻¹)	$b_1 \times 10^6$ (Pa ⁻¹)	q_2 (mmol.g ⁻¹)	$b_2 \times 10^5$ (Pa ⁻¹)	n	t	Max. P (kPa)	Method	Ref.
Zeolites											
4A (Binderless)	303	DSL	3.47	2.012	0	0	-	-	≈900	G	[18]
5A	303	Sips	3.13	2.082	-	-	1.074	-	≈1000	G	[1, 2]
5A	303	Toth	10.068	1.59	-	-	-	0.588	≈5900	G	[19]
13X	303	Toth	5.3	1.302	-	-	-	1	≈500	G	[20]
13X	303	Sips	4.094	1.368	-	-	0.988	-	≈1000	V	[21]
CaX	303	Sips	5.723	0.582	-	-	1.815	-	≈1000	G	[1, 2]
Chabazite	303	Toth	3.6	18.767	-	-	-	0.4	≈3000	V	[22]
Clinoptilolite (Raw)	303	Toth	1.087	14.064	-	-	-	0.482	≈800	G	[23]
Sr ²⁺ Clinoptilolite	303	Toth	1.25	61.643	-	-	-	0.621	≈800	G	[23]
Cs ⁺ Clinoptilolite	303	Toth	0.519	18.169	-	-	-	0.594	≈800	G	[23]
Fe ³⁺ Clinoptilolite	303	Toth	0.992	8.152	-	-	-	0.718	≈800	G	[23]
DD3R	303	DSL	1.71	2.697	1.54	0.004	-	-	≈7000	G	[24]
H-β	303	Langmuir	4.39	1.159	-	-	-	-	≈410	BT	[25]
HiSiV3000	303	Sips	1.867	3.247	-	-	1.082	-	≈1000	G	[26]
LiX	303	Sips	3.807	1.881	-	-	1.178	-	≈1000	V	[17]
H-Mordenite	303	Toth	2.43	3.016	-	-	-	0.85	≈2000	V	[27]
NaY	303	Toth	4.424	0.705	-	-	-	1.348	≈1000	V	[28]
ZSM-5	302	Sips	2.17	5.7	-	-	1.042	-	≈3000	G	[29]

Table A.2 (cont.)- Adsorption equilibrium isotherm parameters of CH₄ over the screened adsorbent materials.

Adsorbent	T (K)	Isotherm	q_i (mmol·g ⁻¹)	$b_1 \times 10^6$ (Pa ⁻¹)	q_2 (mmol·g ⁻¹)	$b_2 \times 10^5$ (Pa ⁻¹)	n	t	Max. P (kPa)	Method	Ref.
Zeolites											
CAU-1	303	Toth	5.505	0.82	-	-	-	1.175	≈6000	G	[19]
CuBTC	303	Langmuir	7.25	1.417	-	-	-	-	≈700	G	[42]
Cu-MOF	303	Langmuir	0.804	13.4	-	-	-	-	≈120	V	[41]
MIL-53(Al)	303	Sips	8.31	0.563	-	-	1.2	-	≈3300	G	[39, 40]
MIL-100(Al)	303	Toth	9.051	0.33	-	-	-	1.08	≈5000	G	[19]
MIL-100(Fe)	303	Toth	8.984	0.35	-	-	-	1.36	≈5000	G	[19]
MIL-101(Cr)	303	Langmuir	8.708	0.257	-	-	-	-	≈800	V	[38]
MIL-125(Ti)	303	Toth	8.707	0.62	-	-	-	1.258	≈5000	G	[19]
MIL-125(Ti)-NH ₂	303	Langmuir	7.093	0.797	-	-	-	-	≈700	G	[37]
MIL-127(Fe)	303	Toth	7.373	1.14	-	-	-	1.202	≈5000	G	[19]
MOF-508b	303	Langmuir	18.34	0.287	-	-	-	-	≈450	BT	[36]
Ni-MOF-74	298	DSL	7.513	1.38	1.301	3.193	-	-	≈1000	G	[11]
Co-MOF-74	298	DSL	4.474	0.538	4.206	0.665	-	-	≈1000	G	[11]
Mg-MOF-74	298	DSL	11.355	0.467	1.355	3.742	-	-	≈1000	G	[11]
MOF Al-Fumarate	303	Langmuir	4.5	2.183	-	-	-	-	≈800	G	[35]
UiO-66(Zr)	303	Toth	6.186	0.46	-	-	-	0.867	≈4700	G	[19]
UiO-66(Zr)-NH ₂	303	Toth	7.071	0.78	-	-	-	0.676	≈4100	G	[19]
UiO-66(Zr)-(COOH) ₂	303	DSL	1.486	1.069	0.416	0.642	-	-	≈6000	G	[34]
UTSA-16	303	DSL	2.148	1.475	0.772	0.149	-	-	≈4000	V	[33]
ZIF-8	298	DSL	5.399	0.244	5.4	0.024	-	-	≈1000	V	[32]
ZIF-94	298	Langmuir	3.07	6.696	-	-	-	-	≈120	V	[30, 31]

Table A.3 - Adsorption equilibrium isotherm parameters of CO₂ over the screened adsorbent materials.

Adsorbent	T (K)	Isotherm	q_1 (mmol·g ⁻¹)	$b_1 \times 10^6$ (Pa ⁻¹)	q_2 (mmol·g ⁻¹)	$b_2 \times 10^5$ (Pa ⁻¹)	n	t	Max. P (kPa)	Method	Ref.
Carbon-based materials											
2GA-H2J	303	Sips	8.19	2.963	-	-	1.295	-	≈1000	V	[17]
AC	303	Sips	19.855	0.351	-	-	1.24	-	≈3500	G	[16]
AC Beads	303	Sips	10.66	2.009	-	-	1.3	-	≈5000	G	[15]
BPL	303	Langmuir	4.25	8.138	-	-	-	-	≈300	BT	[14]
CMS 3A	303	Sips	4.86	3.058	-	-	1.7	-	≈1500	V	[13]
CMS 3K	303	DSL	2.914	1.95	1.385	5.854	-	-	≈2000	G	[12]
DARCO	298	DSL	7.478	1.343	0.762	4.543	-	-	≈1000	G	[11]
Degussa F30-470	303	Toth	10.173	5.064	-	-	-	0.687	≈5000	V	[10]
Norit R1 Extra	298	Sips	13.419	1.422	-	-	1.216	-	≈6000	G	[9]
Norit R2030	303	Sips	5.321	5.665	-	-	1.232	-	≈700	G	[8]
Norit RB3	303	Toth	55.363	0.65	-	-	-	0.343	≈600	BT	[6, 7]
Maxsorb	298	Langmuir	55.7	0.442	-	-	-	-	≈4000	V	[5]
PCB	303	Sips	7.587	2.955	-	-	1.141	-	≈1500	V	[4]
WV1050	303	Langmuir	19.586	0.61	-	-	-	-	≈3700	G	[3]
Xtrusorb A754	303	Sips	10.092	2.105	-	-	1.403	-	≈1000	G	[1, 2]
Activated aluminas / Silica Gel											
AA-300	303	Sips	3.672	1.087	-	-	1.822	-	≈1000	G	[1, 2]

Table A.3 (cont.)- Adsorption equilibrium isotherm parameters of CO₂ over the screened adsorbent materials.

Adsorbent	T (K)	Isotherm	q_1 (mmol·g ⁻¹)	$b_1 \times 10_6$ (Pa ⁻¹)	q_2 (mmol·g ⁻¹)	$b_2 \times 10^5$ (Pa ⁻¹)	n	t	Max. P (kPa)	Method	Ref.
Zeolites											
4A (Binderless)	303	DSL	1.81	3.941	3.68	35.915	-	-	≈900	G	[18]
5A	303	Sips	4.328	563.908	-	-	2.529	-	≈1000	G	[1, 2]
5A	303	Toth	19.134	3.86	-	-	-	0.432	≈5900	G	[19]
13X	303	Toth	7.06	607.039	-	-	-	0.48	≈500	G	[20]
13X	303	Sips	5.994	69.428	-	-	1.862	-	≈1000	V	[21]
CaX	303	Sips	6.614	91.208	-	-	1.836	-	≈1000	G	[1, 2]
Chabazite	303	Toth	4.27	1926.32	-	-	-	0.46	≈3000	V	[22]
Clinoptilolite (Raw)	303	Toth	2.168	5062.92	-	-	-	0.288	≈800	G	[23]
Sr ²⁺ Clinoptilolite	303	Toth	2.01	1526.77	-	-	-	0.421	≈800	G	[23]
Cs ⁺ Clinoptilolite	303	Toth	1.894	2576.86	-	-	-	0.316	≈800	G	[23]
Fe ³⁺ Clinoptilolite	303	Toth	1.789	532.149	-	-	-	0.342	≈800	G	[23]
DD3R	303	DSL	2.87	9.843	1.41	0.009	-	-	≈7000	G	[24]
H-β	303	Langmuir	4.39	3.232	-	-	-	-	≈410	BT	[25]
Hisiv3000	303	Sips	2.215	14.898	-	-	1.033	-	≈1000	G	[26]
LiX	303	Sips	8.199	8.36	-	-	3.581	-	≈1000	V	[17]
H-Mordenite	303	Toth	3.9	209.02	-	-	-	0.409	≈2000	V	[27]
NaY	303	Toth	6.532	45.691	-	-	-	0.785	≈1000	V	[28]
ZSM-5	302	Sips	2.67	63.8	-	-	1.493	-	≈3000	G	[29]

Table A.3 (cont.)- Adsorption equilibrium isotherm parameters of CO₂ over the screened adsorbent materials.

Adsorbent	T (K)	Isotherm	q_1 (mmol.g ⁻¹)	$b_1 \times 10^6$ (Pa ⁻¹)	q_2 (mmol.g ⁻¹)	$b_2 \times 10^5$ (Pa ⁻¹)	n	t	Max. P (kPa)	Method	Ref.
Metal-Organic Frameworks											
CAU-1	303	Toth	8.843	2.54	-	-	-	0.938	≈6000	G	[19]
CuBTC	303	Langmuir	15	3.439	-	-	-	-	≈700	G	[42]
Cu-MOF	303	Langmuir	1.009	33.3	-	-	-	-	≈120	V	[41]
MIL-53(Al)	303	Sips	9.039	1.136	-	-	1.437	-	≈3300	G	[39, 40]
MIL-100(Al)	303	Toth	16.812	0.61	-	-	-	1.161	≈5000	G	[19]
MIL-100(Fe)	303	Toth	134	3.39	-	-	-	0.218	≈5000	G	[19]
MIL-101(Cr)	303	Langmuir	22.908	0.349	-	-	-	-	≈800	V	[38]
MIL-125(Ti)	303	Toth	12.254	1.52	-	-	-	1.499	≈5000	G	[19]
MIL-125(Ti)-NH ₂	303	Langmuir	8.509	0.345	-	-	-	-	≈700	G	[37]
MIL-127(Fe)	303	Toth	10.268	3.67	-	-	-	1.329	≈5000	G	[19]
MOF-508b	303	Langmuir	18.34	0.983	-	-	-	-	≈450	BT	[36]
Ni-MOF-74	298	DSL	8.261	3.39	4.649	14.331	-	-	≈1000	G	[11]
Co-MOF-74	298	DSL	7.523	3.019	6.111	5.599	-	-	≈1000	G	[11]
Mg-MOF-74	298	DSL	9.498	3.026	6.206	34.46	-	-	≈1000	G	[11]
MOF Al-Fumarate	303	Langmuir	5.9	5.474	-	-	-	-	≈800	G	[35]
UiO-66(Zr)	303	Toth	8.5	1.87	-	-	-	0.756	≈4700	G	[19]
UiO-66(Zr)-NH ₂	303	Toth	18.73	7.07	-	-	-	0.329	≈4100	G	[19]
UiO-66(Zr)-(COOH) ₂	303	DSL	3.159	3.579	0.273	4.791	-	-	≈6000	G	[34]
UTSA-16	303	DSL	4.079	48.17	1.289	0.054	-	-	≈4000	V	[33]
ZIF-8	298	DSL	135.777	0.038	83.324	0.003	-	-	≈2000	G	[32]
ZIF-94	298	Langmuir	3.248	26	-	-	-	-	≈120	V	[30, 31]

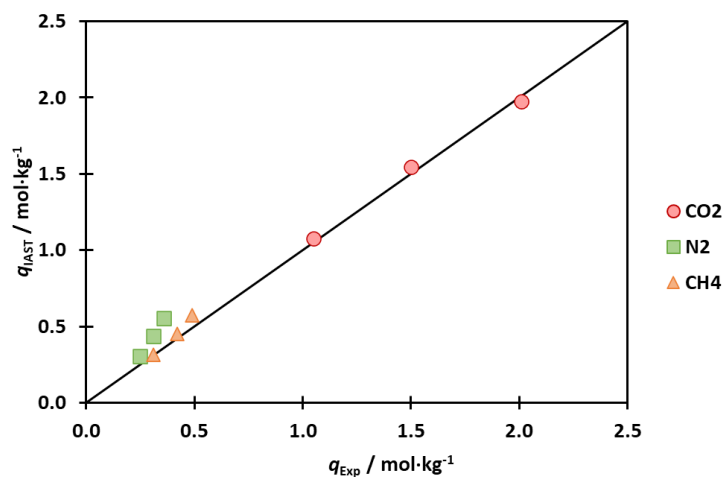


Figure A.1 - Comparison of experimental ternary adsorption equilibrium data with IAST predictions for the Norit R1 Extra adsorbent at 298 K. Experimental data taken from [9].

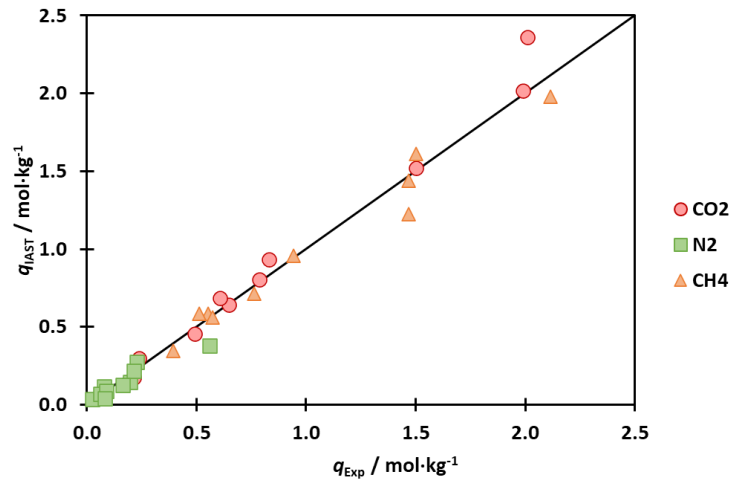


Figure A.2 - Comparison of experimental ternary adsorption equilibrium data with IAST predictions for the MOF-508b adsorbent at 303 K. Experimental data taken from [36].

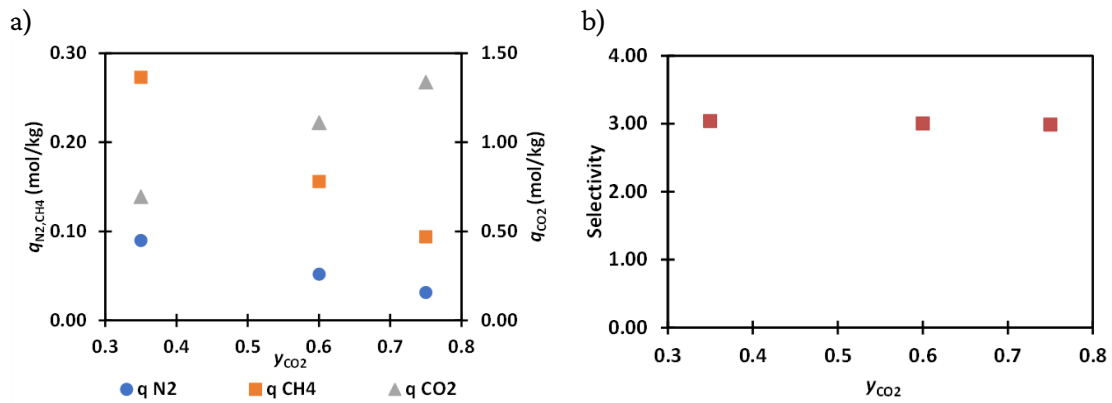
AC Sutcliffe Speakman

Figure A.3 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the AC (Sutcliffe Speakman) adsorbent.

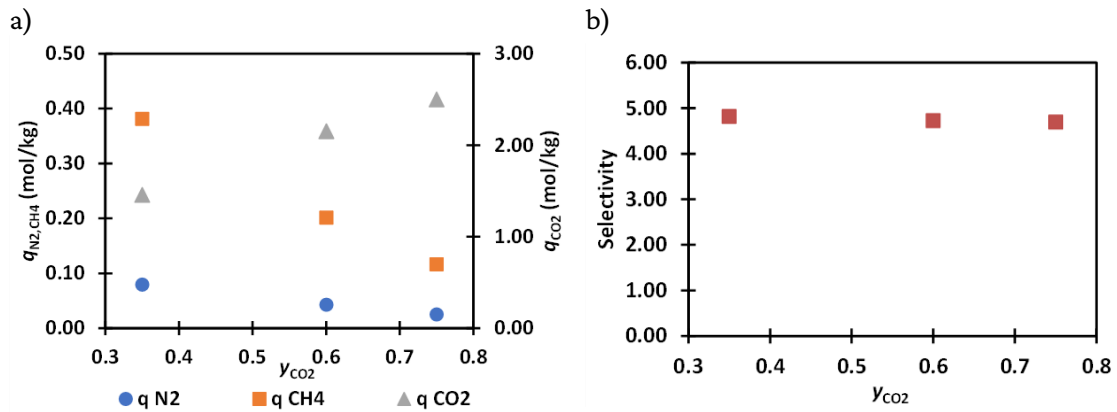
AC Beads

Figure A.4 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the AC Beads adsorbent.

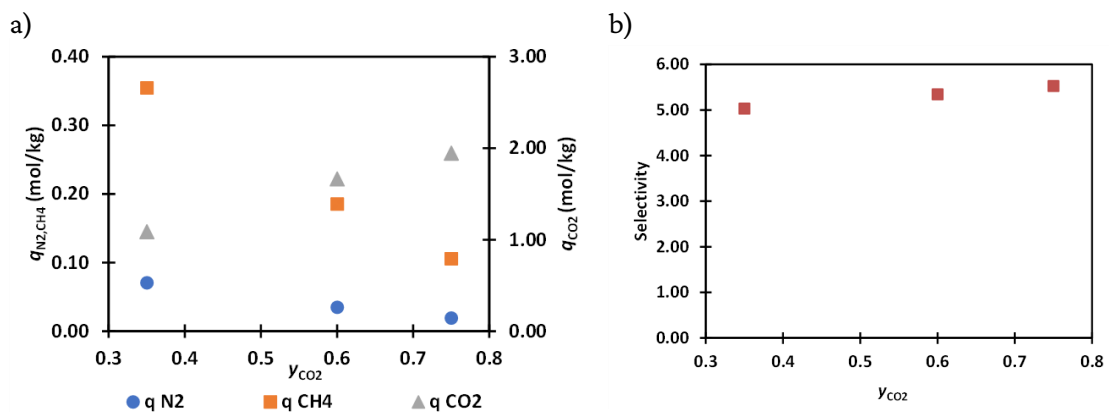
AC BPL

Figure A.5 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the BPL adsorbent.

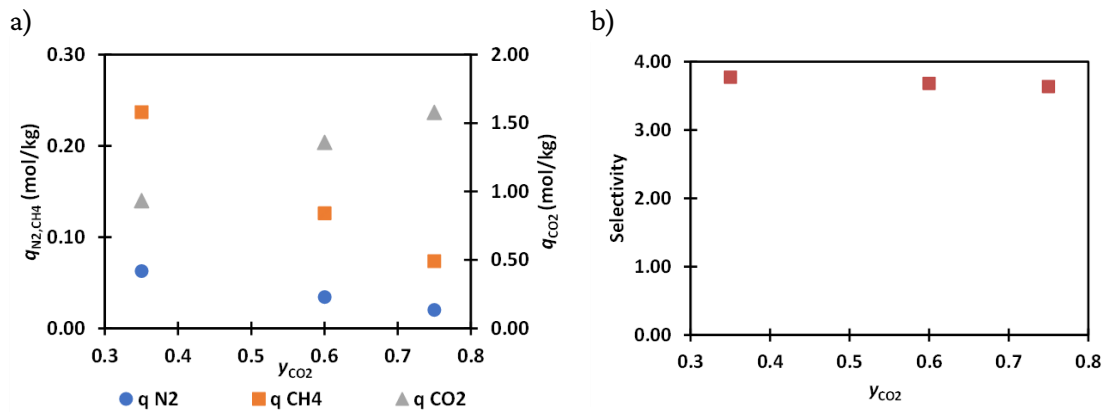
AC Darco

Figure A.6 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the AC Darco adsorbent.

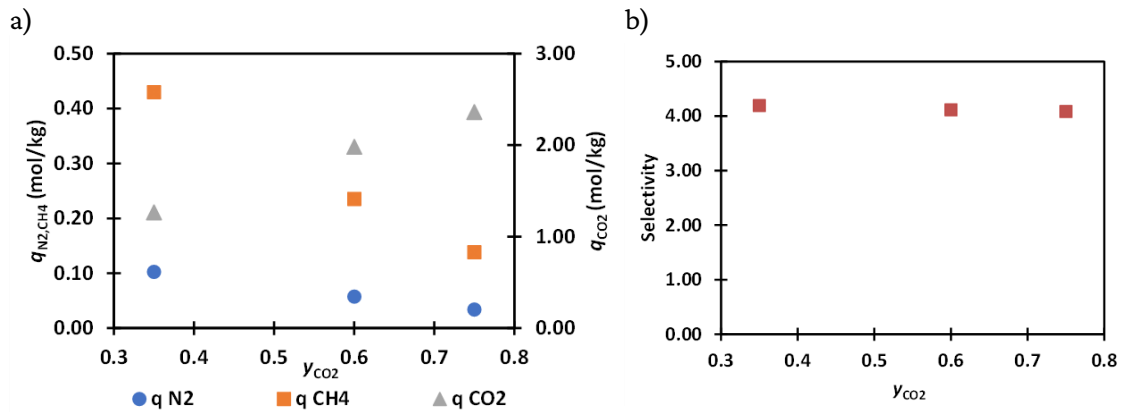
AC Norit R1 Extra

Figure A.7 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Norit R1 Extra adsorbent.

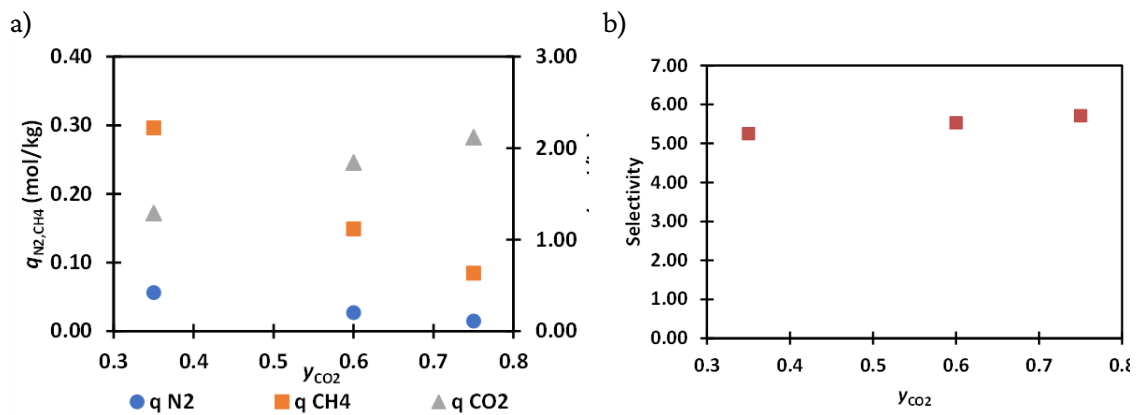
AC Norit R2030

Figure A.8 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Norit R2030 adsorbent.

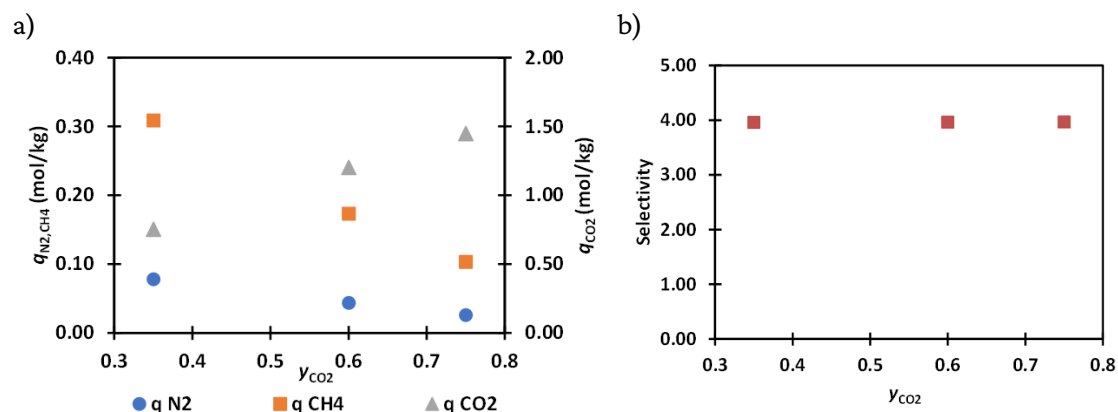
AC Norit RB3

Figure A.9 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Norit RB3 adsorbent.

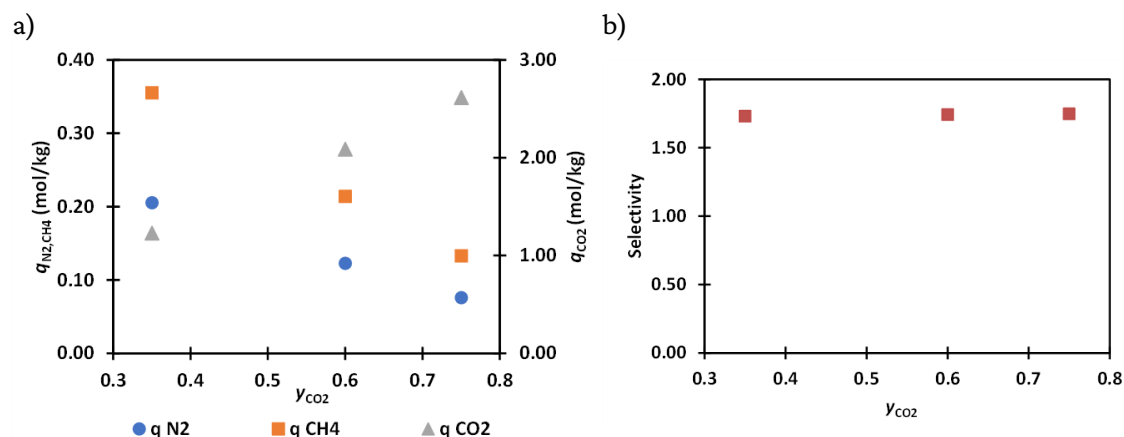
AC Maxsorb

Figure A.10 - Effect of the desorbent fraction onto a) the amount adsorbed and b) adsorption selectivity for the Maxsorb adsorbent.

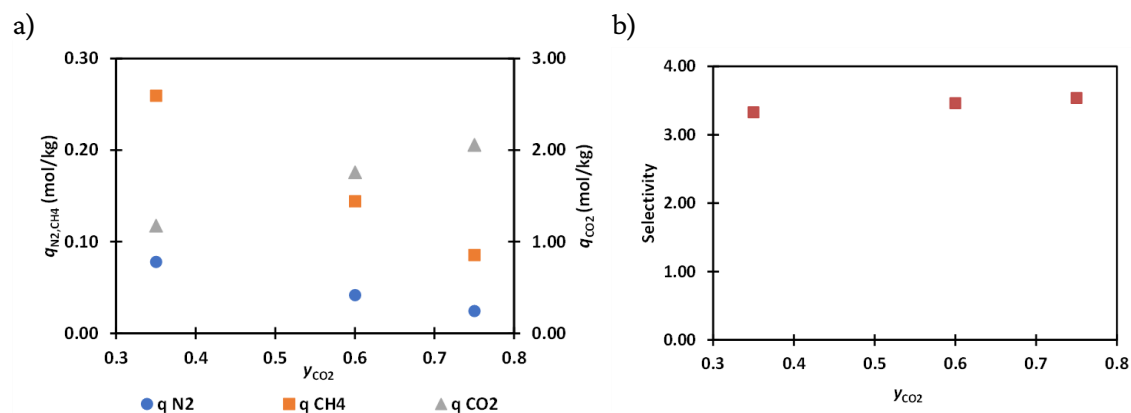
AC PCB

Figure A.11 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the AC PCB adsorbent.

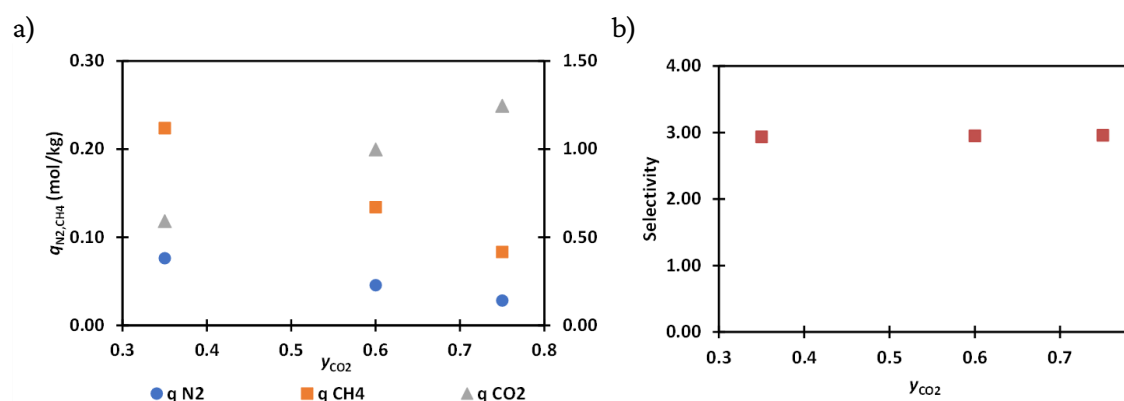
AC WV1050

Figure A.12 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the AC WV1050 adsorbent.

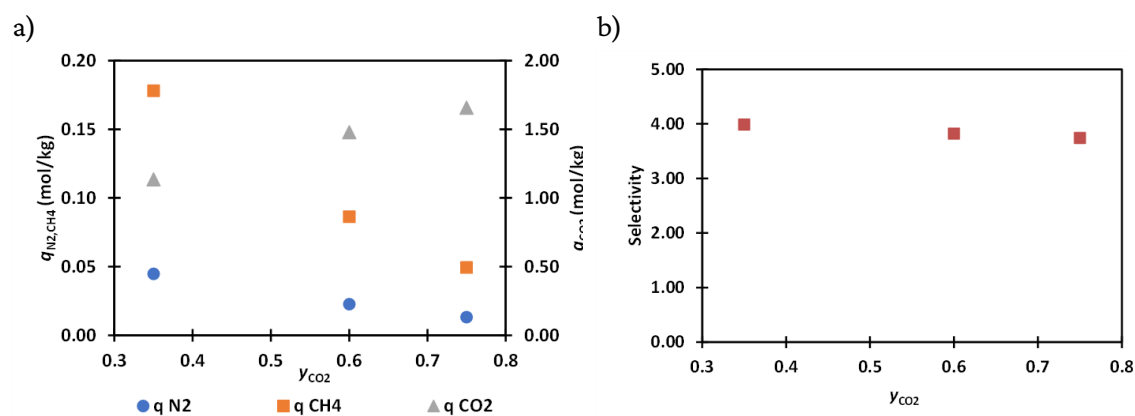
CMS 3A

Figure A.13 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the CMS 3A adsorbent.

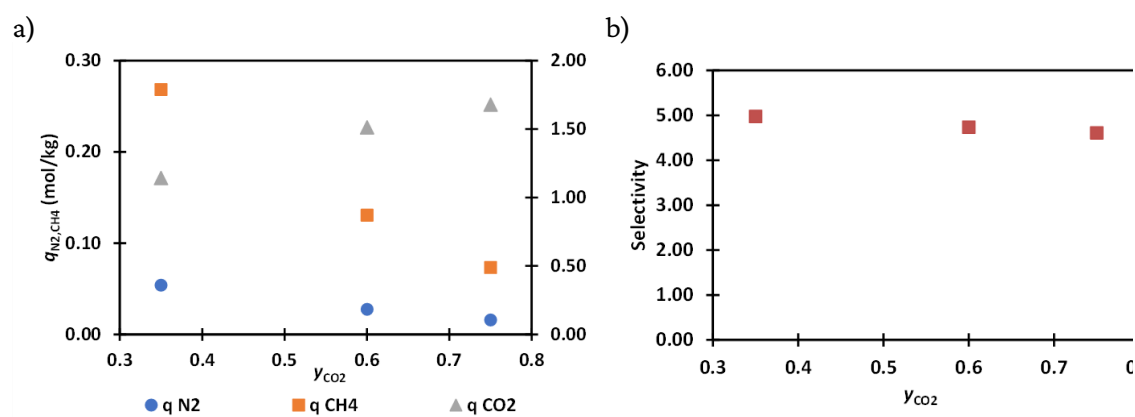
CMS 3K

Figure A.14 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the CMS 3K adsorbent.

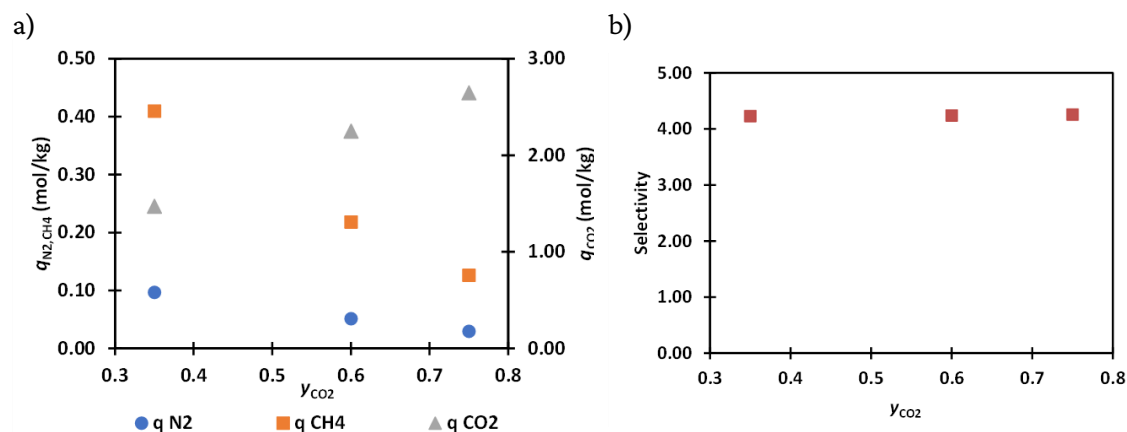
Degussa F30-470

Figure A.15 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Degussa F30-470 adsorbent.

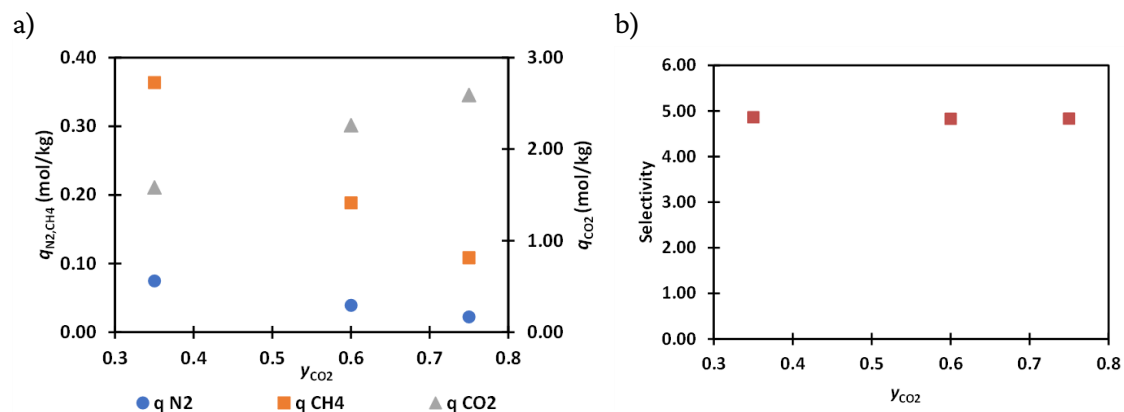
AC Xtrusorb A754

Figure A.16 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Xtrusorb A754 adsorbent.

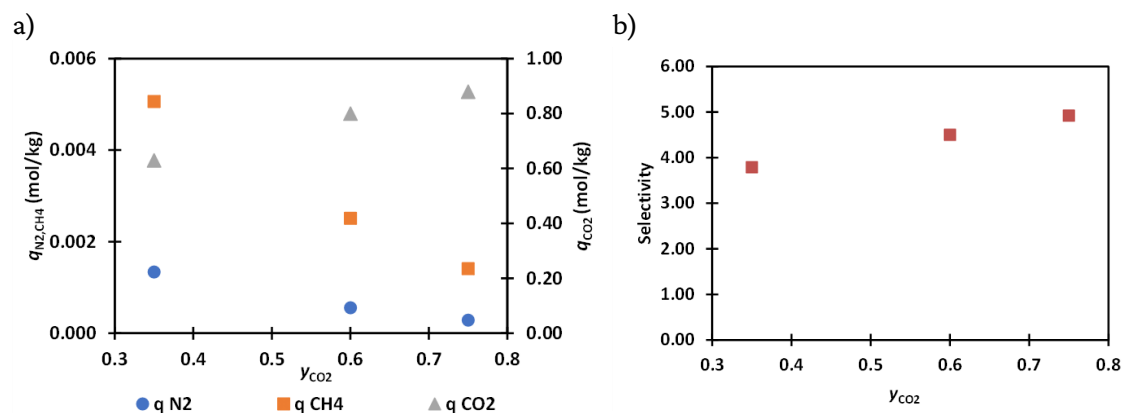
Activated Alumina AA300

Figure A.17 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the AA300 adsorbent.

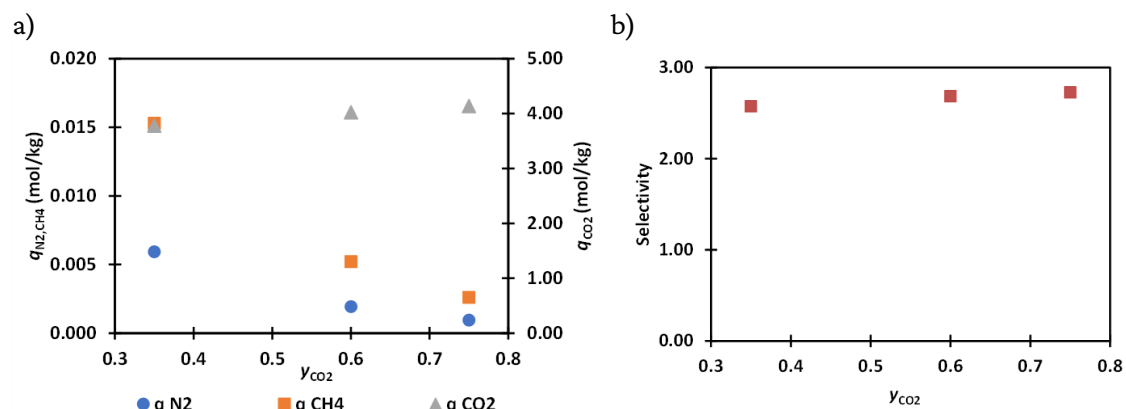
Zeolite 4A Binderless

Figure A.18 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the binderless Zeolite 4A adsorbent.

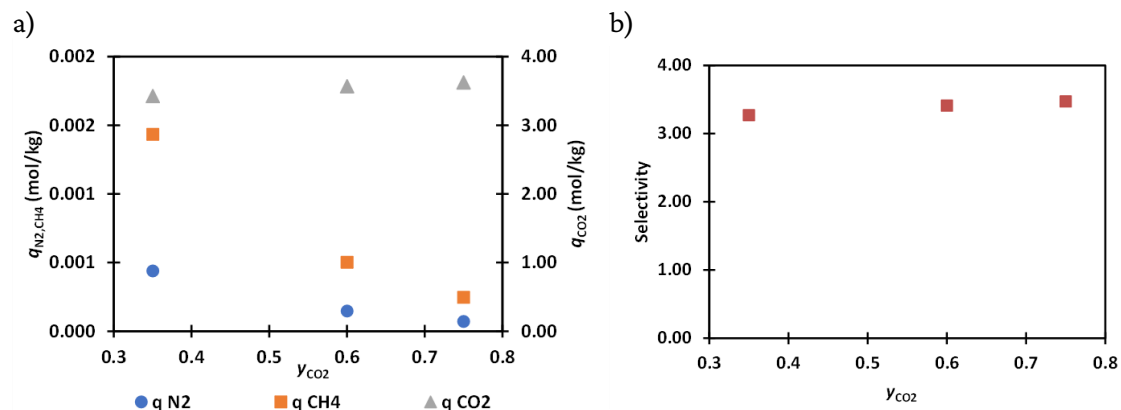
Zeolite 5A (Union Carbide)

Figure A.19 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Zeolite 5A (Union Carbide) adsorbent.

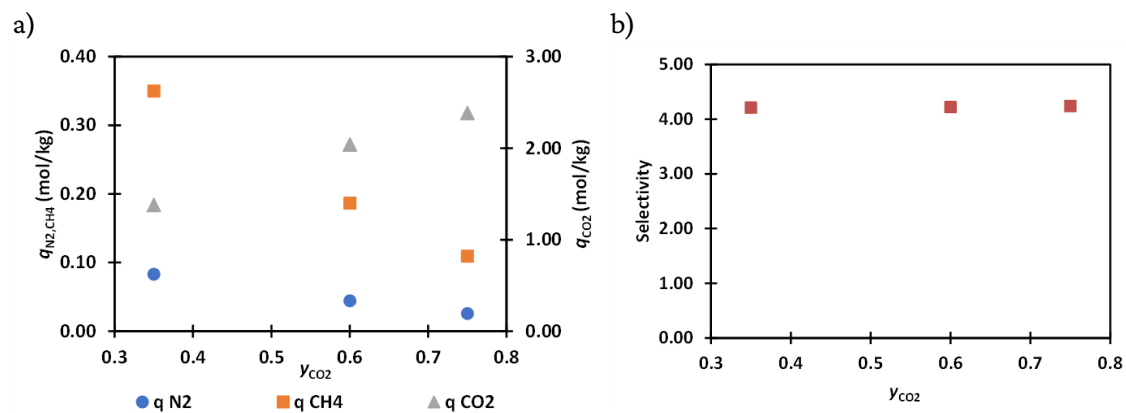
Zeolite 5A (Takeda)

Figure A.20 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Zeolite 5A (Takeda) adsorbent.

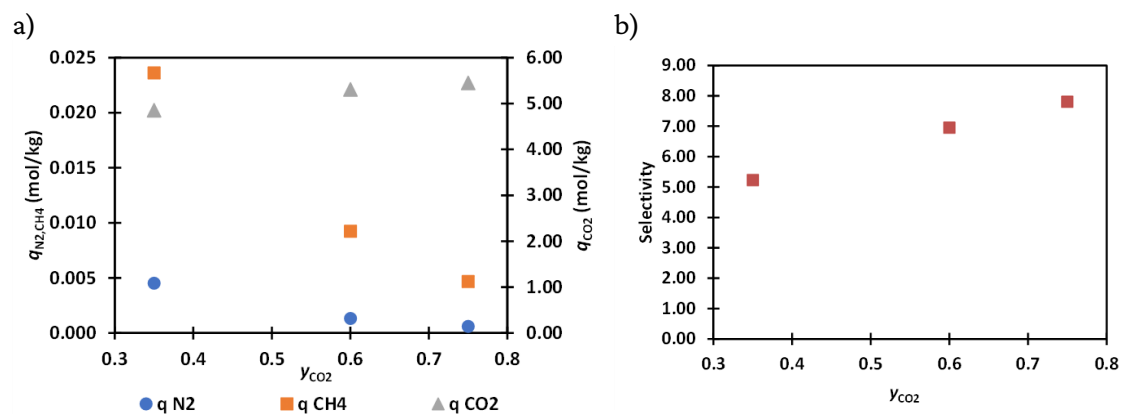
Zeolite 13X (CECA)

Figure A.21 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Zeolite 13X (CECA) adsorbent.

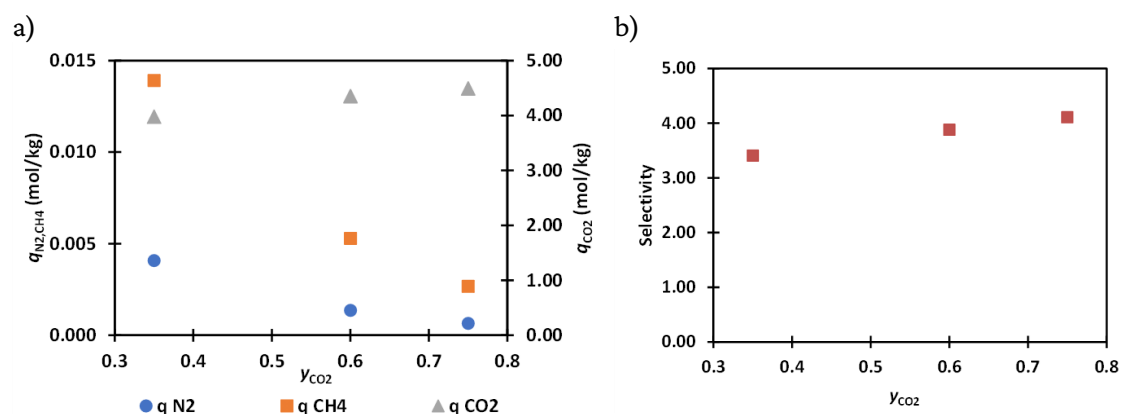
Zeolite 13X (UOP)

Figure A.22 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Zeolite 13X (UOP) adsorbent.

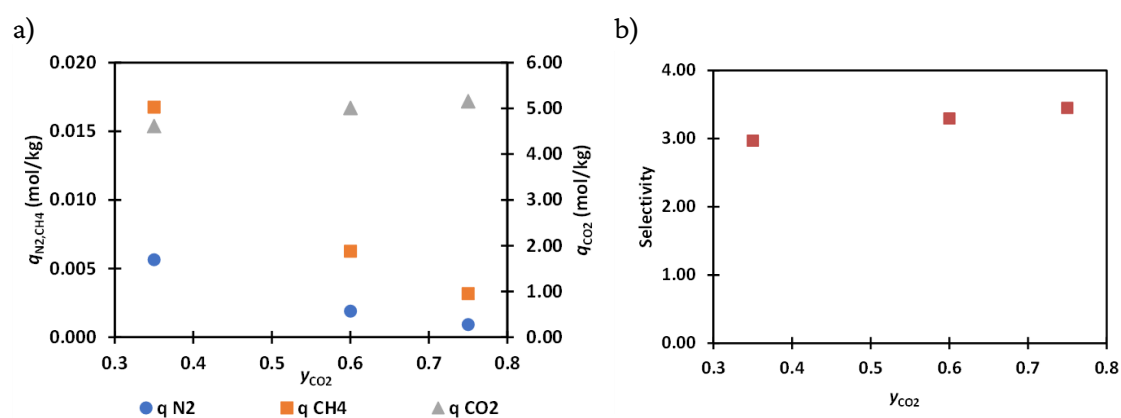
CaX

Figure A.23 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the CaX adsorbent.

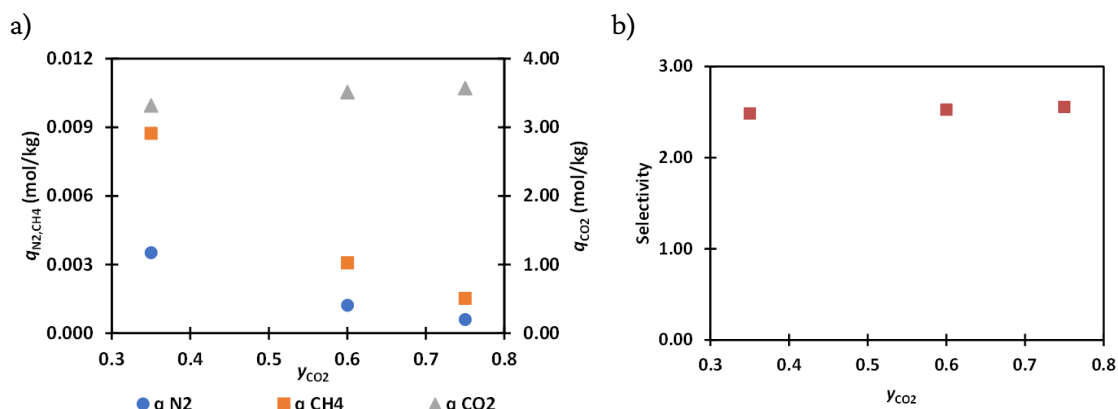
Chabazite

Figure A.24 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Chabazite adsorbent.

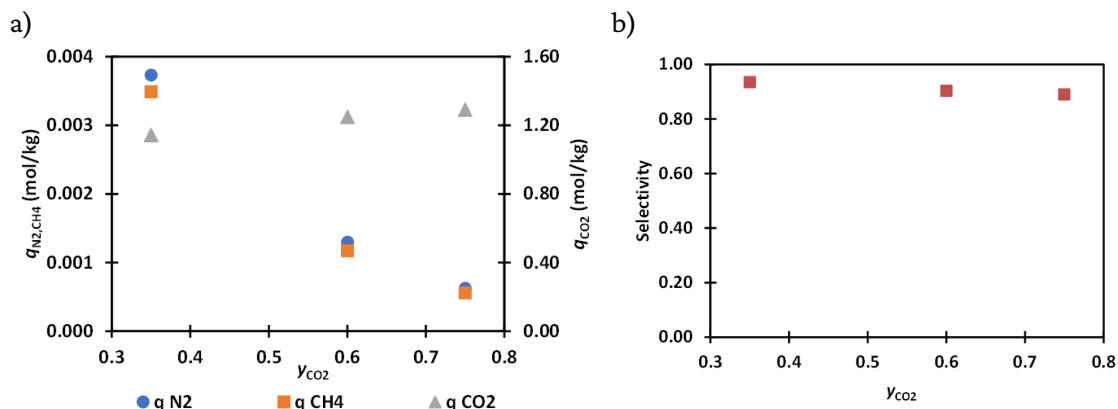
Clinoptilolite (Raw)

Figure A.25 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Clinoptilolite adsorbent.

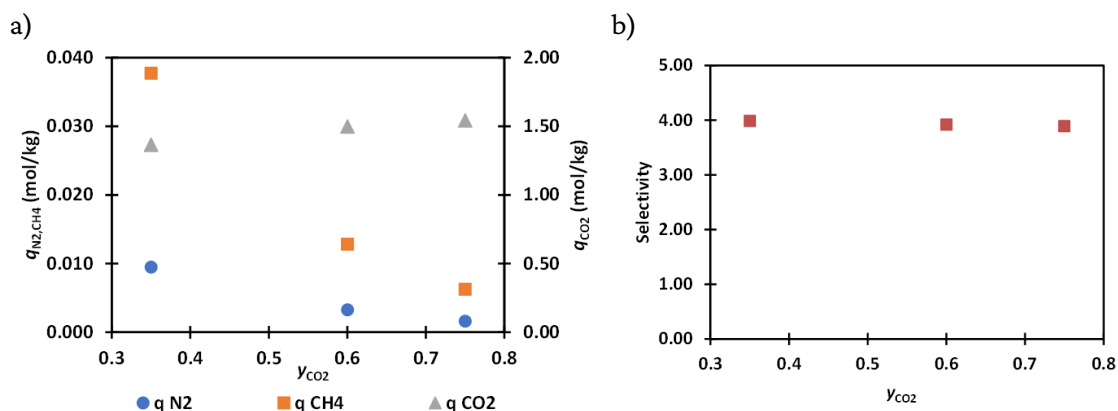
Sr-Clinoptilolite

Figure A.26 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Sr-Clinoptilolite adsorbent.

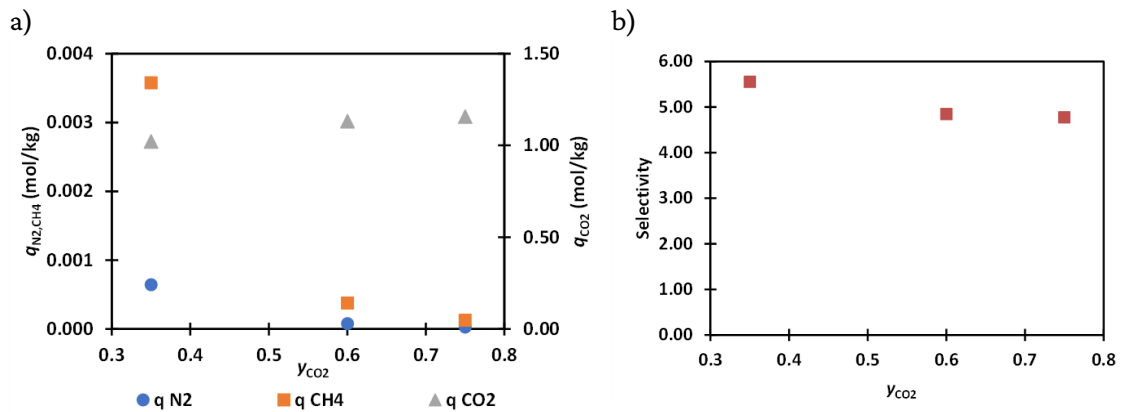
Cs-Clinoptilolite

Figure A.27 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Cs-Clinoptilolite adsorbent.

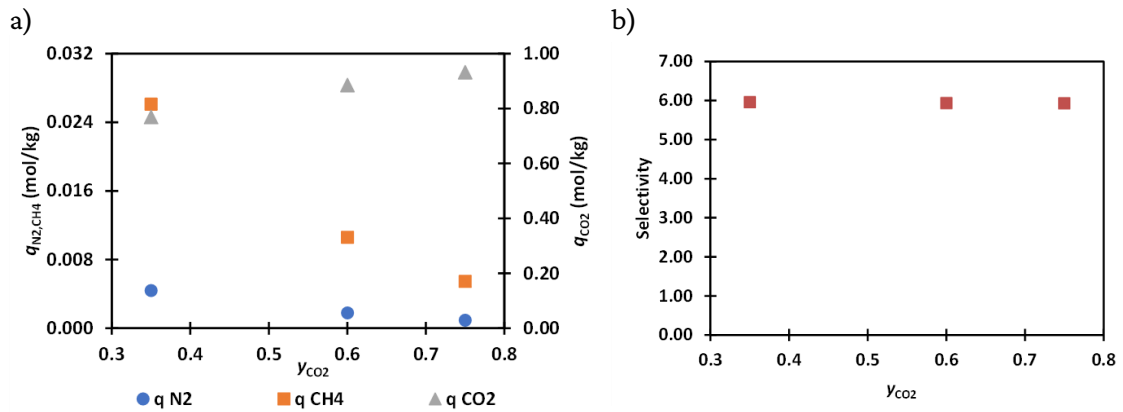
Fe-Clinoptilolite

Figure A.28 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Fe-Clinoptilolite adsorbent.

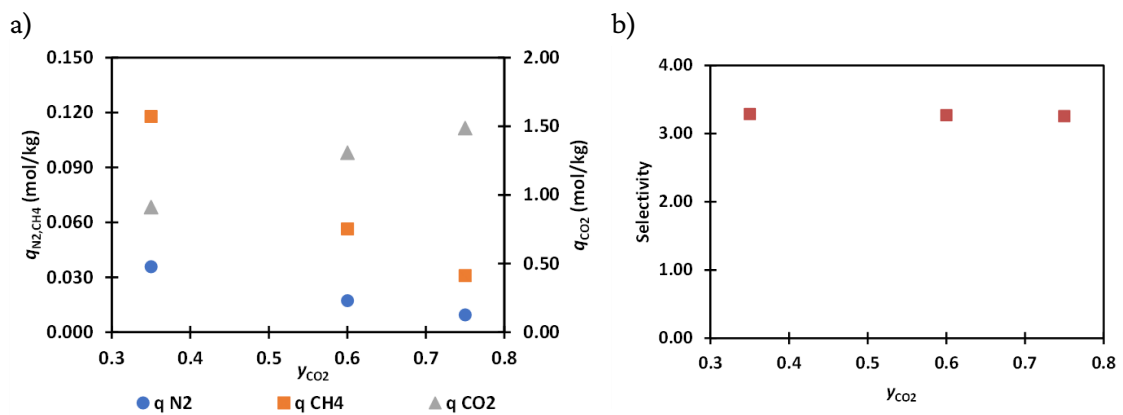
DDR3

Figure A.29 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the DDR3 adsorbent.

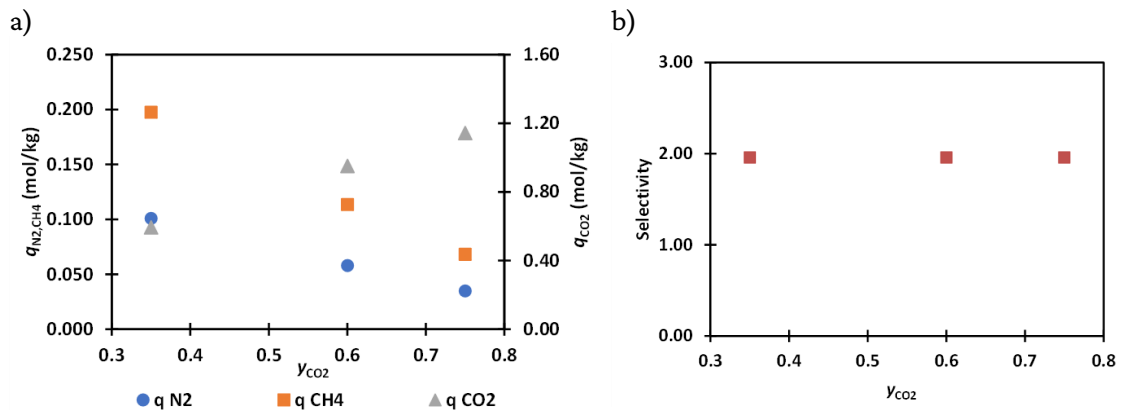
H-BETA-25

Figure A.30 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the H-BETA-25 adsorbent.

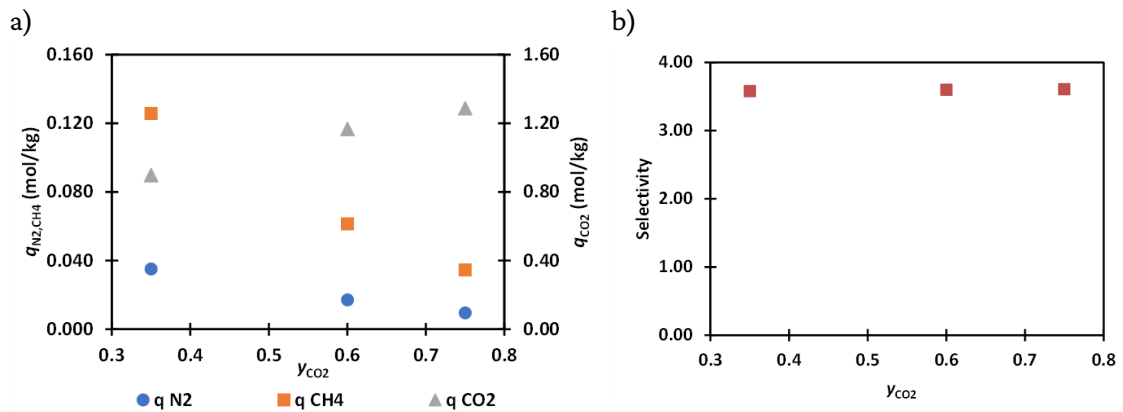
HiSiv3000

Figure A.31 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the HiSiv3000 adsorbent.

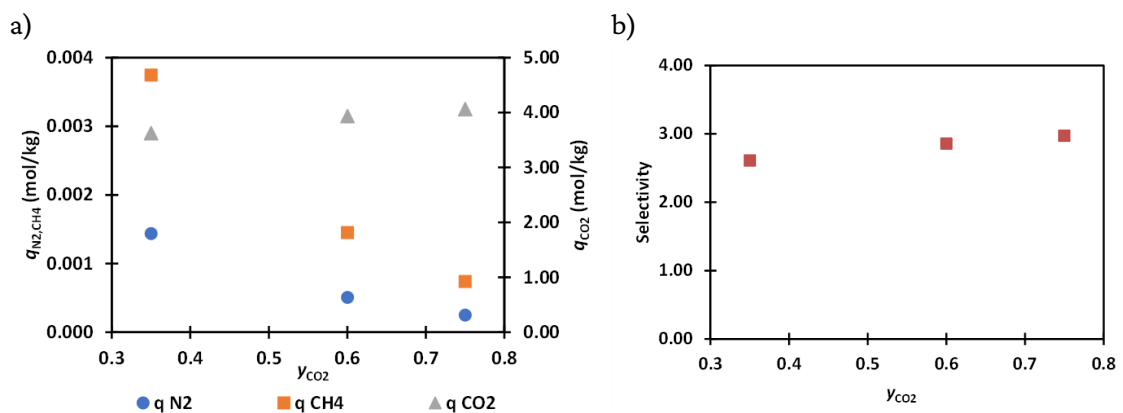
LiX

Figure A.32 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the LiX adsorbent.

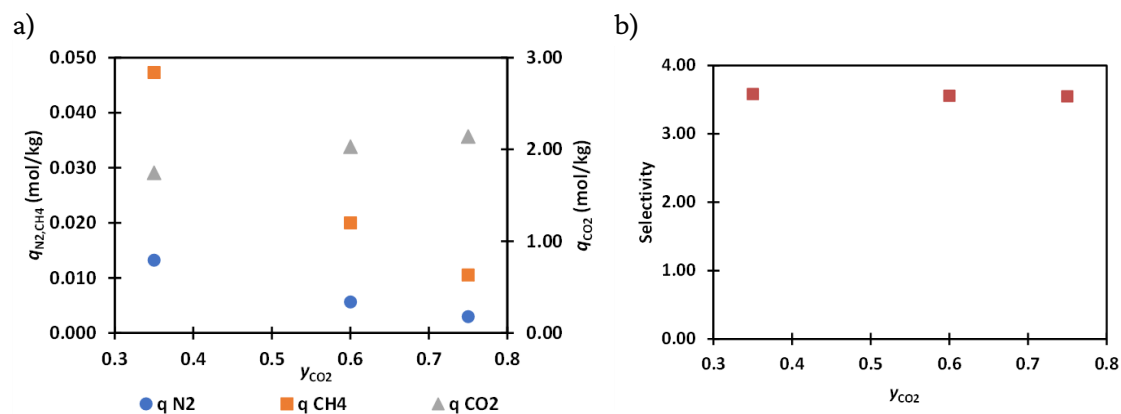
Mordenite

Figure A.33 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Mordenite.

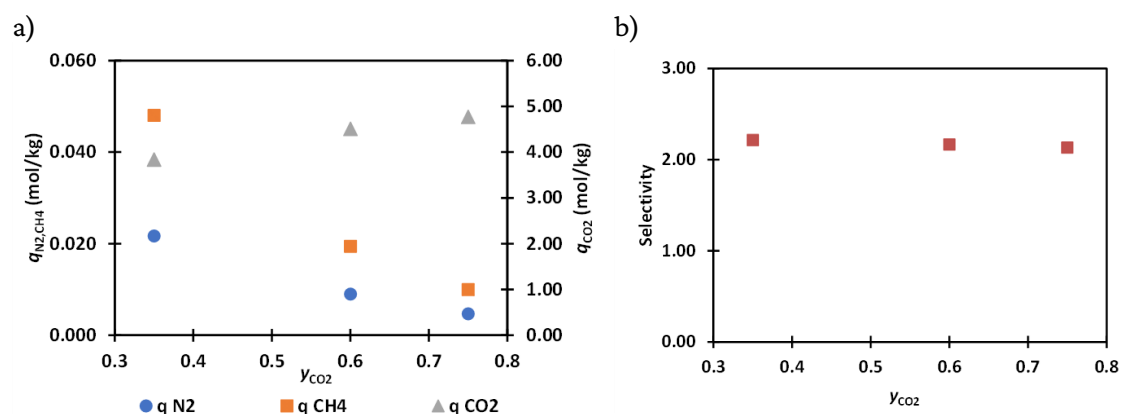
NaY

Figure A.34 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the NaY.

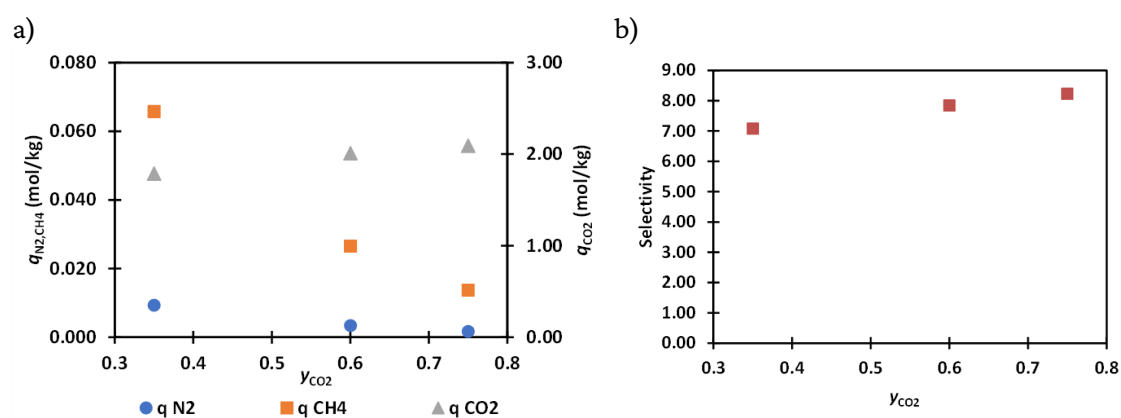
ZSM-5

Figure A.35 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the ZSM-5.

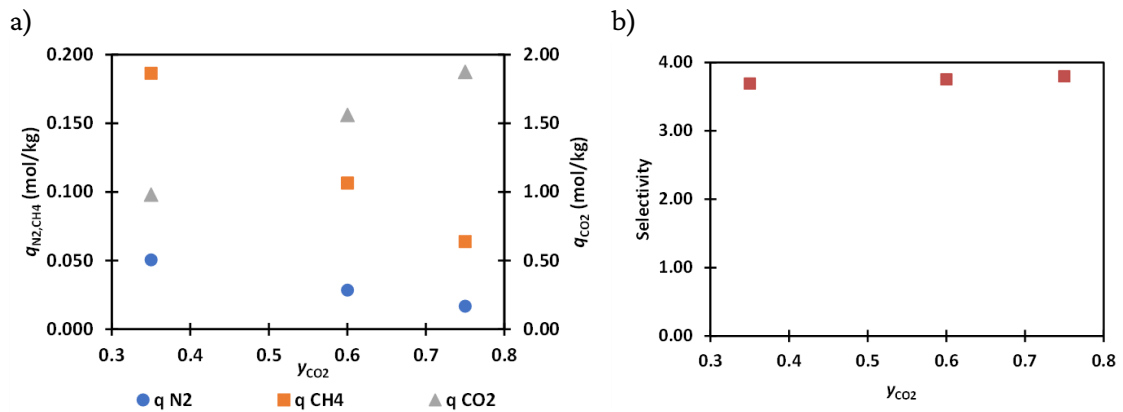
CAU-1

Figure A.36 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the CAU-1.

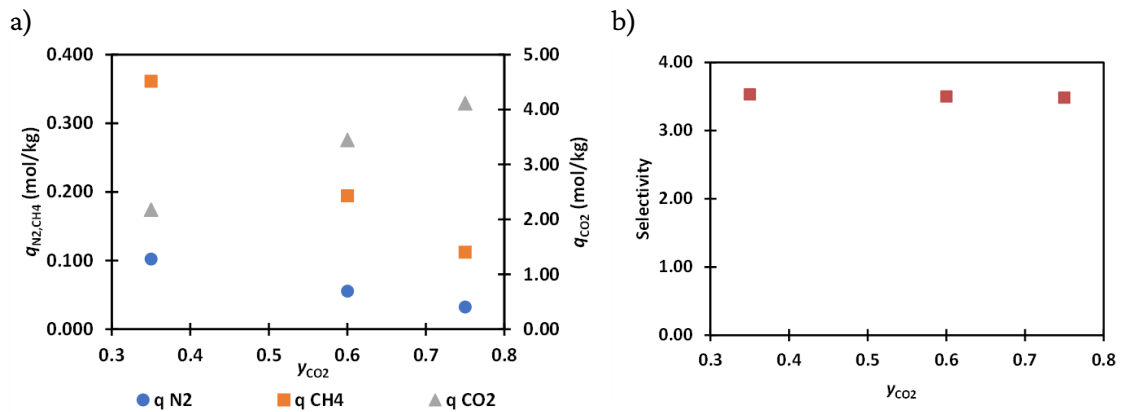
CuBTC

Figure A.37 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the CuBTC.

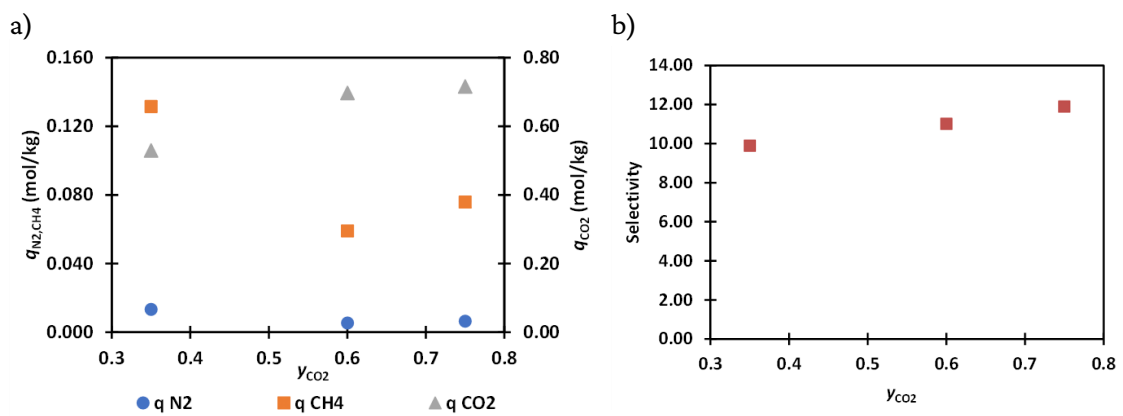
Cu-MOF

Figure A.38 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Cu-MOF.

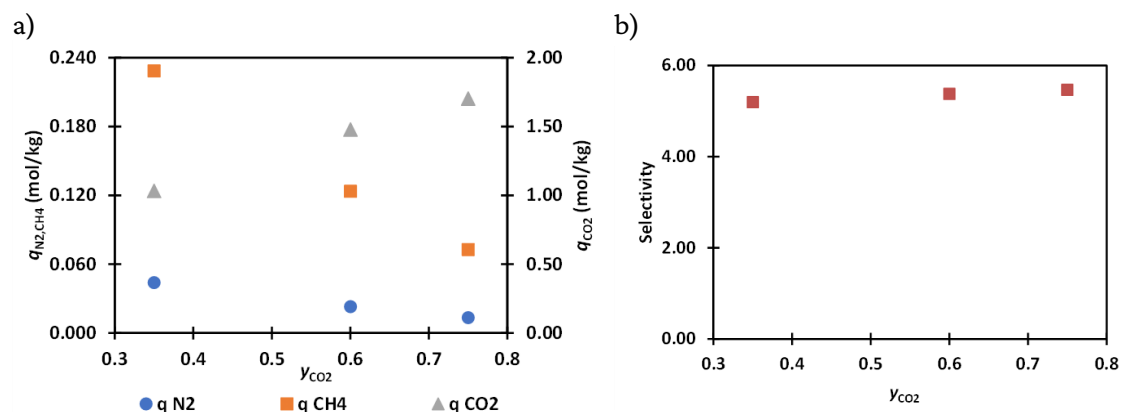
MIL-53(Al)

Figure A.39 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the MIL-53(Al).

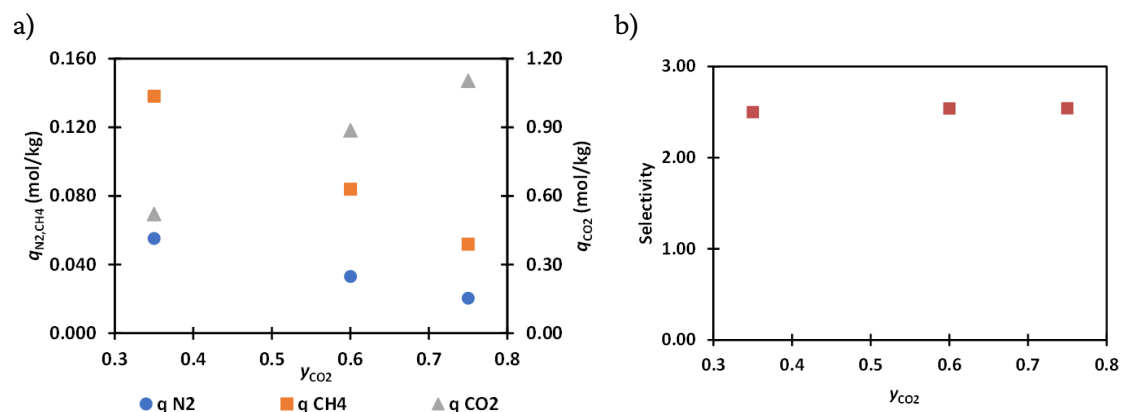
MIL-100(Al)

Figure A.40 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the MIL-100(Al).

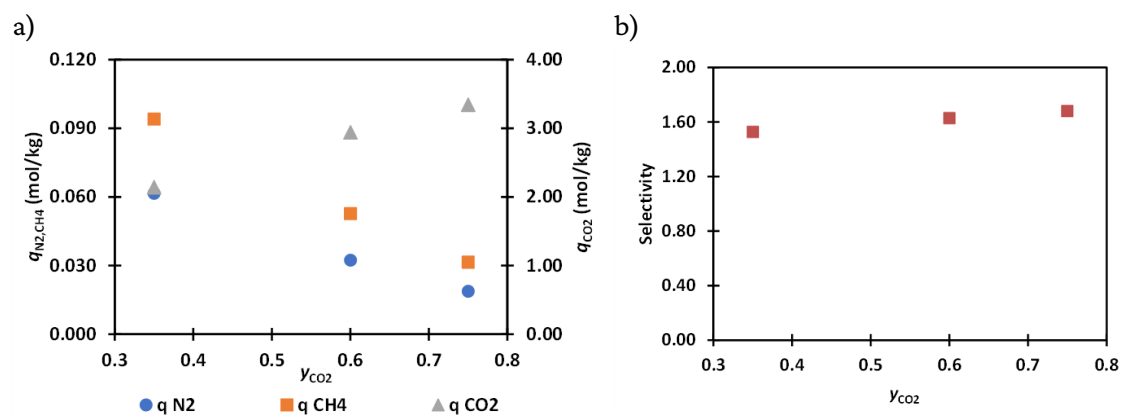
MIL-100(Fe)

Figure A.41 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the MIL-100(Fe).

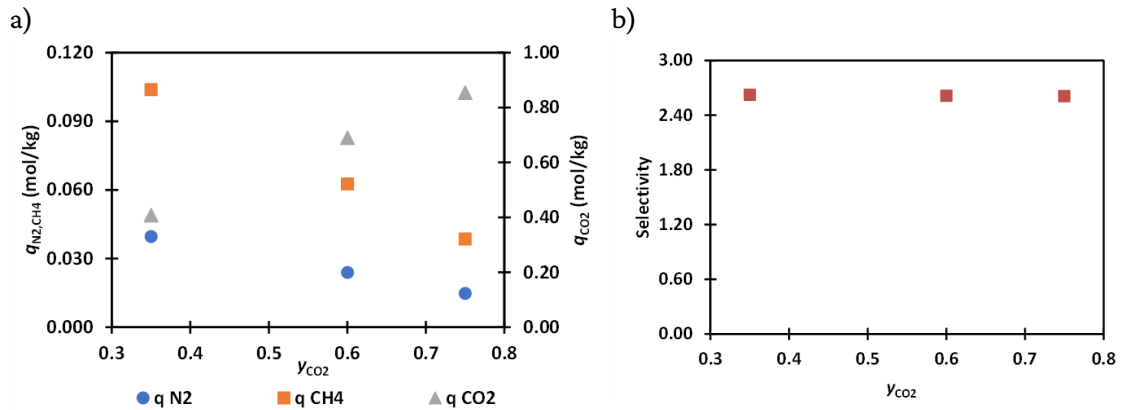
MIL-101(Cr)

Figure A.42 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the MIL-101(Cr).

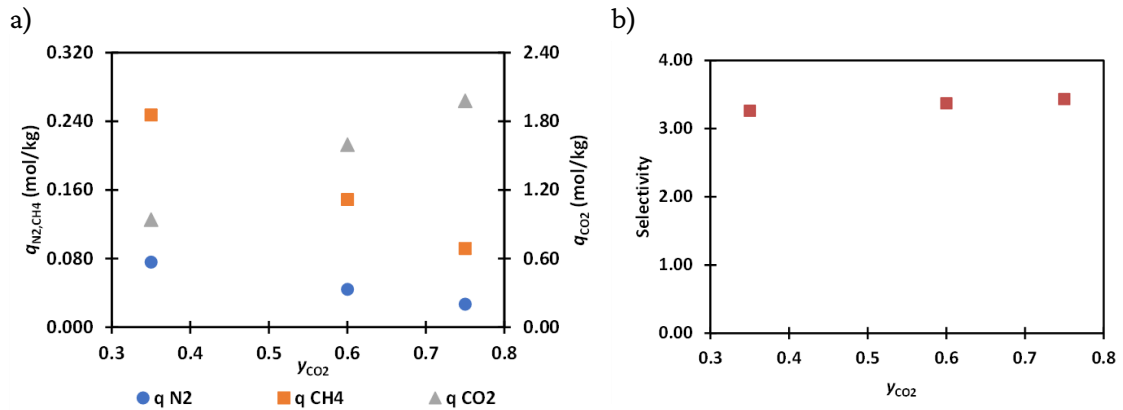
MIL-125(Ti)

Figure A.43 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the MIL-125(Ti).

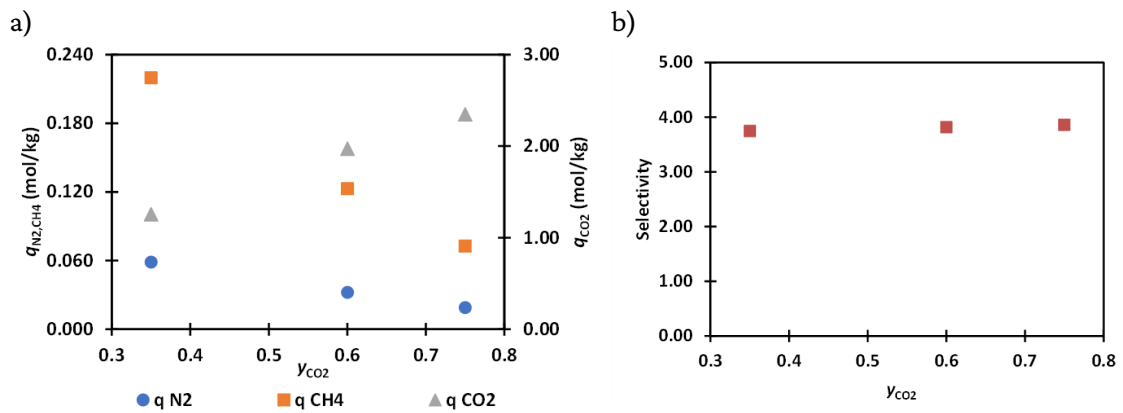
MIL-125(Ti)-NH₂

Figure A.44 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the MIL-125(Ti)-NH₂.

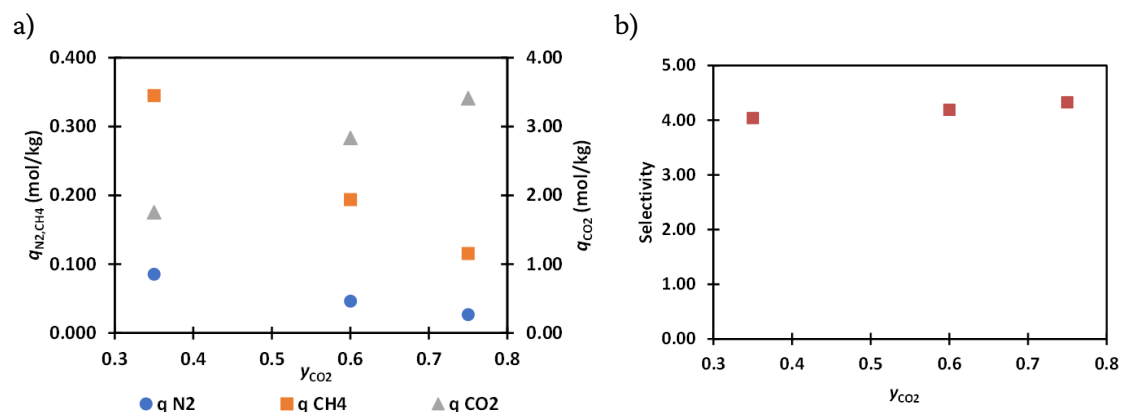
MIL-127(Fe)

Figure A.45 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the MIL-127(Fe).

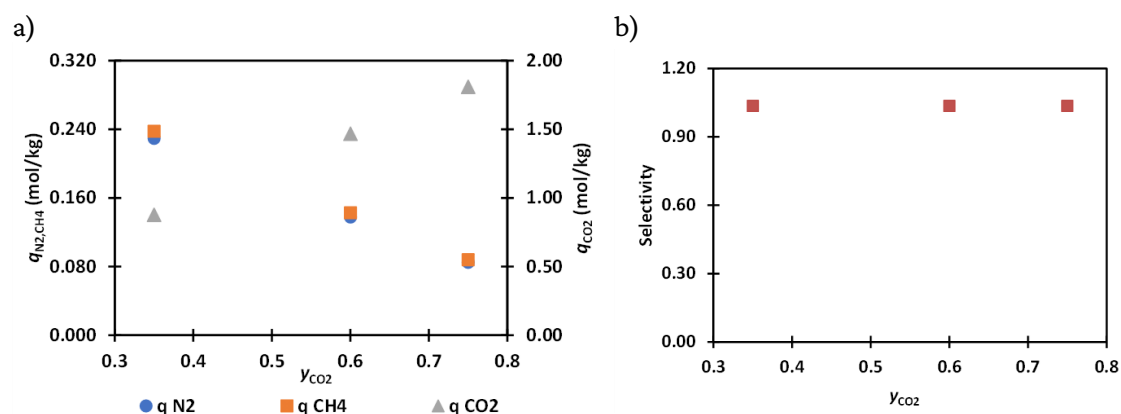
MOF-508b

Figure A.46 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the MOF-508b.

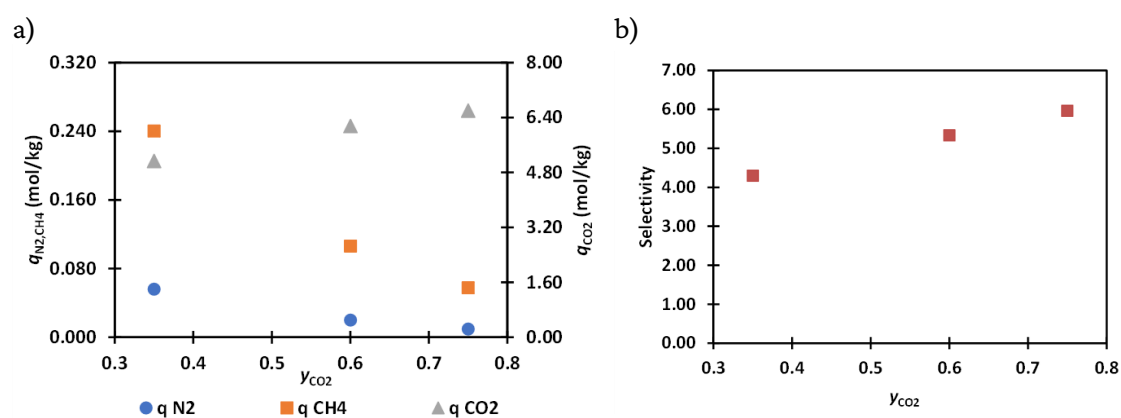
Ni-MOF-74

Figure A.47 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Ni-MOF-74.

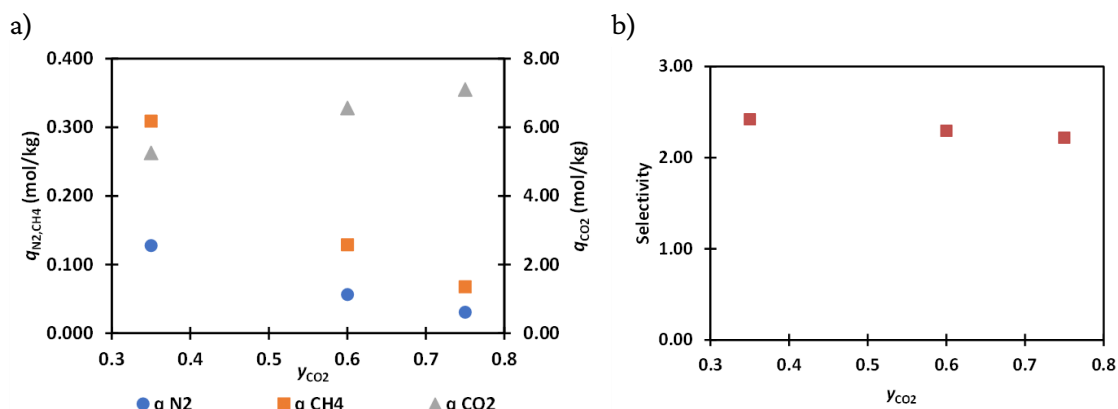
Co-MOF-74

Figure A.48 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Co-MOF-74.

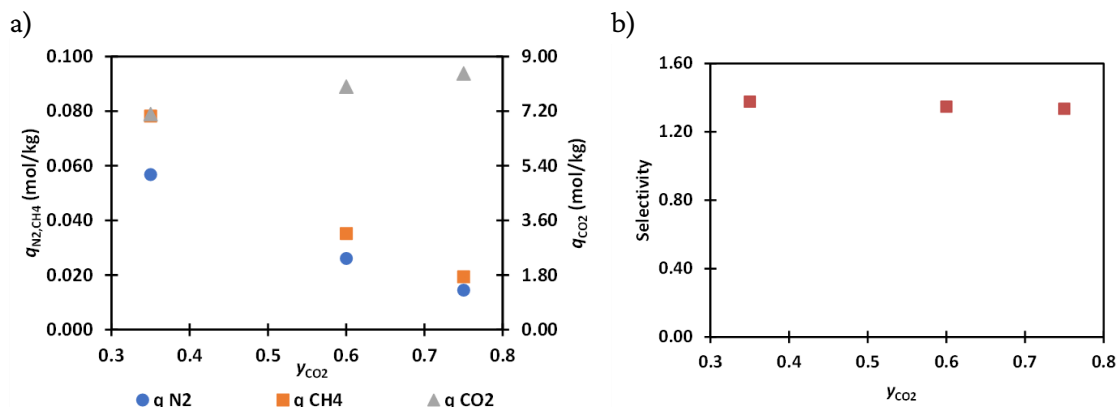
Mg-MOF-74

Figure A.49 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Mg-MOF-74.

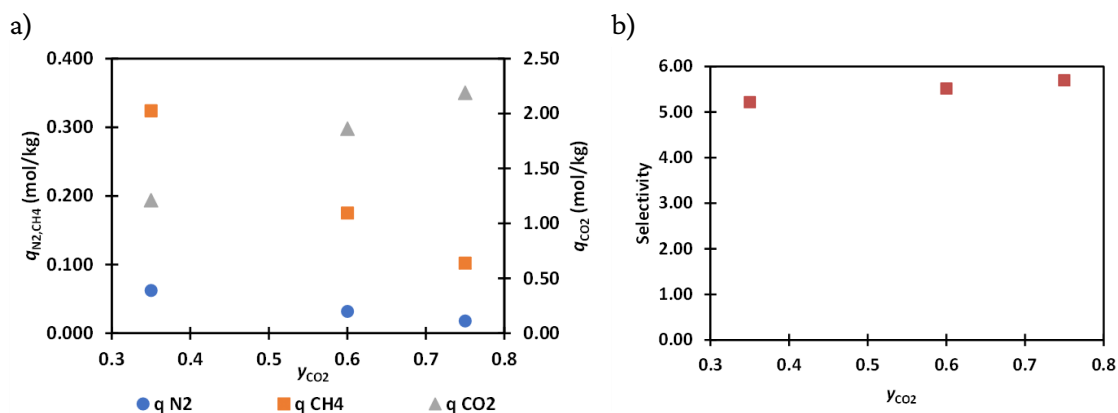
Al-Fumarate

Figure A.50 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the Al-Fumarate.

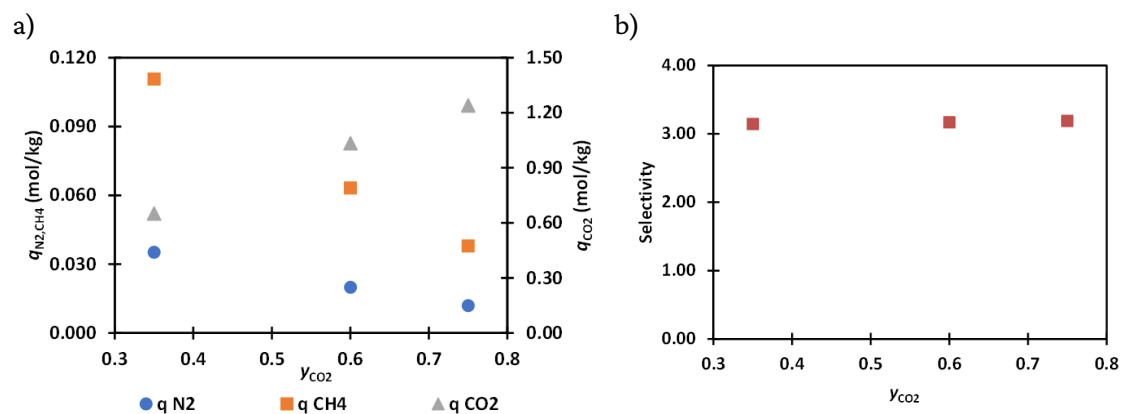
UiO-66(Zr)

Figure A.51 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the UiO-66(Zr).

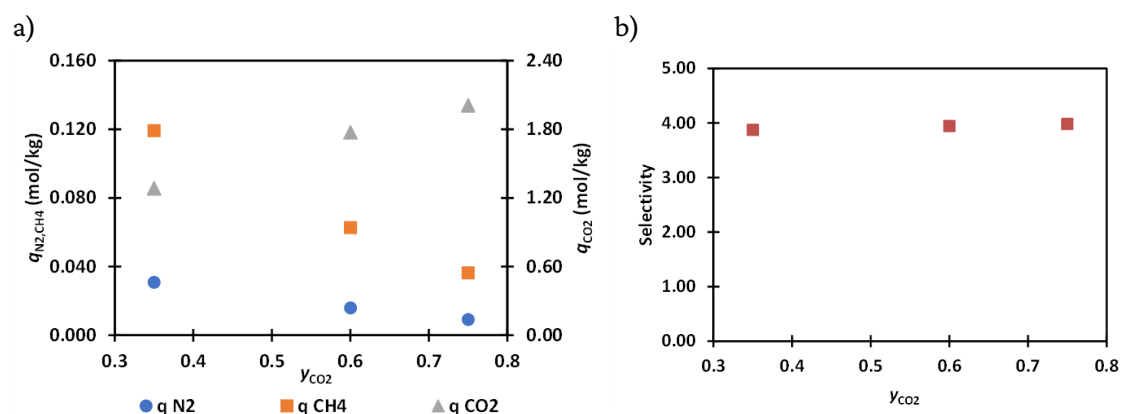
UiO-66(Zr)-NH₂

Figure A.52 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the UiO-66(Zr)-NH₂.

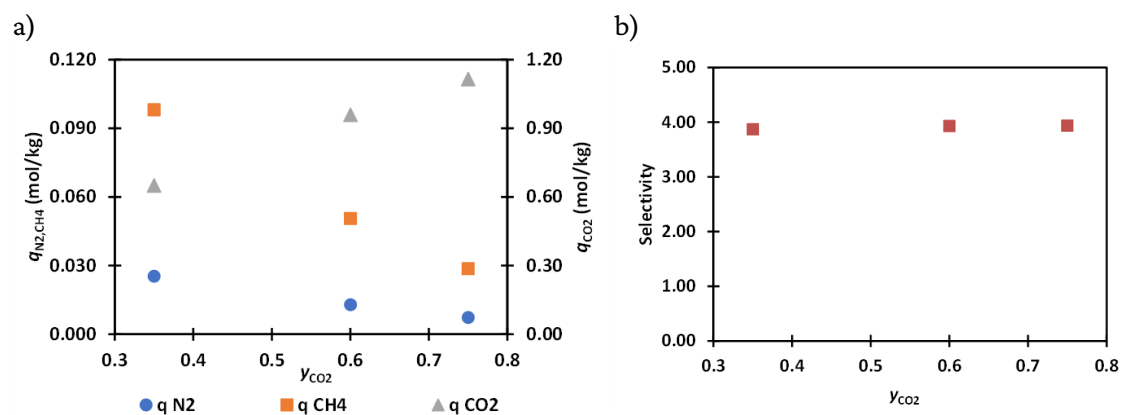
UiO-66(Zr)-(COOH)₂

Figure A.53 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the UiO-66(Zr)-(COOH)₂.

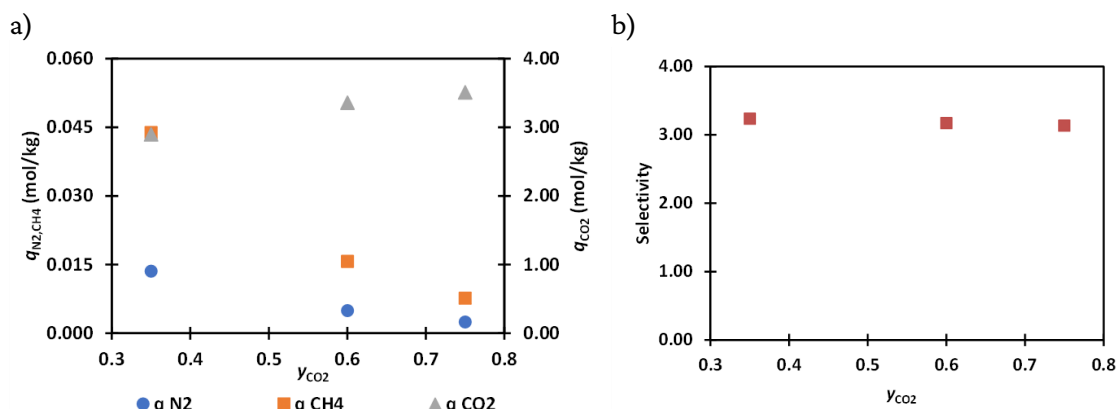
UTSA-16

Figure A.54 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the UTSA-16.

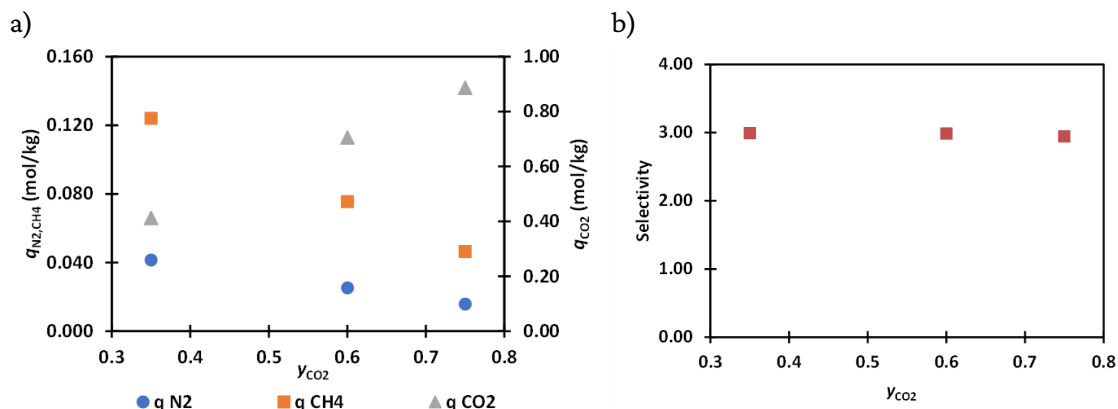
ZIF-8

Figure A.55 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the ZIF-8.

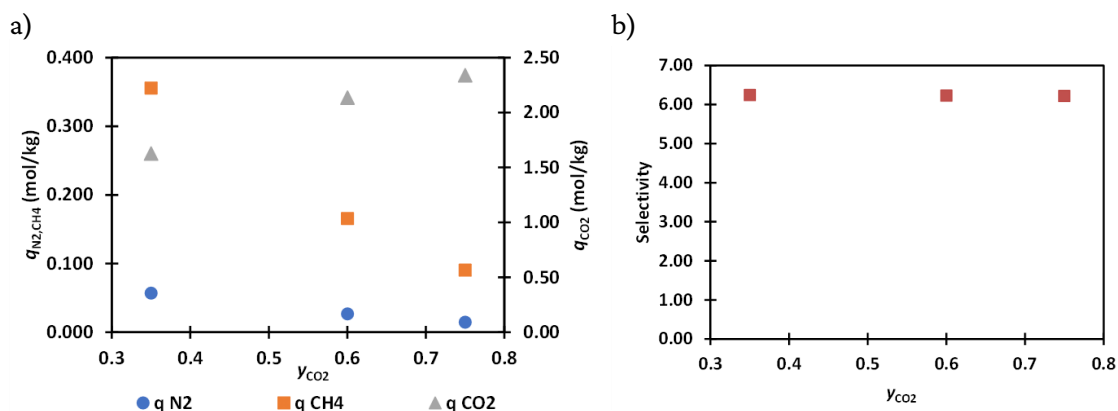
ZIF-94

Figure A.56 - Effect of the desorbent fraction onto a) the amount adsorbed and b) CH_4/N_2 adsorption selectivity for the ZIF-94.

Table A.4 - Fitting parameters of the DSL model for CO₂ adsorption equilibrium on the adsorbents.

Adsorbent	$q_{m,A}$ (mmol/g)	$q_{m,b}$ (mmol/g)	$b_{A,\infty} \times 10^5$ (bar ⁻¹)	$b_{B,\infty} \times 10^5$ (bar ⁻¹)	$-\Delta H_A$ (J/mol)	$-\Delta H_B$ (J/mol)
2GA-H2J	6.02	1.25	1.20	8.28	25388	26665
AC Sutcliffe Speakman	13.99	0.80	1.92	32.01	20271	21068
BPL	4.26	0.00	4.00	0.42	24978	34461
Norit RB3	11.36	1.09	3.84	64.21	19015	19082
H-Beta	2.27	2.12	15.86	117.2	19356	13974
HiSiv3000	1.04	1.85	4.90	1336.0	28881	7660
CuBTC	14.83	0.54	3.61	4.57	22920	24153
MIL-53(Al)	5.48	0.65	0.93	4.83	25588	29661
Al-Fumarate	5.61	0.32	14.56	3.77	20612	25852
UiO-66(Zr)_BTEC	3.18	0.34	0.54	2.28	27776	30286

Table A.5 - Fitting parameters of the DSL model for CH₄ adsorption equilibrium on the adsorbents.

Adsorbent	$q_{m,A}$ (mmol/g)	$q_{m,b}$ (mmol/g)	$b_{A,\infty} \times 10^5$ (bar ⁻¹)	$b_{B,\infty} \times 10^5$ (bar ⁻¹)	$-\Delta H_A$ (J/mol)	$-\Delta H_B$ (J/mol)
2GA-H2J	4.66	1.29	7.45	0.66	17872	29857
AC Sutcliffe Speakman	10.47	0.83	5.97	62.89	15924	17181
BPL	2.52	0.49	35.80	0.51	17235	31414
Norit RB3	5.55	1.32	6.28	63.37	16519	17249
H-Beta	3.59	0.80	190.4	167.9	10341	10710
HiSiv3000	1.27	1.07	173.1	3494.0	13778	3226
CuBTC	1.55	5.81	21.75	18.84	14995	16919
MIL-53(Al)	7.28	0.62	2.11	33.69	19947	19955
Al-Fumarate	3.27	1.39	86.23	53.54	13298	16114
UiO-66(Zr)_BTEC	1.92	0.43	0.94	2.65	22498	25662

Table A.6 - Fitting parameters of the DSL model for N₂ adsorption equilibrium on the adsorbents.

Adsorbent	$q_{m,A}$ (mmol/g)	$q_{m,b}$ (mmol/g)	$b_{A,\infty} \times 10^5$ (bar ⁻¹)	$b_{B,\infty} \times 10^5$ (bar ⁻¹)	$-\Delta H_A$ (J/mol)	$-\Delta H_B$ (J/mol)
2GA-H2J	4.14	1.39	6.17	23.95	15222.4	17110
AC Sutcliffe Speakman	10.58	0.90	11.81	173.3	11662.2	11106
BPL	1.46	0.65	40.92	3.56	13552.8	23258
Norit RB3	5.86	1.23	3.52	83.00	14493.3	13301
H-Beta	4.29	0.07	442.1	109.3	6553.4	10100

HiSiv3000	1.20	1.17	1783	3060	4948.3	0
CuBTC	2.75	5.37	25.10	25.84	11276.5	12839
MIL-53(Al)	4.81	0.66	10.98	38.64	12261.1	16150
Al-Fumarate	0.50	2.34	45.97	30.89	11239.8	14167
UiO-66(Zr)_BTEC	1.97	0.43	2.50	50.97	16900.8	14300

Table A.7 - Values of the SPI and performance values taken from the separation zones.

Adsorbent	SPI	$\sqrt{\text{Area}}$	$\gamma_{F,\max}$
2GA-H2J	0.37	2.97	4.33
AC Sutcliffe Speakman	0.24	2.43	3.46
BPL	0.43	3.52	5.54
Norit RB3	0.32	3.01	4.75
H-BETA-25	0.09	0.56	0.93
HiSiv3000	0.09	0.72	1.04
CuBTC	0.22	2.43	3.03
MIL-53(Al)	0.26	2.37	3.81
Al-Fumarate	0.39	3.08	4.75
UiO-66(Zr)-(COOH) ₂	0.02	0.25	0.16

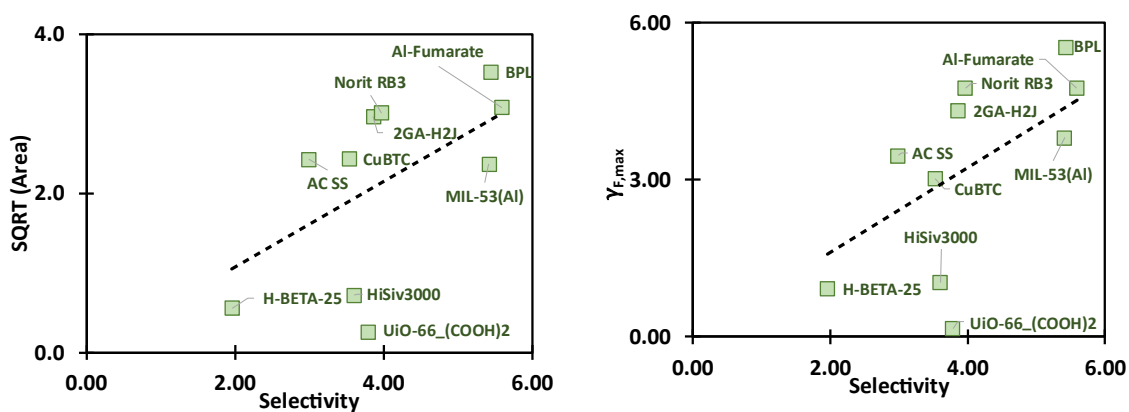


Figure A.57 - Competitive selectivity vs performance values given by the separation regions.

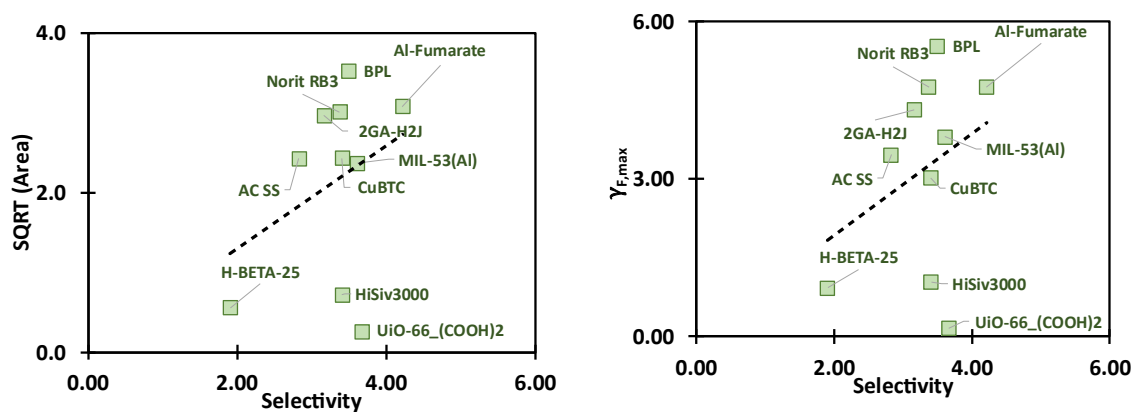


Figure A.58 - Pure component selectivity vs performance values given by the separation regions.

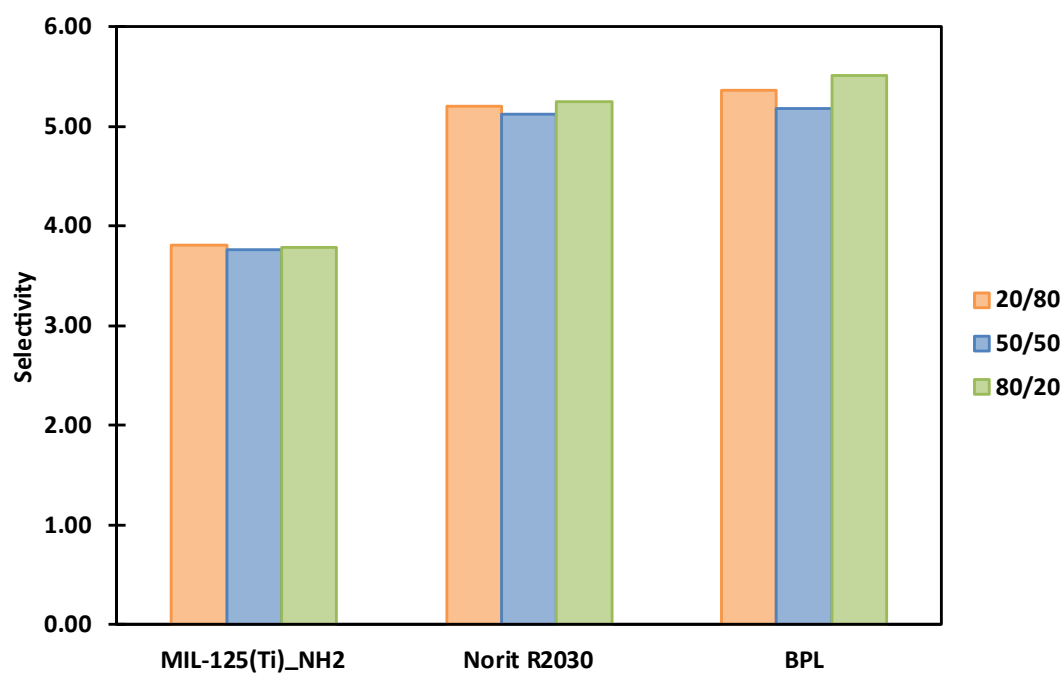


Figure A.59 - Effect of the composition in the selectivity for the three materials presented in Figure 4.17.

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