

Master in Chemical Engineering

Techno-economic study of a C3 splitter replacement for a VPSA unit

Master's dissertation

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Abstract

This work focus on the economic assessment of a Vacuum Pressure Swing Adsorption unit as a potential low-cost alternative to partially or totally replace the conventional C3 distillation column to obtain propylene with polymeric grade concentration (purity > 99.5 %) from a stream of 50 % of propylene and 50 % of propane.

Aspen Adsorption™ was used to simulate the VPSA unit, while the C3 distillation was simulated using Aspen Plus™. The VPSA characteristics was based on a 4-column pilot scale unit packed with a 4A zeolite. The 12-step VPSA unit was optimized based on a design of experiments approach, where adsorption time, vacuum pressure and feed pressure were used as factors. It was demonstrated that reducing the evacuation pressure benefits the propylene recovery and purity, while rising the feed pressure increases the propylene recovery but decreases the purity. The adsorption time revealed to have a minor influence in propylene recovery, generally, the purity is lower for low adsorption times. Under optimized conditions ($P_{\text{low}} = 0.05$ bar, $P_{\text{feed}} = 3$ bar and $t_{\text{ad}} = 90$ s) it was also a 99.5 % propylene stream obtained with a recovery of 63.8 %, $0.074 \text{ kW}\cdot\text{h}^{-1}$ of power consumption and a productivity of $7.63 \text{ mol}\cdot\text{h}^{-1}\cdot\text{kg}_{\text{zeolite}}^{-1}$. The scale-up of the unit was performed based on these results.

The capital cost to produce $10\,000 \text{ m}^3\cdot\text{h}^{-1}$ of purified propylene by VPSA is 28.6 M€ per year and by distillation 3.3 M€ per year. The estimated VPSA OPEX (excluding LOC) is 93.90 € per ton of propylene, mainly due to the vacuum pump consumption, which contributes with 84 % of the OPEX cost. Despite having a higher capital cost, the C3 distillation system presents a lower OPEX (*ca.* 73.01 € per ton of propylene). When the LOC is considered, the OPEX distillation raises to 252 € per ton of propylene, which turns the VPSA not attractive from the economic point of view.

Keywords: Propylene/propane separation, distillation column, adsorption, VPSA.

Resumo

Este trabalho foca-se no estudo económico com vista á aplicação de uma unidade de adsorção com modelação de pressão como potencial alternativa de baixo custo para substituir a coluna de destilação convencional, cujo objectivo é obter propileno de grau polimérico (pureza > 99,5 %) a partir de uma corrente de 50 % de propeno e 50 % de propano.

O trabalho foi desenvolvido simulando cada unidade individualmente, tendo-se utilizado o *software Aspen Adsorption™* na simulação do VPSA e *Aspen Plus™* para a coluna de destilação. As características do VPSA baseiam-se numa unidade piloto, tendo sido utilizado um zeólito 4A comercial como adsorvente. A unidade de VPSA é constituída por 12 passos sendo otimizada com base num conjunto de experiências, onde o tempo de adsorção, a pressão de vácuo e a pressão de alimentação foram usadas como variáveis. Foi demonstrado que a redução da pressão de vácuo beneficia a recuperação e pureza do propileno, o aumento da pressão de alimentação aumenta a recuperação do propileno enquanto que a sua pureza é reduzida. O tempo de adsorção revelou ter uma influência menor na recuperação de propileno e muito significativa na pureza sendo menor para menores tempos de adsorção. Tendo em conta o ótimo adquirido (pressão de vácuo de 0.05 bar, pressão de alimentação de 3 bar e um tempo de adsorção de 90 s), obteve-se um caudal com 99,5 % de propileno, uma recuperação de 63,8 %, 0,074 kWh relativo ao consumo energético e uma produtividade de $7,63 \text{ mol} \cdot \text{h}^{-1} \cdot \text{kg}_{4\text{Azeolite}}^{-1}$. A adaptação para a escala industrial é baseada nos resultados descritos.

O custo de capital para produzir $10\,000 \text{ m}^3 \cdot \text{h}^{-1}$ de propileno através de um VPSA é de 28,6 M € por ano, é significativamente mais barato quando comparado com a destilação que custa 3,3 M € por ano. O OPEX (excluindo o LOC) relativo ao VPSA é de 93,90 € por tonelada de propeno, sendo que 84 % reflete-se no consumo da bomba de vácuo. Apesar de ter um custo de capital mais elevado, a coluna de destilação apresenta um OPEX inferior (cerca de 73,01 € por tonelada de propileno). Quando o LOC é contabilizado, o OPEX aumenta para 252 € por tonelada de propileno, o que torna o VPSA não atrativo do ponto de vista económico.

Palavras-chave: Separação Propileno/propano, coluna de destilação, adsorção, VPSA.

Declaration

I hereby declare, on my word of honor, that this work is original and that all non-original contributions were properly referenced with source identification.

Diogo André Pereira Botelho

Porto, 1st of July 2019

Nomenclature

a_i	Number of neighboring sites occupied	
C_i	Partial molar concentration of component i	$\text{mol}\cdot\text{m}^{-3}$
C_p	Molar constant pressure specific heat of the gas mixture	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
C_v	Molar constant for a volumetric specific heat of the gas mixture	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
C_{valve}	Valve constant	$\text{mol}\cdot\text{bar}\cdot\text{s}^{-1}$
d_p	Particle diameter	m
d_c	Column diameter	m
D_{axial}	Axial dispersion coefficient	$\text{m}^2\cdot\text{s}^{-1}$
D_c	Crystal diameter of the particle	m
D_i	Internal diameter	m
h_f	Heat-transfer coefficient between the gas and solid phases	$\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$
K_i	Adsorption affinity constant	bar^{-1}
K_i^0	Adsorption affinity constant at infinite temperature	bar^{-1}
k_{LDF}	Linear drive force coefficient	s^{-1}
L	Column length	m
p	Partial pressure	bar
P_d	Design pressure	bar
P_o	Operation pressure	bar
P_{in}	Pressure before the evacuation step	bar
P_{low}	Evacuation pressure	bar
P_{high}	Feed pressure	bar
P_{BS}	Initial bed pressure	bar
P_{BE}	End bed pressure	bar
P_{EE}	External end pressure	bar
P_{ES}	External start pressure	bar
$q_{i,\text{max}}$	Maximum adsorbed phase concentration of component i	$\text{mol}\cdot\text{kg}^{-1}$
q_i^*	Total amount adsorbed of component i	$\text{mol}\cdot\text{kg}^{-1}$
$\bar{q}_i$	average concentration in the adsorbed phase	$\text{mol}\cdot\text{kg}^{-1}$
r_p	Particle radius	m
r_c	Crystal radius	m
R_g	Ideal gas constant	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
t	Time	s
t_{ad}	Adsorption time	s

t_{cycle}	Cycle time	s
t_{step}	Step time	s
T_{feed}	Feed temperature	K
T_g	Gas temperature	K
T_g	Solid phase temperature	K
T_0	Initial bed temperature	K
V_{ef}	Effective bed volume	m ³
$\dot{V}_{\text{out}}$	Molar flow rate	mol·h ⁻¹
u_i	Interstitial velocity	m·s ⁻¹
u_0	Superficial velocity	m·s ⁻¹
u_c	Velocity concentration wave front	m·s ⁻¹
z	Axial position	m

Greek Letters

ε_b	Bed porosity	
ε_p	Particle porosity	
λ	Heat axial dispersion coefficient	W·m ⁻² ·K ⁻¹
ΔH_i	Heat of adsorption of component i	J·mol ⁻¹
μ	Gas viscosity	Pa·s
ρ_b	bulk density	kg·m ⁻³
ρ_g	Gas density	kg·m ⁻³
ρ_p	Particle density	kg·m ⁻³
ρ_s	Solid density	kg·m ⁻³
Ω	PSA parameter	

List of Acronyms

IUPAC	International Union of Pure and Applied Chemistry
LDF	Linear Drive Force
PSA	Pressure Swing Adsorption
TSA	Temperature Swing Adsorption
VLE	Vapor-Liquid Equilibrium

VPSA	Vacuum Pressure Swing Adsorption
OPEX	Operation expense
CAPEX	Capital expenditure
LOC	Lost Opportunity Cost
CEPCI	Chemical Engineering Plant Cost Index

Index

1	Introduction.....	1
1.1	Framing and presentation of the work.....	1
1.2	Presentation of the company.....	1
1.3	Organization of the thesis	2
2	Context and State of the art.....	3
2.1	Propylene	3
2.1.1	Global market	3
2.2	Petrochemical process.....	4
2.3	C3 Splitter	5
2.4	State of Art for C3 splitter.....	6
2.4.1	Distillation.....	6
2.4.2	Adsorption	6
3	Adsorption	9
3.1	Adsorption equilibrium models	9
3.1.1	Langmuir	9
3.1.2	Toth	10
3.1.3	Dual-Site Langmuir.....	10
3.2	Adsorption kinetics	11
3.2.1	Macropores diffusion	11
3.2.2	Microporous diffusion	11
3.2.1	Linear driving force (LDF)	12
3.3	Adsorbent.....	12
3.3.1	Zeolites.....	12
3.3.2	Carbon molecular sieves.....	13
3.4	Breakthrough	13
3.5	Pressure-swing adsorption (PSA).....	14

4	Materials and Methods.....	17
4.1	Distillation column simulation.....	17
4.2	Adsorbents.....	18
4.2.1	CMS.....	18
4.2.2	4A zeolite.....	19
4.3	VPSA.....	20
4.3.1	Design of Experiments.....	23
4.4	VPSA model and Aspen simulation.....	23
5	Results and discussion.....	27
5.1	Distillation column.....	27
5.2	Simulation results for CMS.....	27
5.3	Simulation results for zeolite 4A.....	28
5.4	Economic analysis.....	32
6	Conclusion.....	37
6.1	Assessment Objectives Achieved.....	38
6.2	Recommendations for Future Work.....	38
	Appendix A - Distillation columns sizing and costs.....	44
	Appendix B - Scale up and cost for the VPSA unit.....	43

List of Figures

<i>Figure 1 - Block flow diagram of a typical olefin planta¹².</i>	5
<i>Figure 2 – Ideal profile of a favorable isothermal concentration.</i>	13
<i>Figure 3 - Four steps Skarstrom cycle⁴¹.</i>	14
<i>Figure 4 - Graphical representation of the effect of pressure regeneration.</i>	14
<i>Figure 5 - Scheme of DSTWU (upper) and RADFRAC (down) column models</i>	17
<i>Figure 6– a) Propylene isotherms on CMS and b) Propane isotherms on CMS at: 298 K, 318 K, and 338 K. The lines represent the Dual-Site Langmuir isotherm fitting.</i>	18
<i>Figure 7 – Dual-Site Langmuir isotherms for a) propane and b) propylene on zeolite 4A for 400 K.</i>	19
<i>Figure 8 – a) Elementary steps of the VPSA cycle and b) Typical pressure history VPSA cycle.</i>	21
<i>Figure 9 – Schematic representation of the VPSA.</i>	25
<i>Figure 10 - Comparison of simulation breakthrough curves for a) non-isotherm conditions and b) isotherm conditions.</i>	28
<i>Figure 11 - Comparison of simulation breakthrough curves for a) non-isotherm conditions, and b) isotherm conditions.</i>	28
<i>Figure 12 – Influence of vacuum pressure, adsorption time and pressure on a) propylene recovery and b) propylene purity.</i>	30
<i>Figure 13 – Propylene composition in the three exit streams (W, PROD and PROD2) accordingly the steady state.</i>	31
<i>Figure 14 – Economical profile for distillation columns and VPSA capital and operation cost without LOC factor for 0.05 vacuum pressure VPSA.</i>	34
<i>Figure 15 - Economical profile for distillation columns and VPSA capital and operation cost with LOC factor for 0.05 vacuum pressure VPSA 66.7% recovery rate.</i>	34
<i>Figure 16 – Economical profile for distillation columns and VPSA capital and operation cost without LOC factor 0.2 bar of vacuum pressure VPSA.</i>	35
<i>Figure 17- Economical profile for distillation columns and VPSA capital and operation cost with LOC factor 0.2 bar of vacuum pressure VPSA and 66.7 % of recovery.</i>	35
<i>Figure 18 - Economical profile for distillation columns and VPSA capital and operation cost with LOC factor 0.2 bar of vacuum pressure VPSA and a recovery rate of 97 %.</i>	36

List of Tables

<i>Table 1 - Top 5 main chemical products in Portugal ¹⁰</i>	<i>3</i>
<i>Table 2 - Equilibrium and isotherm parameters for propylene and propane.....</i>	<i>19</i>
<i>Table 3 – Physical characterization for the 4A zeolite and isotherm parameters for propylene and propane for the Dual-Site Langmuir model Grande et al. (2010) and Dual-Site Langmuir isotherm model²⁷.....</i>	<i>20</i>
<i>Table 4 – Input for one column loaded with 4A zeolite (*Temperature was based in Grande et al (2010).).....</i>	<i>20</i>
<i>Table 5 – VPSA cycle sequence: 1) Adsorption, 2) co-current pressure equalization depressurization, 3) counter-current blowdown, 4) co-current pressure equalization depressurization, 5) evacuation, 6) counter-current pressure equalization pressurization counter-current pressure equalization pressurization, 7) counter-current pressure equalization pressurization and 8) co-current feed pressurization.....</i>	<i>22</i>
<i>Table 6 – Active specifications for valves</i>	<i>25</i>
<i>Table 7 - RadFrac column results for 50 % propylene/50 % propane. (* input data from DSTWU model)</i>	<i>27</i>
<i>Table 8 – Design of experiments and for the VPSA simulator.</i>	<i>29</i>
<i>Table 9 - Parameters of second order polynomial Equation.....</i>	<i>30</i>
<i>Table 10 – Scale up dimensions for one column.</i>	<i>32</i>
<i>Table 11 – Capital expenditure, operation expenses and LOC for each separation unit.</i>	<i>33</i>
<i>Table 12 – VPSA cycle sequence: 1) Adsorption, 2) co-current pressure equalization depressurization, 3) co-current blowdown, 4) evacuation, 5) counter-current pressure equalization pressurization 6) co-current feed pressurization.</i>	<i>38</i>
<i>Table 13 - Data for the cooling water annual cost estimation.</i>	<i>42</i>
<i>Table 14 - Data needed to determine the steam cost.</i>	<i>42</i>
<i>Table 15 – Datasheet for the column with Feed stream (50%propylene/50%propane)</i>	<i>42</i>

1 Introduction

1.1 Framing and presentation of the work

Separation operations play an important role in all types of industry including petrochemical, pharmaceutical, food, cosmetic, recycling, etc¹. Unfortunately, separation process is commonly associated to an elevated energy consumption, present in both thermal energy and work forms, turning into a major concern due to the high cost and consequent environmental impacts. Among the various separation processes, distillation stands out in terms of energy consumption. In the United States, distillation processes consume the equivalent of about 100 000 barrels of oil per day, corresponding to approximately 40 % of the total energy consumed in chemical and petrochemical industries².

Despite having low thermodynamic efficiency, distillation is still the most common technology to separate hydrocarbons. Particularly, propylene/propane separation is currently performed on very large-scale distillation processes and is defined as the most energy intensive distillation process due to their close boiling point. In fact, it is estimated that purification of propylene and ethylene accounts for 0.3 % of global energy use, which is equivalent to the energy consumed annually in Singapore³. Therefore, finding alternative technologies for such separation is of great importance in order to minimize the energy consumption supplying the huge demand of propylene. Less energy-intensive separation technologies such as extraction, adsorption and membrane separation have been considered to replace distillation. Among them, vacuum pressure swing adsorption is an attractive approach owing as advantages, continuous operation and reduced energy consumption⁴.

The main objective of this work is to conduct a techno-economic study for the replacement of a C3 splitter with a VPSA unit to produce 99.5 % propylene (polymeric degree) at an acceptable recovery rate. To sustain the main objective, the VPSA unit and the C3 distillation column will be simulated to estimate the capital costs and respective energy consumption in order to compare the OPEX and CAPEX factors.

1.2 Presentation of the company

Amnis Pura, Ltd, is a spin-off of FEUP dedicated to hydrogen sector developing technologies, including PEMFC's and Pressure Swing Adsorption (PSA) units for hydrogen purification. The PSA units allow obtaining fuel cell grade hydrogen at high recovery rate when packed with a suitable adsorbent and operated under an optimized cycle. Amnis Pura is also dedicated to the development of new adsorbents, including activated carbons, zeolites, carbon molecular sieves, etc. Based on a sustainable future, fuel

cells are the next motor vehicle where energy efficiency and zero GHG emissions are unmatched by any other technology.

1.3 Organization of the thesis

This thesis begins, in Chapter 1, with a short description of the work, presenting the relevance and motivation and the objectives.

Chapter 2 focus on propylene and propane economics, the conventional C3 splitter in industry and the state of art for propylene purification. In this last, the pressure swing adsorption process and the adsorption fundamentals is given.

Chapter 3 regards the materials and methods, where the 4A zeolite characterization can be found along with the mathematic model applied in both simulators. A brief explanation about the VPSA operation is also given in this chapter, including the 12-cycle implementation.

In Chapter 4 the results and discussion in the simulation results can be found. The economic analysis for both VPSA and conventional C3 splitter is also given.

Chapter 5 is composed by the conclusions.

Finally, Chapter 6 respects to the assessments of the work done as objectives, limitations and future work.

2 Context and State of the art

2.1 Propylene

2.1.1 Global market

Global annual production of light olefins exceeds 200 million tones, representing an equivalent quantity of 30 kilograms for each person. Among these, approximately 50 % is attributed to propylene, whose production is expected to boost to 165 million tons by 2030, at an estimated rate of 6 % per year⁸. Its market is mainly controlled by China, United States and Western Europe, with a total share of 74 % of global consumption. The enhancement of living conditions and structures improvement in under development countries have a huge contribute for the 66 % of all the propylene consumption that is directed to polypropylene production. This polymer is an important thermal plastic material used in a wide range of industries including in automotive industry, consumer goods and furniture market, which represents the biggest fluctuation in the global demand of propylene⁸.

According to Portuguese national statistics, INE, in 2014 the national production of chemical products accounted for a total of 236 products. The most significant increase in the five main products was observed in propylene, whose values production grew 17.0% in relation to 2013, as shown in Table 1⁹. In Portugal, propylene is mainly produced by REPSOL Polymers, a refinery located in Sines. In 2016, the production capacity reached to 200 000 tons per year of polymeric degree propylene (99.5 % purity), mostly exported to European countries⁹.

Table 1 - Top 5 main chemical products in Portugal¹⁰.

Rank	Product	Quantity produced (tonnes)	Quantity exported (tonnes)	Growth 2013-2014
1	Biofuels	356 458	355 855	6 %
2	Resins	162 050	159 771	12 %
3	Aniline	180 514	177 703	9 %
4	Naphthalene and mixtures of aromatic hydrocarbons	439 571	249 359	13 %
5	Propene	162 887	158 645	17 %

Due to the high economic value (1164 € per ton) and his wide range of applicability, propylene is considered as the component of interest in propane/propylene separation⁵. In turn, propane is commonly used as thermal utility in industry and domestic heating, with a market price of 445 € per tonne⁵.

Three commercial grades of propylene can be pointed: refinery-grade (50 – 70 %), chemical-grade (95.0 %) and polymer grade (99.5 %). Refinery-grade propylene can be used for thermal energy production; as an octane-enhancing and as raw-material in cumene and isopropanol production. Chemical-grade propylene is extensively used for most chemical derivatives, such as oxo alcohols and acrylonitrile. Finally, polymer-grade propylene is mainly targeted to polypropylene production. Regarding propane, HD5 grade is considered the "consumer grade" and is the most widely sold and distributed grade of propane, specified with a minimum purity of 95 %⁵.

2.2 Petrochemical process

Propylene is commonly extracted from naphtha and is submitted to a complex process for purification. Thermal cracking and steam cracking are considered the state-of-art in propylene production, although steam cracking represents 56 % of all the production. Production methods including propane dehydrogenation, olefin metathesis and coal olefins processes may also be found in industry¹¹. For a better understanding of the complexity of the steam cracking process, a typical olefin plant is depicted in the block diagram of Figure 1. In the steam cracking reaction, the hydrocarbon feedstock is firstly heated to the cracking temperature (773-923 K) and pressure of 3 bar, is cooled down afterwards to prevent secondary reactions. The resulting mixture is sent to a fractionator to remove heaviest components, which can be used as fuel oil. After the fractionator, a sequence of 4 to 6 compressors are found, where an acid removal step is placed before the last compressor, reacting caustic soda (NaOH) with hydrogen sulfide (H₂S) and carbon dioxide (CO₂). After the last compressor stage, the stream is conducted to a chilling and drying process using molecular sieves. Methane and hydrogen are then removed in the first fractionator, while the bottom stream, with a high content of C1+ is fed to the deethaniser. In the deethaniser, a C2 stream is produced as overhead product and a C2+ stream is the bottom product. The overhead stream is hydrogenated to remove acetylene and then fractionated to recover ethylene on the top and ethane on the bottom, which generally is recycled to the steam cracking reactor. The bottom product of the deethaniser is fed to the depropaniser, where a C3 stream is produced overhead and a C3+ stream is the bottom product. The overhead stream is hydrogenated to remove methylacetylene and propadiene and then fractionated to recover propylene on the top and propane on the bottom, which generally is recycled to the reactor as well. The fractionation process can continue after the depropaniser, (if economically viable), but usually a debutanizer is only used when a liquid feedstock is processed. Since the present work is focused on propane/propylene separation, a greater emphasis will be given to C3 splitter.

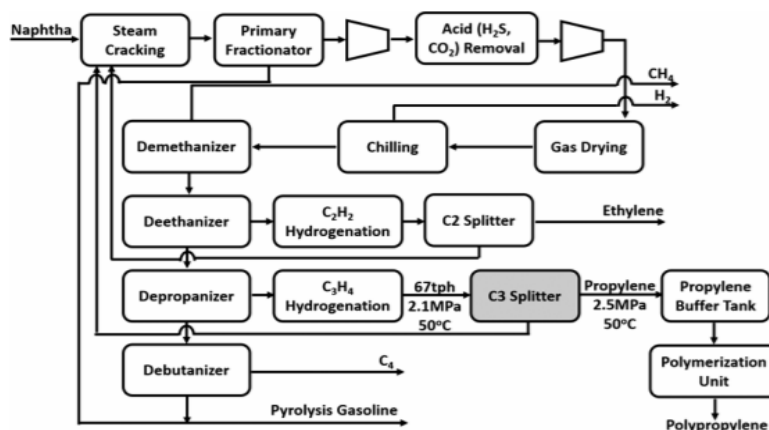


Figure 1 - Block flow diagram of a typical olefin plant¹².

2.3 C3 Splitter

Typically, a distillation process brings up two product streams, top (or distillate product) and the bottom product, whose compositions differ from the feed. The mechanism underlying the distillation is vapor-liquid equilibrium (VLE), formed by the contact of both phases, liquid and vapor. The ease of separating the components of a mixture through distillation essentially depends on the difference in vapor pressure, or volatility. Propylene-propane binary mixture have low relative volatility range (1.09 to 1.15) due to their close boiling points, 225.4 K and 231 K, to propylene and propane respectively. Consequently, propane/propylene separation is claimed as one of the hardest separations in industry¹³.

In the distillation process, the mass transfer phenomena occur between the vapor phase and the liquid. Consequently, a high energy consumption is associated to the exchange elements, the reboiler and the condenser¹². The reboiler is a heat exchanger used to provide thermal energy to the bottom of distillation columns. In the reboiler, part the vapor phase returns to the column and the remaining liquid is routed as bottom product. In the condenser, the vapor from the top of the distillation column is condensed (total or partially), where a fraction of the product returns to the column (reflux) above the top tray. The remaining stream is the distillate. The location where the mixture enters the column is denoted as feed tray and the zone above the feed is referred to as the rectification section, while the zone below is referred as stripping section. The distillation column can be considered a series of equilibrium stages that successively promote the enrichment of the vapor phase for the most volatile component. While the vapor phase rises in the column and is recovered as top product, the liquid phase enriches in the less volatile components and is recovered in the bottom¹³.

In order to overcome hard separations, two main approaches can be implemented: cryogenic and high-pressure distillation. Cryogenic distillation operates typically at 243 K and 3 bars, requiring the use of a special refrigerant fluid below -263 K to condensate the distilled product. In high-pressure distillation columns, water is commonly used to condensate the propylene due to its accessibility as

refrigerant fluid, while steam is used to continuously provide thermal energy to the reboiler. High pressure distillation towers for propylene/propane binary mixture have a minimum number of 100 to 200 theoretical plates, operating from 12 and 22 bar and high reflux ratio (approx. 18 to 25) in the bottom head (reboiler). The large column dimensions and high reflux ratio lead to high capital and operational costs¹³.

2.4 State of Art for C3 splitter.

Among the technologies available for propylene-propane separation, the most viable choice depends on a wide range of factors including the desired recovery, purity, energy consumption and others¹³. During the last decades, a great attention has been paid to four types of technology for obtaining propylene with polymeric degree (purity > 99.5%): distillation, adsorption, membranes and absorption. Since the present work is focused on replacing a C3 distillation tower using a VPSA unit, a greater attention is given to C3 distillation process and adsorption technologies.

2.4.1 Distillation

As previously mentioned, distillation is the state-of-art in industry for propane/propylene separation. Despite being a well-established technology, multiple studies have been developed to reduce the energy consumption, most of them by changing the process configuration. For instance, Nguyen concluded that low pressure increases the relative volatility, leading to a low condenser temperature around 278 K, however the use of water is unappropriated appealing to more expensive refrigeration fluids¹⁴. Olujić applied self-heat recuperation to a variety of distillation, showing approximately 20-50 % reduction in energy consumption¹⁵. Asprion proposed a new configuration of vapor recompression column, adapting reboilers to an intermediated stage recovering a small quantity of energy¹⁶. Kumar *et al.* (2013) suggested a heat pump system directing the energy provided by the cooling and condensation, reducing the energy requirements by 15 %¹⁷. Kazemi, A. *et al.* (2018), proposed a configuration reducing the total utility requirements for a conventional distillation column by 52.7 %.

2.4.2 Adsorption

Pressure Swing Adsorption (PSA) has a wide range of applications in industry, including air separation (as an alternative to cryogenic distillation), biogas upgrading, hydrogen purification, etc. In the case of propane/propylene separation, a vacuum step is introduced to the PSA cycle, thus operating in VPSA mode (vacuum pressure swing adsorption). During the last decade, several studies using VPSA for propylene/propane separation have been performed. A 5-step VPSA cycle packed with a 4A zeolite adsorbent was tested by Rodrigues, obtaining a propylene stream of 99.50 % purity at recovery rate of

84.3 % from a feed of 46.3/44.1/9.6 % propylene/propane/nitrogen mixture. A. Grande studied a system improve propylene recovery, a 2-stage VPSA unit with 4A zeolite with different crystal sizes in each stage, aiming to separate a mixture of 38.9/61.1 % propylene/propane. Propylene with a purity of 99.6 % purity was obtained with a recovery of 95.9 %. In its turn, Khalighi et al (2013) created an VPSA unit packed with a silica adsorbent producing a 99.0 % purity propylene stream at 98.0 % recovery from a feed stream of 84.4/15.6 % propylene/propane.

Commercially available adsorbents, such as the ones used in the studies mentioned above, typically present a higher than the separation factor towards propylene. This means that propylene is preferably adsorbed during the PSA cycle and is recovered in the PSA off-gas side during the blowdown and evacuation steps (see section 3.5), while the raffinate product is enriched in propane. Nonetheless, a few cases of propane selective adsorbents can be found in literature²⁵. To check the PSA cycle viability, have been tested a wide range absorbers, zeolites (4A^{26–28}, 5A²⁹, 13X³⁰), silica gel³¹, activated carbon^{31,32}, carbon molecular sieves⁶ and metal organic framework (MOF)^{33,34}. From all the selectivity's relative to propylene, that stand out with the best performance is the zeolite topology denominated Deca-dodecasil-3R (DDR)³⁵. Recent studies in metal-organic frameworks (MOFs) revealed interesting properties, including elevated surface area, facility in pore dimension controlling and a thermal stability when compared to zeolites. Among them, sMIL-100(Fe) stand out due to its high surface area (2000 m²·g⁻¹), good hydrothermal stability and accessible scale-up²⁴.

For a better understanding adsorption-based processes, a brief introduction to adsorption concepts will be given in the next chapter.

3 Adsorption

Adsorption is the phenomenon where the molecules of a gas or a liquid phase (adsorbate) are transferred to the surface of a solid phase (adsorbent). Depending on the nature of the interactions involved, two types of adsorption mechanisms are commonly distinguished³⁸:

- Chemical adsorption (chemisorption), which is characterized by a strong adsorption to the solid surface involving the formation of chemical bonds, generally covalent. In this type of adsorption, there is only one molecular layer (monolayer) and the adsorption force decrease as the surface area occupation increases³⁹.
- Physical adsorption, or physisorption, involves Van Der Waals interactions, which are translated into weaker bonds when compared to chemisorption. Nevertheless, physisorption is strong enough to form successive molecular layers. The adsorption force decreases as the number of layers increases³⁹.

From the practical point of view, physical adsorption is commonly preferred, since it allows the adsorbent regeneration by a simple “pressure-swing” and avoiding the use of elevated temperatures due to its lower heat of adsorption. Besides, adsorption kinetics in physisorption is typically faster than those found in chemisorption. In terms of separation, adsorption can be controlled by one of three different mechanisms. Steric effect, where the pores only allow passage to molecules of a specific molecular size and configuration; kinetic mechanism, based on the difference between the diffusion constants of the molecules present in the fluid; and equilibrium, which is related to the total quantity adsorbed of each component when reaching equilibrium between the fluid and solid phase⁴⁰. The equilibrium quantity depends on the interactions between adsorbate and adsorbent and varies with temperature and pressure. The relation of the quantity adsorbed with the pressure at a given temperature is the so-called adsorption equilibrium isotherm.

3.1 Adsorption equilibrium models

3.1.1 Langmuir

Langmuir model settles in a kinetic base, assuming that the rate of adsorption and the rate of desorption from the surface at equilibrium are equal¹⁸. The model is based in three main assumptions:

- The surface is homogeneous, punctual adsorption energy is held constant.
- Each site can accommodate only one molecule or atom.
- There is no lateral interaction between adsorbed molecules.

The Langmuir isotherm is expressed by the Equation (1)¹⁸:

$$q_i^* = q_{i,max} \frac{K_i P}{1 + K_i P} \quad (1)$$

where, q_i^* is the amount in component adsorbed phase of, $q_{i,max}$ is the maximum amount adsorbed of component i corresponding to a complete monolayer coverage, K_i is the affinity constant expressed in Equation (3) and P is the partial pressure of the gas.

Accordingly, for high or lower pressures, the Langmuir model can be simplified as described below¹⁸:

- If the pressure is very low, $1 \gg K_i P$ the isotherm follows the Henry law: $\frac{q_i^*}{q_{i,max}} = K_i P$, where the amount adsorbed increases linearly with the pressure.

At high pressures the amount adsorbed is maximum and corresponds to a total site occupation,

so, $K_i P \gg 1$ then, $\frac{q_i^*}{q_{i,max}} = 1$.

•

3.1.2 Toth

Toth Equation, described by Equation (2) is an empirical isotherm model and which properly describes systems with a monolayer coverage⁴⁰:

$$q_i^* = q_{i,max} \frac{K_i P}{1 + ((K_i P)^n)^{\frac{1}{n}}} \quad (2)$$

where, q_i^* and $q_{i,max}$ are the amount adsorbed and the maximum amount adsorbed of component i , P is the gas partial pressure and n is the heterogeneity parameter to characterize the adsorbent. Low values of n mean that the material is more heterogeneous. Like in Langmuir model, K_i is the adsorption constant dependent of the temperature and can be described by the Equation (3):

$$K_i = K_i^0 \cdot e^{\frac{-\Delta H_i}{R_g T}} \quad (3)$$

where K_i^0 is the infinite adsorption constant, T is the temperature, R_g is the universal gas constant, ΔH_i is the isosteric heat of adsorption at zero loading owning always a negative value because the adsorption is an exothermal mechanism.

3.1.3 Dual-Site Langmuir

The Dual-Site Langmuir model represented in Equation (4) has the same specifications as the Langmuir model presented in Equation (1), but assumes the presence of two types of active sites⁴⁰:

$$q_i^* = q_{max,1} \frac{K_1 P}{1 + K_1 P} + q_{max,2} \frac{K_2 P}{1 + K_2 P} \quad (4)$$

3.2 Adsorption kinetics

The rate of adsorption is mainly controlled by diffusional limitations instead the faster equilibrium rate in the surface. The diffusion of gases inside the adsorbent particles until the adsorption centers involve different mass transfer mechanisms: the gas has to diffuse through distribution channels (macropores) and then diffuse inside the micropores before they reach their adsorption location⁴⁰. Regarding to its sorption kinetics, adsorbents can be defined as homogeneous or composite. While homogeneous particles have a good ramification section of pores, the composite pellets are formed by agglomeration of small microparticles. Three types of mass transfer mechanisms can be found in composite adsorbents. From the practical point of view, the external film resistance is commonly neglected, so adsorption and desorption rate are typically controlled by macropore or micropore resistance³⁸.

The size of the pore stay between critical diameter of propene (4.3 Å) and propane (4.5 Å)²⁷. Considering the critical diameter differences, propene is adsorbed and propane is nearly excluded, causing the high selectivity towards propene. The presence of adsorption molecules with a critical diameter dimensions in the pore openings cause a limited diffusion, leading low mass transfer and adsorption rates⁴². The range of pore size according to the classification recommended by IUPAC is: micropores ($d < 2$ nm), mesopores ($2 < d < 50$ nm) and macropores ($d > 50$ nm). The most important characteristic of an adsorbent is its high porosity because particles can be designed with a specific pore size and size distribution in order to act for a specific separation, thus physical characterization is often more relevant than chemical characterization²⁶.

3.2.1 Macropores diffusion

The transport in macropores can be rolled by four diffusion mechanisms: molecular diffusion, Knudsen diffusion, Poiseuille diffusion and surface diffusion⁴⁰. When the pore diameter is larger than the distance between molecular collisions, molecular diffusion is the dominant mechanism. When the pore diameter is equal or minor than the distance between collisions, pore wall and the molecules collide and Knudsen diffusion is the controller mechanism. In addition, a contribution to the flux from forced flow may also be present, commonly named as Poiseuille flow, with happens when the pores are large enough⁴⁰. Surface diffusion is similar to microporous diffusion, explained in the next section.

3.2.2 Microporous diffusion

The microporous diffusion is due to the closer dimensions between the molecular diameter and the pore diameter. In this phase the force field applied by the pore wall is so strong that the diffusing

molecules cannot escape and will eventually be adsorbed in the wall, so the molecules present in the microporous are denominated as adsorbed phase⁴⁰.

3.2.1 Linear driving force (LDF)

The use of diffusion Equation to model adsorption kinetics involves solving an additional differential Equation with associated boundary conditions. Solving this Equation, in addition to the mass and energy balance in the gas phase, can be computationally very time-consuming. It has been shown that the linear driving force assumption (LDF), proposed by Glueckauf and Coates (1947), is equivalent to assuming a concentration profile within the particles. The concentration difference between bulk gas and the solid phase sets the mass transfer driving force (mass transfer coefficient). The intraparticle mass transfer model is therefore given by the following Equation:

$$\frac{\partial \bar{q}_i}{\partial t} = k_{\text{LDF}}(q_i^* - \bar{q}_i) \quad (5)$$

where the LDF coefficient can be estimated according to Equation (6):

$$k_{\text{LDF}} = \frac{\Omega \times D_{c,i}}{r_c^2} \quad (6)$$

where $D_{c,i}$ is the apparent diffusion time constant and the value of Ω is 15 when related to the PSA unit.

3.3 Adsorbent

The adsorbent is the most critical factors in adsorption-based processes. Accordingly, several factors must be taken into account when selecting the adsorbent material, including: multicomponent adsorption equilibrium capacities, selectivity, kinetics, high mechanical resistance, high stability and low cost. Good adsorbents have good adsorptive capacity and kinetics so, thus high surface areas or micropore volume and a high porosity are commonly found⁴¹.

3.3.1 Zeolites

Zeolites are crystalline materials classified as aluminosilicates, which can be constituted by sodium, potassium or calcium. The stoichiometric formula is defined by: $M_{x/n} [(AlO_2)_x(SiO_2)_y]zH_2O$ where x and y are integer numbers, n is the valence of cation M and z is the number of water molecules in each unit cells. The tetrahedra of silicon and aluminum, SiO_4 and AlO_4 , are the primary structural units. These atoms (Si and Al) are connected through shared oxygen atoms helping the formation of a channel grid. This crystalline structure has openings where the molecules can diffuse²⁷. About 150 types of zeolites have been synthesized and classified but only a few are commercially important.

3.3.2 Carbon molecular sieves

Carbon molecular sieves (CMS) are a modified type of activated carbon with a more uniform pore size distribution. In fact, the objective during CMS synthesis is to obtain a material with a homogeneous pore size distribution. CMS have a high internal surface area and a molecular sieving capability, with pore size of several angstroms⁴⁴, ranging from 4 to 9 angstroms (Å)⁴⁰. The carbonization of the coal and the coating of coke on the coal char are the basic procedures in their synthesis, while the pyrolysis and activation steps are determinant in the micropore size⁴⁴. The gas separation factor using this type of adsorbents is typically based on the different adsorption kinetics of the gases⁴³.

3.4 Breakthrough

A breakthrough curve is the concentration front profile of the gas concentration at the outlet of a fixed bed adsorbent column. Starting from the component mass balance, neglecting the axial dispersion, the mass transfer resistances, and the temperature variations, the velocity of the concentration wave front (u_c) in the column is given by Equation (7)⁴⁰.

$$u_c = \frac{u_i}{1 + \left(\frac{1 - \varepsilon_b}{\varepsilon_b} \right) \frac{dq}{dC}} \quad (7)$$

From the Equation above the u_c is function of the interstitial velocity, u_i and the slope of the isotherm ($\frac{dq}{dC}$). In the case of a favorable isotherm, its derivative decreases as the concentration increases, leading to an increase in the velocity of the wave. Thus, an initially dispersive wave, compresses as it flows through the column to a point of discontinuity (shock) where there is no dispersive effect⁴⁰, as represented in Figure (2). This behavior is the so-called self-sharpening behavior.

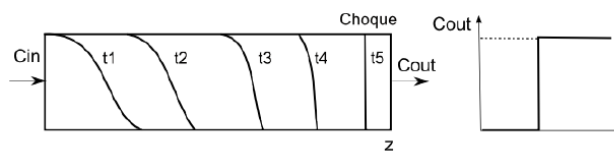


Figure 2 – Ideal profile of a favorable isothermal concentration.

If the axial dispersion and the mass transfer resistance are added, the dispersive effects will be in competition with the compressive effect, whereby a steady wave is generated when the two effects are in equilibrium⁴⁰. This effect is called the constant pattern behavior. In the case of a non-favorable isotherms, their self-dispersive nature will further enhance axial dispersion and transfer mass resistance effects⁴⁰.

3.5 Pressure-swing adsorption (PSA)

PSA process was firstly described in 1932 in a patent disclosed by Finlayson and Sharp⁴⁴, though Skarstrom often receives the credits due to his patent filled in 1958 for oxygen enrichment⁴⁵. A PSA unit is composed by a system of at least two packed adsorbent beds operating in parallel and controlled by a valve system, which open and close according to the cycle⁴⁰. The “core” cycle consists in four steps showed in Figure 3: pressurization, adsorption, countercurrent blowdown, and countercurrent purge, and uses the total pressure as the thermodynamic variable to cause desorption of the adsorbent. An additional pressure equilibration step and the increase of number of columns allows to increase the recovery and to save power⁴⁰.

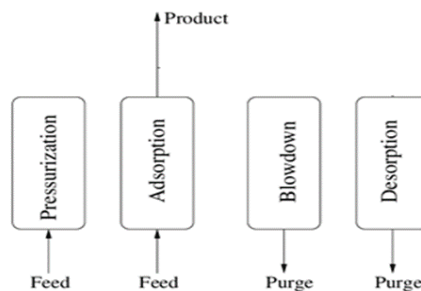


Figure 3 - Four steps Skarstrom cycle⁴¹.

The pressurization step consists in the pressurization of the column to the maximum pressure. In the end of this step, the column is ready to start the adsorption step. The pressurization can be performed through the product side (also called backfill) or using the feed stream.

In the adsorption step, the more strongly adsorbed species are retained in the adsorbent and the product is enriched in the less adsorbed component. The step ends before the column gets fully saturated. During the blowdown step, the pressure decreases and the adsorbent is regenerated. This is possible because the equilibrium quantity at the surface q_1 drops to a new value q_2 , resulting in a lower adsorption capacity, as shown in Figure 4.

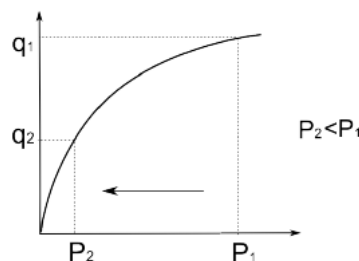


Figure 4 - Graphical representation of the effect of pressure regeneration.

A fraction of the product can be used to purge the column, lowering the adsorbed species partial pressure and thus enhancing the adsorbent regeneration. Alternative ways to regenerate the adsorbent includes the use of a vacuum pump and the implementation of an evacuation step (VPSA), or by raising

the temperature of the adsorbent causing a decrease in the adsorption capacity (TSA). Heating of the adsorbent is caused directly by a hot purge fluid, or indirectly through heat transfer elements inserted in the column. Because of the poor heat transfer capabilities of the adsorbent, TSA cycles are slow, so it is practical to treat low concentration adsorbent fluids, such as in the purification or drying processes. Since temperature has a strong effect on equilibrium, it becomes suitable for the treatment of strongly adsorptive species⁴⁰.

In this type of regeneration there is no need for cooling or heating steps, since the adsorption and desorption heats cancels each other. To achieve the same efficiency of the TSA in reducing the equilibrium, it is necessary to apply high pressure drops, which in many cases at a higher cost coupling compressor. Thus, in general, PSA have a lower capacity than TSA, and also have limitations on strongly adsorbed species since they require very low pressure to desorb. On the other hand, a very important aspect in PSA is the rapid response of the adsorbent to pressure variations, which allow faster cycles. An PSA with a rapid cycling makes it ideal for separations with concentrated mixtures, since a fast adsorption process follows a rapid desorption. Another characteristic of the PSA is the obtaining of a product of high purity and need for long beds. The major applications of PSA are in the purification of gases⁴⁰. When the regeneration needs low-pressure at vacuum level, the designation is adjusted to VPSA, vacuum pressure swing adsorption due to the high pressures for the adsorption process and the low pressures for regeneration.

4 Materials and Methods

4.1 Distillation column simulation

Aspen Plus was used to simulate the conventional distillation process. A C3 splitter was projected for a feed stream of 50/50 (%V/V) C_3H_6/C_3H_8 , based a steam cracker product, the most commonly used method for propylene production. A feed temperature of 303 K and a pressure of 18 bar were used at a feed flowrate of 220 000 tons of propylene per year. This feed flowrate was used to match the major national producer. The propane was adjusted according to the feed compositions mentioned above. The selected thermodynamic model was Peng-Robinson, a well-established and suitable model to hydrocarbon separation.

For each feed conditions, two columns were placed in parallel, one representing the DSTWU column model and the other RADFRAC column, according to the scheme presented in Figure 5. The DSTWU unit operation is designed for single feed, two product distillation processes. This column completes calculations using Gilliland's, Winn's, and Underwood's methods that are shortcuts methods to estimate the reflux ratio, propylene recovery (distillated and bottom product), feed stage location and the condenser and reboiler duties present in Table A.1. These calculations are completed based on two assumptions, constant molar overflow and constant relative volatilities. In turn, the RADFRAC column represents the "real" column having more inputs origin more mathematic variables and rigorous methods. The inputs are taken from the DSTWU results. For the column simulation heat losses were assumed to be negligible and a total condenser has been assumed because the reflux ratio is related to the reboiler so the distillation only needs the condensation process.

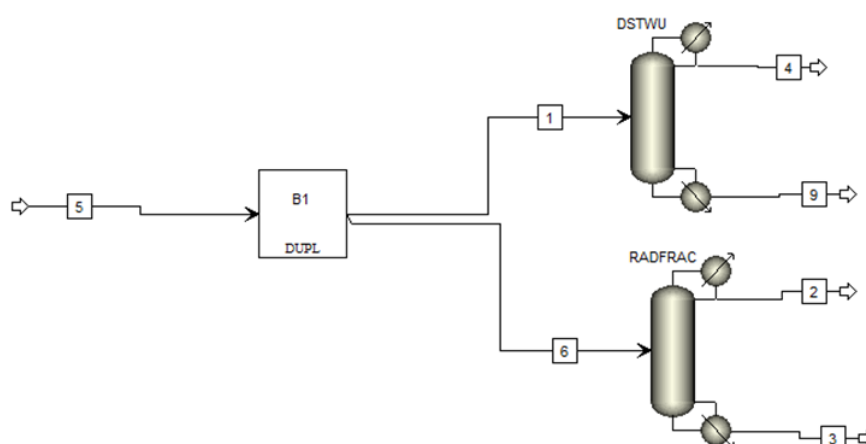


Figure 5 - Scheme of DSTWU (upper) and RADFRAC (down) column models

4.2 Adsorbents

In the present work, two adsorbents were considered for packing a VPSA unit for propylene purification, a 4A zeolite and a carbon molecular sieve produced by Amnis Pura, hereafter named only as CMS. The 4A choice was based on a literature results using VPSA for propylene purification. All the zeolite 4A properties, including kinetic data, adsorption parameters and adsorbent properties were taken from the study of Grande *et al.* (2010)³⁶. The CMS properties required for simulation purposes were provided by the Amnis Pura.

4.2.1 CMS

Monocomponent adsorption equilibrium isotherms of propylene and propane on CMS were available at three different temperatures, 298 K, 318 K and 338 K. The experimental results (previously obtained by the company) were fitted by Dual-Site Langmuir isotherm, according to Equation (4). The isotherms are shown in Figure 6 a) for propane and Figure 6 b) for propylene and the model parameters are presented in Table 2.

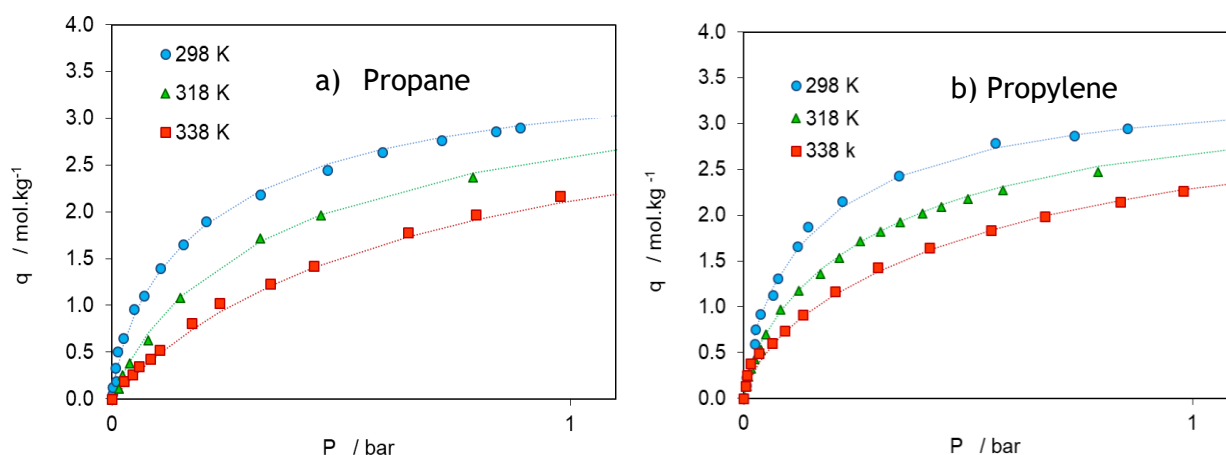


Figure 6– a) Propylene isotherms on CMS and b) Propane isotherms on CMS at: 298 K, 318 K, and 338 K.

The lines represent the Dual-Site Langmuir isotherm fitting.

Comparing the propylene and propane isotherms at the same temperature, it is possible to observe that propylene shows a slightly higher adsorption. However, this difference is not enough for an equilibrium-based separation by PSA due to its lower separation factor, *ca.* 1.07 at 1 bar and 318 K. On the other hand, comparing the apparent diffusivity for both gases presented in Table 2, a kinetic selectivity of 20.8 for propane is obtained, which turns the CMS suitable for a kinetic-based separation by PSA.

Table 2 - Equilibrium and isotherm parameters for propylene and propane.

Parameter	Propylene	Propane
$q_{\max,1} \text{ (mol}\cdot\text{kg}^{-1}\text{)}$	1.126	2.990
$K_1^0 \times 10^{-3} \text{ (bar}^{-1}\text{)}$	0.0043	0.1434
$\Delta H_1 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	-32331	-26083
$q_{\max,2} \text{ (mol}\cdot\text{kg}^{-1}\text{)}$	2.38	0.500
$K_2^0 \times 10^{-3} \text{ (bar}^{-1}\text{)}$	0.0233	2.467
$\Delta H_2 \text{ (J}\cdot\text{mol}^{-1}\text{)}$	-32331	-26083
Apparent diffusion (s^{-1})	0.0015	0.0312

4.2.2 4A zeolite

Monocomponent adsorption isotherms of propylene and propane on 4A zeolite at 400 K were obtained from Grande. These authors give the parameters for the Multi-Site Langmuir model, which were used to fit Dual-Site Langmuir isotherm model. The isotherms are shown in Figure 7 for propane and propylene and the model parameters are presented in Table 3.

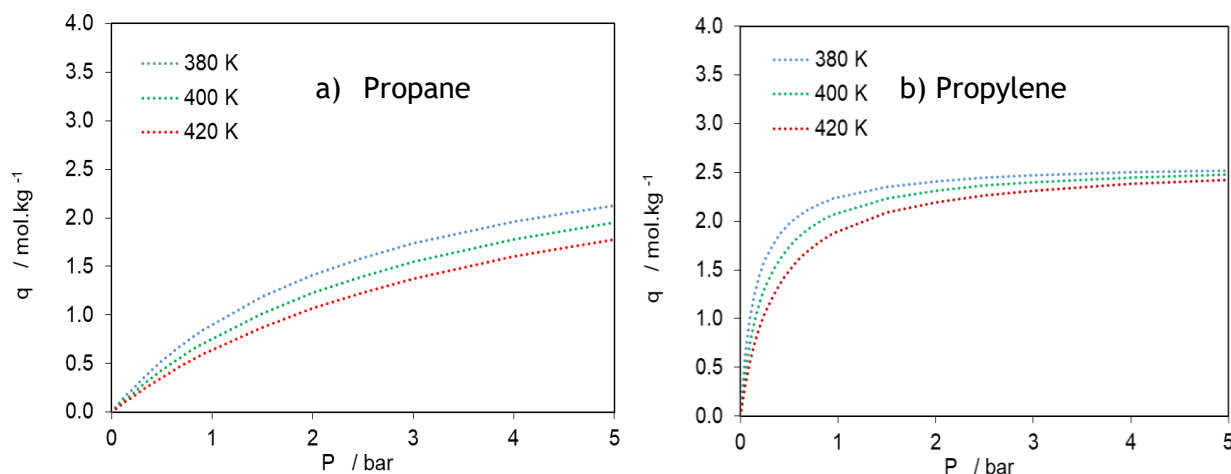


Figure 7 – Dual-Site Langmuir isotherms for a) propane and b) propylene on zeolite 4A for 400 K.

Comparing the propylene and propane isotherms at 400 K, it is possible to verify that propylene shows a higher adsorption. The separation factor for an equilibrium-based separation by PSA is 2.96, calculated at 1 bar and 400 K for comparing the apparent diffusivity for both gases presented in Table 3, a kinetic selectivity of 226 for propane is obtained.

Table 3 – Physical characterization for the 4A zeolite and isotherm parameters for propylene and propane for the Dual-Site Langmuir model and Dual-Site Langmuir isotherm model²⁷.

Parameter	Dual-Site Langmuir model		Multi-Site Langmuir model	
	Propylene	Propane	Propylene	Propane
$q_{\max,1}$ (mol·kg ⁻¹)	1.937	3.092	2.600	3.103
$K_1^0 \times 10^{-3}$ (bar ⁻¹)	2.39	2.58	0.844	2.81
ΔH_1 (J·mol ⁻¹)	-18439	-10887	-28200	-15600
$q_{\max,2}$ (mol·kg ⁻¹)	1.17	1.26	—	—
$K_2^0 \times 10^{-3}$ (bar ⁻¹)	0.41	0.29	—	—
ΔH_2 (J·mol ⁻¹)	-18439	-10887	—	—
a_i	—	—	2.612	2.189
Adsorbent radius (m)	0.0008			
Adsorbent density (kg·m ⁻³)	1210			
Adsorbent porosity	0.34			

Before running PSA simulations, fixed-bed experiments breakthrough curves were simulated to assess the adsorbent effectiveness for propane/propylene separation. The column was fully regenerated and helium was fed to the column at the operating conditions of 400 K and 3 bar. At time t_0 , the feed stream was changed to 50 %/50 % C₃H₈/C₃H₆ at 400 K, 2 L·min⁻¹ and 3 bar.

4.3 VPSA

A VPSA process was simulated aiming to obtain polymer grade propylene (+99.5 %). The simulated unit comprises four columns packed with 4A zeolite, whose dimensions were based on the lab-scale VPSA and are described in Table 4.

Table 4 – Input for one column loaded with 4A zeolite (*Temperature was based in Grande et al (2010).)

Column length (m)	0.34
Column radius (m)	0.016
Bulk porosity	0.4
Temperature (K)	400*
Adsorbent bulk density (kg·m ⁻³)	758

A 12-steps cycle with 8 elementary steps was implemented as sketched in Figure 8 a). Figure 8 b) shows a typical pressure history along the VPSA cycle. Because propylene is the most adsorbed species in zeolite 4A, it is mainly recovered as off-gas during the blowdown and evacuation steps.

Adsorption - During the adsorption stage, propylene is selectively adsorbed while propane is recovered in the top end of the column. This step ends before propylene breakthrough.

First depressurization pressure equalization – The column is depressurized through the top and the outlet gas is used to pressurize the column in the second pressurization equalization step.

Blowdown – The column depressurizes co-currently to atmospheric pressure.

Second depressurization pressure equalization – This step makes an approach to the lowest vacuum pressure by equalizing the pressure with the column in the first pressurization equalization step. Performing this step, the power consumption related to the vacuum pump is reduced.

Evacuation - The vacuum pump acts to recover the propylene present in the adsorbed phase. In this step, the column is at the lowest pressure of the cycle.

First pressurization pressure equalization – The column equalizes its pressure with the column in the second depressurization pressure equalization step.

Second pressurization pressure equalization – The column equalizes its pressure with the column in the first depressurization pressure equalization step.

Pressurization – The column is fed to the operating pressure using feed gas.

All the pressure equalization steps are performed from the top (high pressure side) to bottom (low pressure side). This orientation was selected because of the higher partial pressure of propane in the interparticle volume in the top part of the column. Accordingly, propylene is recovered from the bottom with higher purity during the blowdown and evacuation steps.

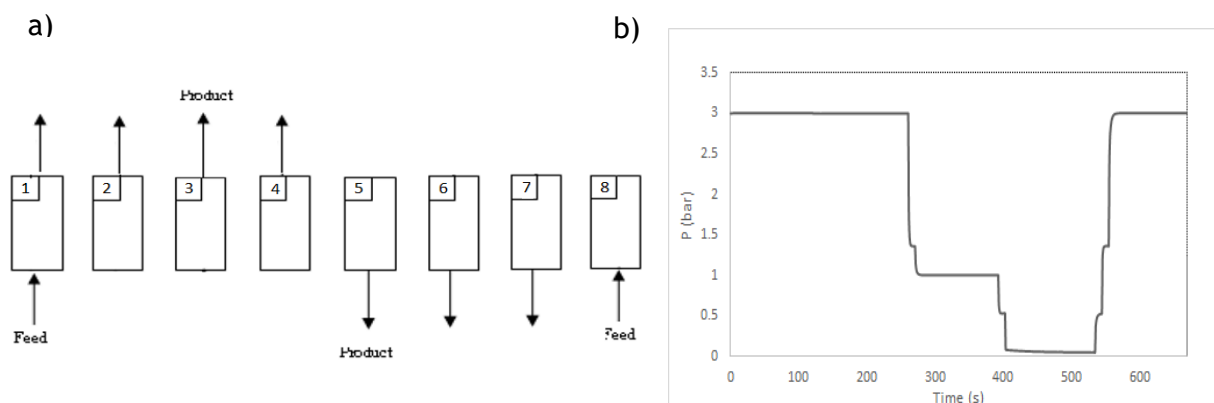


Figure 8 – a) Elementary steps of the VPSA cycle and b) Typical pressure history VPSA cycle.

The VPSA cycle is given in Table 5, where the duration of steps 2, 4, 6,7 was fixed to 10 s, while the remaining steps were adjusted according to the design of experiments described in the next section.

Table 5 – VPSA cycle sequence: 1) Adsorption, 2) co-current pressure equalization depressurization, 3) counter-current blowdown, 4) co-current pressure equalization depressurization, 5) evacuation, 6) counter-current pressure equalization pressurization counter-current pressure equalization pressurization, 7) counter-current pressure equalization pressurization and 8) co-current feed pressurization.

Col 1	1	2	3	4	5	6	7	8
Col 2	7	8	1	2	3	4	5	6
Col 3	5	6	7	8	1	2	3	4
Col 4	2	3	4	5	6	7	8	1

The VPSA performance was assessed based on 4 parameters namely propylene purity, recovery, productivity and power consumption. Propylene purity and recovery were assessed according to Equations (8) and (9), while productivity and power consumption were calculated using Equations (10) and (11).

$$y_{C_3H_6} = \frac{\int_0^{t_{Ev}} C_{C_3H_6} \dot{V}_{out} dt + \int_0^{t_{Bd}} C_{C_3H_6} \dot{V}_{out} dt}{\int_0^{t_{Ev}} C_T \dot{V}_{out} dt} \quad (8)$$

$$Rec_{C_3H_6} = \frac{y_{C_3H_6}}{y_{C_3H_6} + \frac{(y_{C_3H_6,feed} - y_{C_3H_6})(1 - y_{C_3H_6})}{(1 - y_{C_3H_6}) - y_{C_3H_6,feed}}} \quad (9)$$

$$Prod_{C_3H_6} = \frac{\int_0^{t_{Ev}} C_{C_3H_6} \dot{V}_{out} dt + \int_0^{t_{Bd}} C_{C_3H_6} \dot{V}_{out} dt}{t_{cycle} \rho_p L \frac{(1 - \varepsilon_b)}{\varepsilon_b}} \quad (10)$$

$$Power = \frac{1}{\eta_{ev}} \frac{\gamma}{1 - \gamma} \int_0^{t_{ev}} F_{ev} P_{low} \left(\left(\frac{P_{in}}{P_{Low}} \right)^{\frac{1-\gamma}{\gamma}} - 1 \right) dt \quad (11)$$

where $y_{C_3H_6,feed}$ is the fraction of propylene in the PVSA feed, $Rec_{C_3H_6}$ is the propylene recovery, $Prod_{C_3H_6}$ is the productivity of propylene in $\text{mol} \cdot (\text{kg} \cdot \text{h})^{-1}$, P_{in} is the pressure before the evacuation step in Pa, P_{Low} is the minimum vacuum pressure in Pa, F_{ev} is the evacuation molar flowrate, is the mechanical efficiency (η_{ev}), here assumed as 80 % and γ was assumed as 1.15 for a propylene-propane mixture. The outlet concentration was followed along the VPSA cycle and the performance parameters were only taken into account after reaching cyclic steady state (minimum of 50 cycles and a tolerance of 0.001 % between cycles).

4.3.1 Design of Experiments

Design of Experiments (DoE), “defined as a branch of applied statistics that deals with planning, conducting, analyzing, and interpreting controlled tests to evaluate the factors that control the value of a parameter or group of parameters. DOE is a powerful data collection and analysis tool that can be used in a variety of experimental situations.”⁵³. In the present work, software JMP (Statistical Analysis Software) was used to compute a central composite design, combining 2-level factors with central points at midrange-value. After multiple regression analysis of the results, an empirical polynomial model can be obtained, according to Equation (12), as well as the interaction amongst the factors. In this case, the feed pressure (range: 3 to 5 bar), time of adsorption step (range: 63 to 96 s) and vacuum pressure (0.05 to 0.20 bar) were selected as factors. Propylene purity and recovery were the selected response variables. The parameters significance was featured by the p-value used to indicates if the evidence is weak (p-value<0.05) or strong (p-value>0.05) against a null hypothesis, while the coefficient of determination (R^2) and the root-mean-square error (RMSE) were used to estimate the fitness and accuracy of the model.

$$\begin{aligned} \text{Response} = & a_0 + a_1 \times (P_H - 4) + a_2 \times \frac{t_{ads}-79}{16} + a_2 \frac{P_{Low}-0.125}{0.075} + a_7 \times (P_H - 4) \times \frac{t_{ads}-79}{16} + a_4 \times \\ & (P_H - 4) \times \frac{P_{Low}-0.125}{0.075} + a_8 \times \frac{t_{ads}-79}{16} \times \frac{P_{Low}-0.125}{0.075} + a_6 \times (P_H - 4)^2 + a_5 \times \left(\frac{t_{ads}-79}{16}\right)^2 + a_9 \times \\ & \left(\frac{t_{ads}-79}{16}\right)^2 \end{aligned} \quad (12)$$

4.4 VPSA model and Aspen simulation

The VPSA model is described by a set of partial differential Equations including mass, energy and momentum balances. The main assumptions of the model are:

- Ideal gas phase behavior.
- Negligible radial concentration and temperature gradients.
- Axially dispersed plug flow.
- Uniform cross-sectional void fraction.
- Intraparticle mass transport balance described by the linear driving force (LDF) model.
- Non-isotherm conditions.
- Pressure loss described by the Ergun Equation.
- Homogeneous bed porosity along the column.
- Non adiabatic.

Based on these assumptions the component mass balance is described by Equations (13)⁴⁰. Assuming plug flow model with axial dispersion, the molar balance is⁴⁰:

$$-\varepsilon_b D_{axial} + u_i \frac{\partial C_i}{\partial z} + C_i \frac{\partial u_i}{\partial z} + \frac{\partial C_i}{\partial t} + \frac{(1 - \varepsilon_b)}{\varepsilon_b} \rho_s \frac{\partial \bar{q}}{\partial t} = 0 \quad (13)$$

where, u_i is the interstitial velocity, ε_b the bulk porosity, C_i is the concentration of component i , D_{axial} the axial dispersion coefficient and z is the spatial coordinate. The mass balance in the gas phase considers the effects of axial dispersion, the convection term, accumulation on the gas phase and flux to the adsorbent.

The energy balance can be split into two different balances: gas and solid. The column wall energy balance was neglected.

Accordingly, the energy balance for the gas phase is expressed by⁴⁰:

$$\varepsilon_b C_T \frac{\partial T_g}{\partial t} = \frac{\partial}{\partial z} \left(\lambda \frac{\partial T_g}{\partial z} \right) - u_i C_p \frac{\partial T_g}{\partial z} + (1 - \varepsilon_b) h_f a_p (T_g - T_s) \quad (14)$$

where C_T is the total gas phase concentration, T_g is the temperature of the gas phase, T_s is the solid temperature, λ is the axial heat dispersion, C_p is the molar constant pressure specific heat of the gas mixture, C_v is the molar constant volumetric specific heat of the gas mixture h_f is the film heat-transfer coefficient between the gas and solid phases and a_p is the specific area.

The energy balance for the solid phase is expressed by⁴⁰:

$$(\varepsilon_b C C_g + \rho_p (C_{ps} + q C_{vg})) \frac{\partial T_i}{\partial t} - \rho_b \left(\sum_{i=1}^{nc} -\Delta H_{ads} \frac{\partial q_i}{\partial t} \right) = u C C_{vg} \frac{\partial T}{\partial z} + \gamma_g \frac{\partial^2 T}{\partial z^2} - P \frac{\partial u}{\partial z} \quad (15)$$

where, C_{vg} is molar constant volumetric specific heat, C_{ps} is the constant volumetric specific heat of the solid. In turn, Ergun Equation was used to describe the pressure drop along the column, according to Equation (16)⁴⁰:

$$\frac{\partial P}{\partial z} = \frac{150 u \mu (1 - \varepsilon_b)^2}{d_p^2 \varepsilon_b^3} + 1.75 \rho_g \frac{(1 - \varepsilon_b)}{d_p \varepsilon_b^3} u_i |u_i| \quad (16)$$

where P is the total pressure, μ is the gas viscosity of component i , d_p is the particle diameter, and ρ_g is the gas-phase density.

The model was computed using Aspen Adsorption™, where the spatial derivatives are discretized over a fixed and uniform grid (nodes) using algebraic approximations. The resulting ordinary differential Equations are further integrated in time. The final flowsheet of the VPSA is given in Figure 9.

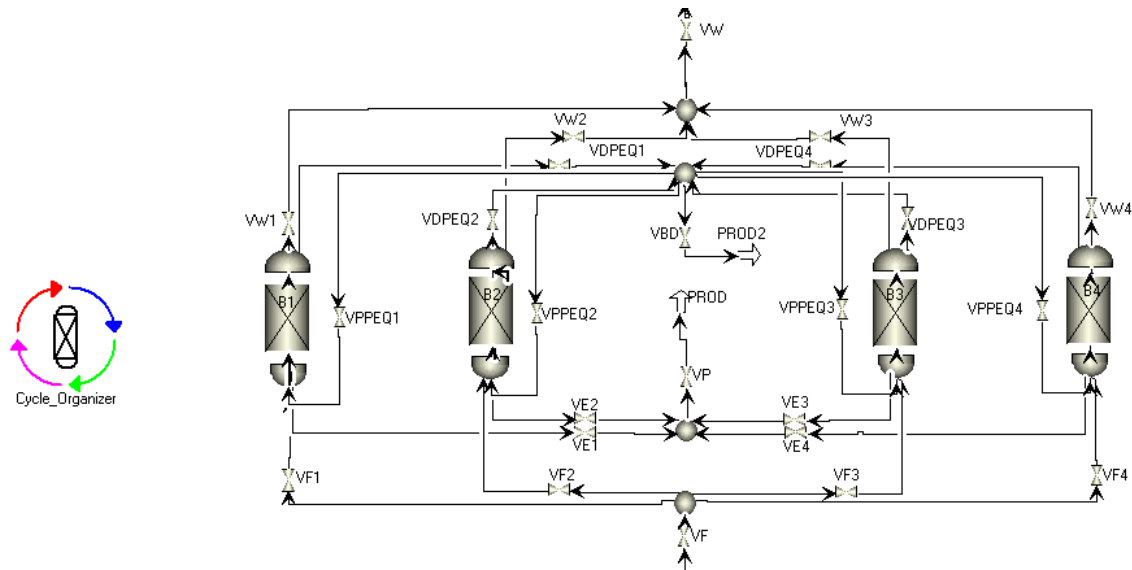


Figure 9 – Schematic representation of the VPSA.

The cycle organizer tool was used to manipulate the valves according to the cycle sequence. Depending on the valves each can be configured in three active specifications, as described in Table 6. An estimation of the valve's constant values C_{valve} is calculated with Equation (17)⁵⁴.

$$C_{valve} = \frac{V_{EB}}{0.0831441 \times T_g * t_{step}} \times \ln \left(\frac{P_{BS} - P_{ES}}{P_{BE} - P_{EE}} \right) \quad (17)$$

where V_{EB} is the effective bed volume, P_{BS} is the initial pressure of the bed, P_{BE} is the final bed pressure t_{step} is the step time, P_{ES} is the external initial pressure and P_{EE} is the external final pressure.

Table 6 – Active specifications for valves

Active specification	Description
0	Valve fully off
1	Valve fully on (valve with high Cv)
2	Valve with a constant value specified for Cv (kmol·bar·s ⁻¹)

5 Results and discussion

5.1 Distillation column

Considering a feed stream of 440 000 tons/h (50 %/50 % - C_3H_6/C_3H_8) at temperature of 303 K and a pressure of 18 bar, the DSTWU model was used to determine the inputs and initial conditions for the RadFrac model. The final design parameters of the distillation column are given on Table 7.

Table 7 - RadFrac column results for 50 % propylene/50 % propane. (* input data from DSTWU model)

Number of trays	202*
Type of tray	Sieve
Feed tray	144*
Reflux ratio	16.1*
D:F ratio	0.517*
Height / m	50.5
Diameter / m	4.85

As it can be observed, to achieve the desired purity of 99.5 %, a very large column is needed, which turns into high capital costs 28.5 M €. Moreover, a high reflux ratio 16.1 was obtained due to the high purity needed and to maximize the recovery, leading to very high operation costs, 16 M€ per year.

5.2 Simulation results for CMS

The breakthrough results for the binary system propylene-propane on CMS adsorbent are depicted in Figure 10. As is can be observed, the adsorbent is able to separate propane from propylene in a 50/50 (% m/m) mixture, under the studied conditions (3 bar, 2 L·min⁻¹ and 303 K). For non-isothermal conditions (Figure 10a)), a rupture time of 348 s was observed for propane, while propylene breakthrough at 301 s. In turn, for isothermal conditions (Figure 10b)), the breakthrough time increases for both gases, 363 s and 318 s for propane and propylene, respectively. This difference is due to the exothermic nature of the adsorption process, leading to a temperature increase in the column and consequent decrease in

adsorption capacity. For the same reason, the shape of the breakthrough curve in non-isothermal conditions present a higher dispersion.

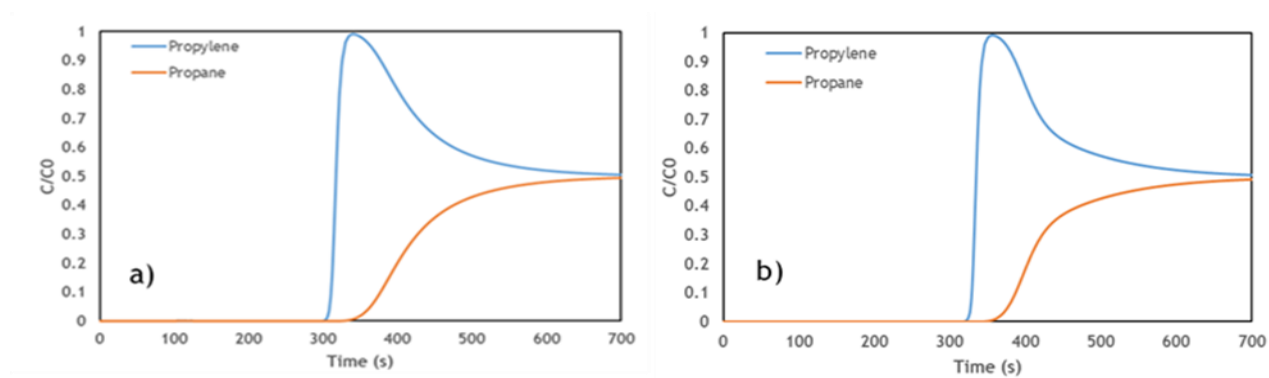


Figure 10 - Comparison of simulation breakthrough curves for a) non-isotherm conditions and b) isotherm conditions.

5.3 Simulation results for zeolite 4A

For the 4A zeolite breakthrough results for the binary system propylene-propane on 4A zeolite adsorbent are depicted in Figure 11. As it can be observed, the adsorbent is able to separate propane from propylene in a 50/50 (% m/m) mixture, under the studied conditions (3 bar, $2 \text{ L} \cdot \text{min}^{-1}$, 400 K). For non-isothermal conditions (Figure 11a), a rupture time of 251 s was observed for propylene, while propane breakthrough happens at 78 s. In turn, for isothermal conditions (Figure 11b), the breakthrough time increases for both gases, 85 s and 269 s for propane and propylene, respectively. Similarly to the breakthrough of the CMS adsorbent the temperature increase inside during the adsorption process decreases the adsorption capacity, thus anticipating the breakthrough time and dispersing the concentration front.

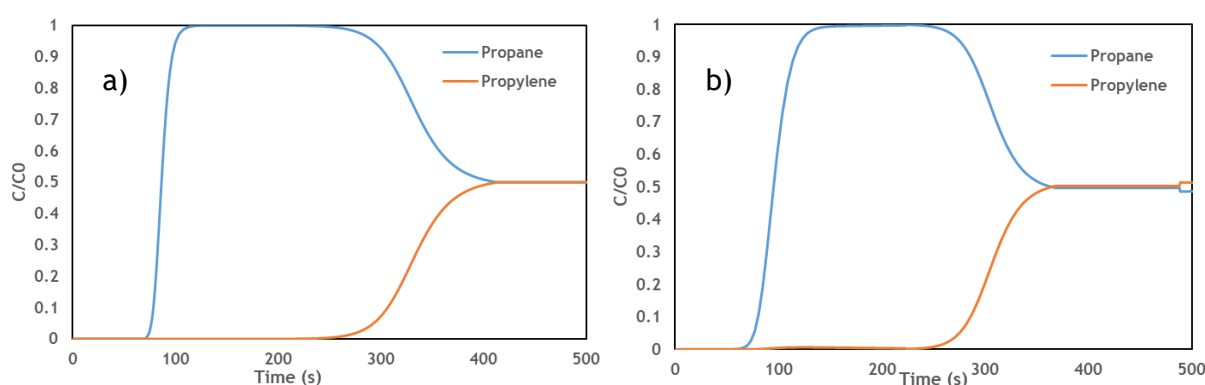


Figure 11 - Comparison of simulation breakthrough curves for a) non-isotherm conditions, and b) isotherm conditions.

Using JMP (Statistical Analysis Software), a central composite design (CCD) was selected to optimize the VPSA unit. A detailed description of the simulated conditions is given in Table 8, where feed pressure (P_{feed}), adsorption time (t_{ad}) and vacuum pressure (P_{low}) were used as factors to study its influence in propylene recovery and purity. It can be observed that propylene can be recovered with +99 % purity with a recovery of approximately 70 %. Nevertheless, polymer grade propylene was only obtained in run # 6 with a recovery of 63.9 %.

Table 8 – Design of experiments and for the VPSA simulator.

DoE Factors				Model prediction			Simulated results		
Run	t_{ad} (s)	P_{feed} (bar)	P_{low} (bar)	C_3H_6	C_3H_6	C_3H_8	C_3H_6	C_3H_6	C_3H_8
				purity (%)	recovery (%)	purity (%)	purity (%)	recovery (%)	purity (%)
1	79	5.00	0.125	98.4	53.2	68.2	99.2	48.3	65.9
2	79	3.00	0.125	99.17	48.3	65.9	98.8	51.3	67.2
3	95	5.00	0.050	99.3	70.0	74.9	99.0	68.8	76.2
4	79	4.00	0.200	98.2	38.4	63.3	98.1	38.8	62.3
5	95	3.00	0.200	99.2	35.8	59.2	99.0	34.5	60.3
6	95	3.00	0.050	99.5	63.0	71.9	99.5	63.9	73.5
7	63	3.00	0.200	98.3	37.9	63.2	98.6	39.4	62.1
8	79	4.00	0.050	99.1	71.0	78.2	99.1	70.2	77.1
9	95	5.00	0.200	98.6	50.1	61.2	98.2	39.0	62.2
10	79	5.00	0.125	98.4	52.7	68.9	98.4	53.2	68.2
11	63	5.00	0.050	98.3	75.4	82.1	98.5	76.8	81.4
12	63	5.00	0.125	97.3	51.4	67.0	96.6	48.4	67.2
13	63	5.00	0.200	96.7	37.2	64.8	97.3	36.5	63.5
14	95	4.00	0.125	98.6	46.8	54.2	99.0	48.0	51.9
15	63	3.00	0.050	98.9	72.0	79.0	98.9	71.9	77.9

Regarding DoE polynomial model, the regression parameters are given in Table 9, where it can be observed that parameters a_5 , a_6 , a_7 and a_8 are not statistically significant ($p\text{-value} > 0.05$) for both models. Nonetheless, these parameters were kept in the model for a better accuracy. In the case of a_9 (quadratic effect of the adsorption time), it is statistically significant for recovery but not for the purity model. Regarding factor's influence, parameters a_1 , a_3 , a_6 and a_7 have a negative value for the recovery model, meaning that the corresponding factor has a negative influence in recovery. For instance, the pressure increase (a_1) leads to a decrease in recovery. On the other hand, the factors associated to the parameters

a_2 , a_6 , a_7 , a_8 and a_9 present a negative effect in propylene purity. For a better understanding, the response surface was plotted in Figure 12 for both recovery, a), and purity, b).

Table 9 - Parameters of second order polynomial Equation.

Regression parameter	Recovery (C ₃ H ₆)	p-value	Purity (C ₃ H ₆)	p-value
a_0	0.5031130	<0.0001	0.985774	<0.0001
a_1	-0.163416	0.0452	-0.004433	0.0086
a_2	0.0443867	0.0306	0.0046889	0.0088
a_3	-0.018366	<0.0001	-0.004708	0.0110
a_4	0.016324	0.2300	-0.002504	0.1032
a_5	0.017045	0.1969	-0.004027	0.1293
a_6	-0.01023	0.0559	0.0027046	0.2773
a_7	-0.01663	0.5894	0.0011634	0.3976
a_8	0.009395	0.2278	0.0009834	0.4698
a_9	0.0069867	0.0146	0.0007296	0.7556
R^2	0.99		0.92265	
RMSE	0.0194		0.0036	
p-value	<0.0001		0.0254	

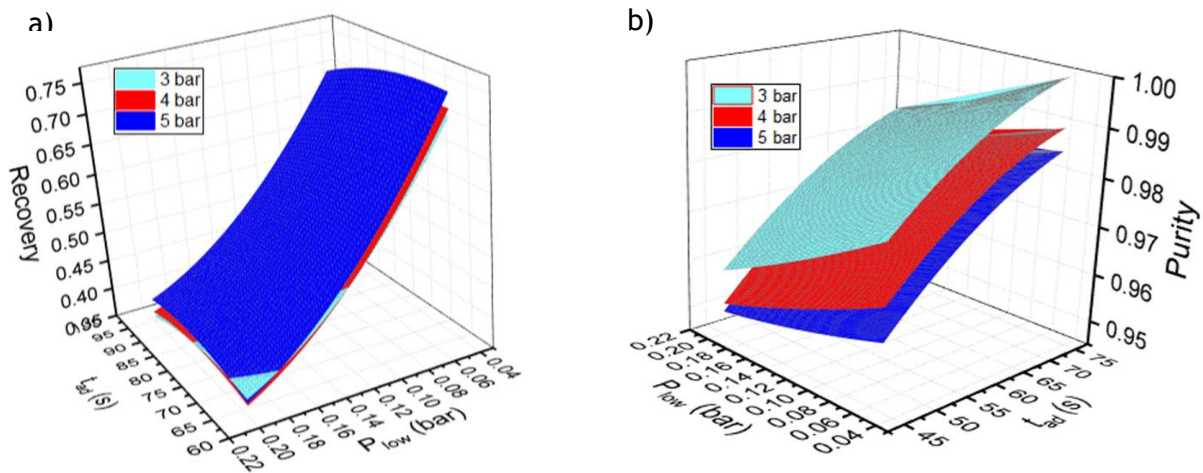


Figure 12 – Influence of vacuum pressure, adsorption time and pressure on a) propylene recovery and b) propylene purity.

Analyzing the response surface given in Figure 12, it can be concluded that the propylene purity is higher for lower feed pressure, becoming less influence for 4 and 5 bar. This behavior is due to the fact that propylene separation factor is higher at lower pressure, 2.29 at 1.5 bar partial pressure (total pressure

= 3 bar) and 1.75 at 2.5 bar partial pressure (total pressure = 5 bar). In the case of recovery the pressure effect is harder to predict. According to the linear effect of pressure in the model Equation, the recovery should decrease with the pressure increase (a_1 is negative). However, the pressure quadratic effect (a_9) has a positive influence in recovery. In the case of the vacuum pressure, lower vacuum pressure (0.05 bar) leads to higher purity propylene and higher yields. Nonetheless, it also means higher operation costs, as it will be further discussed in section 5.4.

Regarding the effect of adsorption time, the purity is maximum in the upper bounds. Because the adsorbent is not completely saturated for smaller adsorption time, the quantity of propylene recovered in evacuation step decreases, resulting in lower purity. On the other hand, when the adsorption time is maximum, the column is saturated and until eventually propylene exit the column.

After the previous analysis, JMP software was used to find the optimum, maximizing the recovery and fixing the purity to 99.5 % (polymer grade propylene). The operating parameters were estimated to 3 bar feed pressure, 0.05 bar vacuum pressure and an adsorption time of 90 seconds. Under these conditions, a recovery of 63.9 % was predicted. This result was validated by simulation, resulting in 99.47 % and 63.8 % of purity and recovery, respectively, at testing the model accuracy.

Figure 13 depicts the exit streams compositions along the VPSA cycle. The propylene average composition present in PROD (evacuation step) is 99.61% with small disturbances due to the residual propane present in the interparticle volume that is evacuated in first seconds. The quantity of propylene adsorbed is considerable higher than propane preventing a significant reduction in the propylene purity.

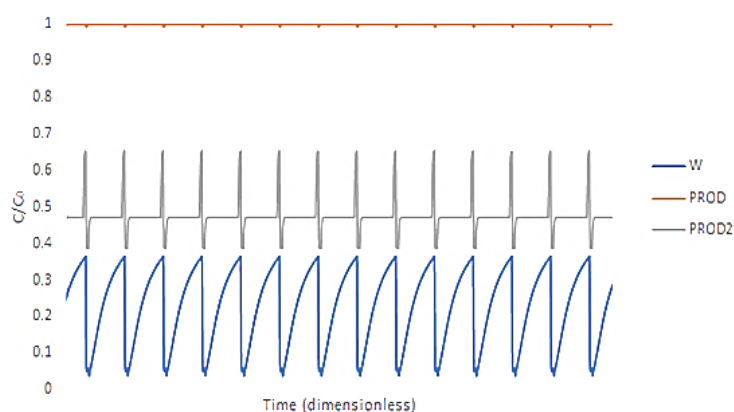


Figure 13 – Propylene composition in the three exit streams (W, PROD and PROD2) accordingly the steady state.

The exit feed (W) presents an average composition of 25 % of propylene, ranging from 6 % to 37 %, due to the bed saturation. Regarding PROD2 (blowdown) the first peak visible on Figure 13 is explained by the faster propylene desorption, while the second is due to the release of propane. For the

calculation of both recovery and purity, the blowdown and evacuation streams were considered together as total product stream.

Based on the optimization results, the pilot scale VPSA was scaled up for an industrial stream, where the scale up dimensions are presented in Table 10. The purity and recovery rate were assumed the same, obtaining a productivity of $7.61 \text{ mol}\cdot\text{h}^{-1}\cdot\text{kg}_{\text{zeolite}}^{-1}$. The Equations used for the scale up dimensions are present in appendix B.

Table 10 – Scale up dimensions for one column.

Variables	Value
Volume (m^3)	135
Diameter (m)	1.50
Length (m)	19.0
Mass of adsorbent (ton)	102

5.4 Economic analysis

The factors that determine the viability of the VPSA unit are capital costs (CAPEX) and operating costs (OPEX). The economic analysis allows us to estimate the profitability of the investment and therefore the degree of attractiveness for potential customers over other alternatives. All the cost results were actualized with a Chemical Engineering Plant Cost Index, (CEPCI), used to account for inflation, 603 (December 2018)⁴⁷.

The economic analysis was performed for two alternatives: a conventional distillation column that can obtain propylene at 99.6 % purity and 99.8 % recovery; and a VPSA packed with 4A zeolite, producing propylene with 99.5 % purity and 63.8 % recovery. The additional equipment costs as piping, insulation instrumentation and others, was estimated as 60 %⁸ of the conventional C3 splitter cost and 20 %⁴ of the VPSA unit. For the distillation column, the installed equipment considered in the economic analysis includes the reboiler, condenser, columns, support structure and number of trays. For VPSA, all the columns, valves, vacuum pump and one heat exchanger to 400 K were considered. The Equations to determine the operation cost and the cost of each component are presented in appendix B for the VPSA. The Equations regarding the C3 distillation column are presented in appendix 1. Operating costs are the continuing requirements in the process, including cooling and heating fluids, electricity, compressors etc. These utilities are proportional to the actual production of the unit. Costs related with the power consumption and cooling water were calculated considering a period of one year, assuming 8000 hours of work per year. Regarding electricity, a price of $0.10 \text{ €}\cdot\text{kWh}^{-1}$ was considered, while $0.0176 \text{ €}\cdot\text{m}^{-3}$ was

established for cooling water. The hot utility used for columns was medium pressure water vapor, which is heated by the combustion of natural gas. A global efficiency of 90 % for the heat transfer between the combustion of natural gas and water to provide energy to the reboiler was assumed. The power for the VPSA was considered as $0.073 \text{ kW} \cdot \text{mol}^{-1}$ of propylene.

According to the simulation results, the distillation column can achieve 99.6 % pure propylene with a recovery of 99.8 %, while the VPSA unit reaches 99.5 % purity with 63.8 % for recovery. To obtain a fair comparison, a lost opportunity factor (LOC) needs to be added, calculating the value for the lost propylene that cannot be recovered. The results of both operating costs (OPEX) and the capital expenditure (CAPEX) are specified in Table 11, where the CAPEX were calculated adding up the grassroots costs of all the equipment for each processual unit.

Table 11 – Capital expenditure, operation expenses and LOC for each separation unit.

Processual unit	P _{low} (bar)	Rec _{C₃H₆} (%)	CAPEX (M €)	OPEX (M € per annum)	LOC (M € per annum)
C3 splitter	—	99.8	28.54	16.26	1.32
	0.050	63.8	3.343	20.5	39.40
VPSA	0.20	63.8	3.343	13.83	39.40
	0.20	99.7	3.343	13.83	1.982

According to the results shown in Table 11, the VPSA has the lowest capital investment reducing 25 million the investment cost when compared with C3 splitter. The distillation process uses more expensive equipment, turning the VPSA a potential alternative. Regarding the operation costs, the propylene production using the conventional C3 splitter, the total annual cost (excluding LOC) is 16.26 M €, or 73.90 € per ton of propylene. In the case of the VPSA, the total annual cost (excluding LOC) is 20.5 M € per year, or 93.01 € per ton of propylene, mainly due to the low pressure that the vacuum pump needs to apply. For the calculation of the LOC factor, it was considered that propylene below the polymer grade can be sold as HD grade propane. The price of HD grade propane is considerably low, 391.6 € per ton, when compared to polymer grade propylene, 1164 €. Accordingly, when considering the LOC, the production costs using the VPSA rises to 39.4 M € per year or 179 € per ton of propylene, due to the low recovery of 63.8 %. On the other hand, the production costs remains nearly the same when considering the LOC for the conventional C3 splitter.

To provide a better understanding, Figure 14 gives the economic profile for both conventional distillation column and VPSA, including capital as initial cost and the operation cost through the time.

Figure 15 plots the same scenarios but including LOC. Comparing the two Figures it becomes clear that LOC plays an important role in the economic scenario, turning the VPSA a non-competitive alternative. Nevertheless, VPSA capital cost is attractive and has a potential cost reduction of 25 million €. The high OPEX for VPSA is explained by the huge power required to reach a vacuum pressure of 0.05 bar.

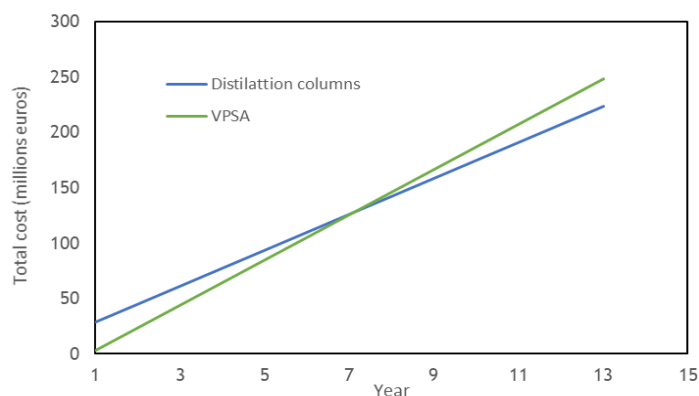


Figure 14 – Economical profile for distillation columns and VPSA capital and operation cost without LOC factor for 0.05 vacuum pressure VPSA.

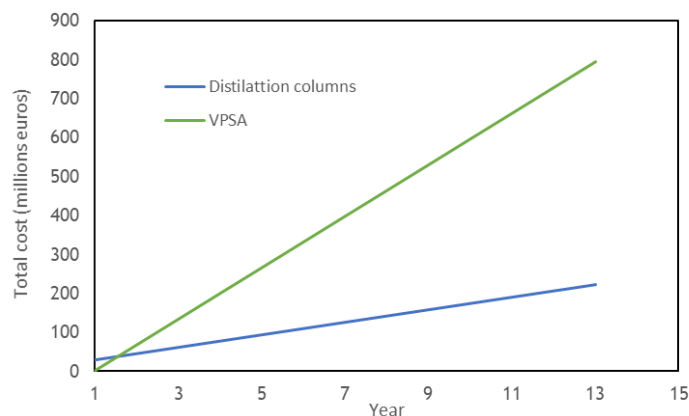


Figure 15 - Economical profile for distillation columns and VPSA capital and operation cost with LOC factor for 0.05 vacuum pressure VPSA 66.7% recovery rate.

To study the low-pressure effect in the OPEX, the vacuum was set to 0.2 bar (assuming that the purity target is accomplished and the recovery was kept at 63.8 %). The total costs as function of the year was plotted in Figure 16, where the OPEX was estimated as 62.86 € per ton (excluding LOC), resulting in a cost-competitive alternative to C3 splitter. However, if the LOC is considered, the distillation column

becomes a more attractive technology, as shown in Figure 17. In fact, to become more viable than the distillation column, a minimum recovery of 97 % is required, as shown in Figure 18.

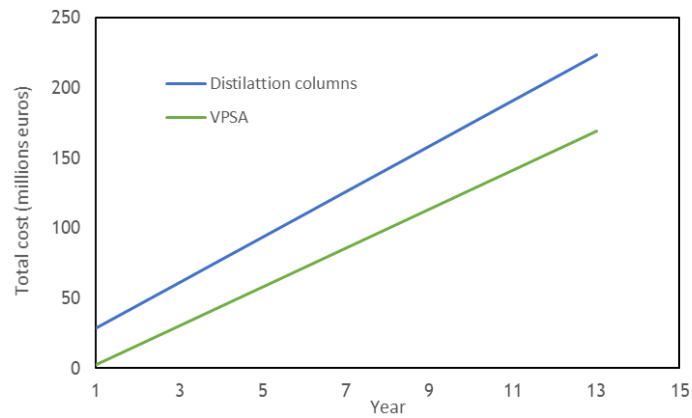


Figure 16 – Economical profile for distillation columns and VPSA capital and operation cost without LOC factor 0.2 bar of vacuum pressure VPSA.

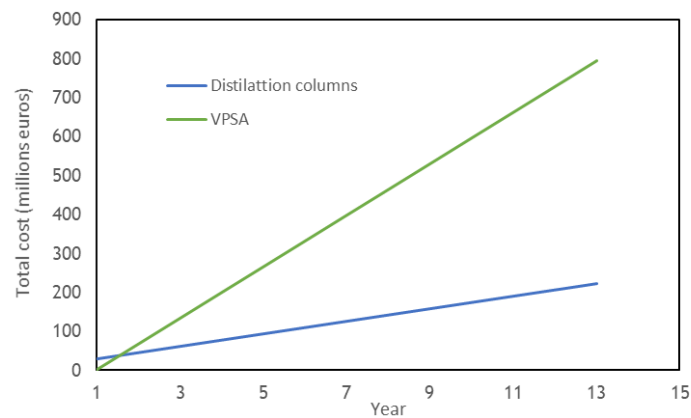


Figure 17- Economical profile for distillation columns and VPSA capital and operation cost with LOC factor 0.2 bar of vacuum pressure VPSA and 66.7 % of recovery.

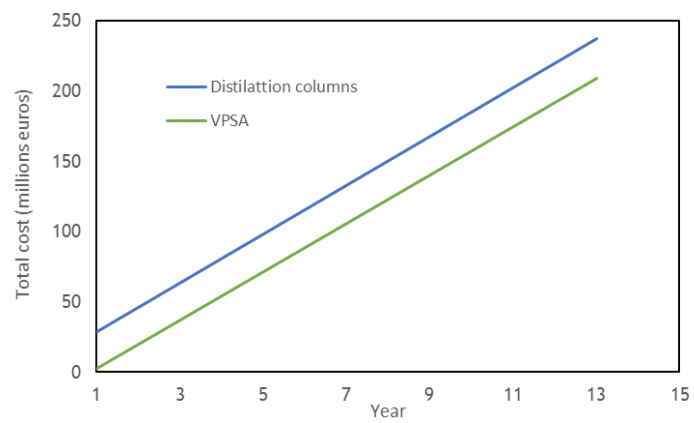


Figure 18 - Economical profile for distillation columns and VPSA capital and operation cost with LOC factor 0.2 bar of vacuum pressure VPSA and a recovery rate of 97 %.

6 Conclusion

This dissertation compares a vacuum pressure swing adsorption unit with a conventional C3 distillation column for the purification of a 50 % propylene / 50 % propane stream to obtain polymeric grade propylene (purity > 99.5 %). The VPSA was simulated using Aspen Adsorption™ and the distillation column was simulated using Aspen Plus™. The simulated distillation column produced a propylene stream with a concentration of 99.5 % and a recovery of 99.6 %, while the VPSA unit packed with a 4A zeolite with 12-step cycle produced a stream with 99.5 % of propylene at 66.7 % recovery.

From the economical point of view, VPSA has the lowest capital investment with a cost of 3.3 M € versus 28.5 M € of the distillation column. Nonetheless, when considering the operating costs, the conventional process provided a better solution, mainly due to the effect of LOC. It was also found that the vacuum power contributes with 83 % of the VPSA OPEX cost. The best OPEX, excluding LOC cost, was 93.90 € per ton of propylene, which is higher than that for the distillation column of 73.01€ per ton of propylene.

The investigation should be proceed to evaluate the possibility of recovering the VPSA waste stream, thus reducing the LOC and improving the global process performance. The use of alternative adsorbents has also a great potential to reduce both LOC and OPEX cost, particularly if propylene is recovered in as the top product.

6.1 Assessment Objectives Achieved

The conventional C3 splitter and the VPSA unit with 4A zeolite were simulated with success achieving the purity target of 99.5%. The VPSA unit was optimized and scaled up properly. The economic analysis was achieved with success for both units enhancing the LOC predominance all over the others cost influences as: vacuum pump, heat exchanger and capital cost.

6.2 Recommendations for Future Work

Conducting a research is usually presupposed by a continuity so, to upgrade the VPSA unit performance's the cycle can be further optimized trying another configuration or implement more pressure equalizations steps to initiate the vacuum pump from the lowest pressure possible reducing the power consumption. Others pressure equalizations configurations as bottom-bottom and bottom top can be tested. Another future work can be the introduction of a recycled stream to recover all the propylene.

In the section 3.5.1, it was shown that using a 4A zeolite requires the implementation of an evacuation step. To achieve high purity propylene and recovery, the vacuum should be as low as 0.05 bar, turning into an expensive process due to the high operation costs. As future work, it is recommended to evaluate the use of CMS from Amnis Pura, a propane selective adsorbent. In this case, propylene is recovered during the adsorption step and the evacuation step is used only to regenerate the adsorbent. Accordingly, milder vacuum conditions can be applied, reducing the operation costs. Alternatively, a purge step can be used to replace vacuum (totally or partially) In the case of using the CMS from Amnis Pura, the VPSA cycle should be adapted. It is important to recall that CMS is propane selective, which means that propylene will be recovered from the top end of the column during the adsorption step.

Thus, the following cycle was proposed:

Table 12 – VPSA cycle sequence: 1) Adsorption, 2) co-current pressure equalization depressurization, 3) co-current blowdown, 4) evacuation, 5) counter-current pressure equalization pressurization 6) co-current feed pressurization.

Col 1	1		2	3	4		5	6
Col 2	5	6	1		2	3	4	
Col 3	4		5	6	1		2	3
Col 4	2	3	4		5	6	1	

Where the second pressure equalization step is not used to avoid contaminating the column that is being pressurized. Moreover, in this cycle the pressure equalization should be performed top-to-top, once it leads to higher recoveries when the component.

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Appendix A - Distillation columns sizing and costs

Using the Aspen Plus V9 tool for the C3 distillation column simulation and based in it is possible to dimension and calculate the associated costs.

Related with the vessel, taking into account that the first and last stages correspond to the condenser and reboiler, the values of the internal diameters and the heights of the different distillation columns were obtained directly by the simulation. These values are given in Table 16 for 50/50 % vol (C₃H₆/C₃H₈).

Firstly, it is necessary to estimate parameters as the design pressure, the thickness and weight to estimate the final cost.

For operation pressures between 10 and 1000 psi the design pressure is calculated from the operating pressure, P_d , with the follow equation:

$$P_d = \exp\{6068 \times 10^{-3} + 91615 \times 10^{-3} \times [\ln(P_0)] + 156.55 \times 10^{-5} \times [\ln(P_0)]^2\} \quad (\text{A.1})$$

It was possible to determine the thickness of each distillation column by the following equation (A.2). The value of S is 15 000 psi and the value of E is 0.85.

$$t_p = \frac{P_d \times D_i}{2 \times S \times E - 1.2 \times P_d} \quad (\text{A.2})$$

The weight, W , depends on the wall thickness of the shell and the two heads. Considering the shell and the two heads with the same thickness the weight of the shell and the two heads is given in Equation (A.3)

$$W = \pi \cdot (D_i + t_p) \cdot (L + 0.8 \cdot D_i) \cdot t_p \cdot \rho \quad (\text{A.3})$$

where the term L accounts for the cylinder length, the term $0.8 \cdot D_i$ accounts for the two heads and ρ is the density of the carbon steel (490 lb·ft⁻³).

To obtain the cost of purchasing this equipment is necessary aggregate the vessel costs, platforms and ladders cost and plate cost by equation (A.4):

$$\text{Total cost} = C_V + C_{PL} + C_T \quad (\text{A.4})$$

The vessel costs for Towers for $9000 < W < 2500000$ lb can be calculated in Equation (A.5):

$$C_V = e^{[7.0374 + 0.18255 \cdot \ln(W) + 0.02297 \cdot \ln(W)^2]} \quad (\text{A.5})$$

The cost for platforms and ladders for towers is determinate through Equation (A.6):

$$C_{PL} = 237.1 \cdot D_i \cdot 0.63316 \cdot L \cdot 0.80161 \quad (\text{A.6})$$

The cost associated with trays is represented by Equation (A.7)

$$C_T = N_T \cdot F_{NT} \cdot F_{TT} \cdot F_{TM} \cdot e^{(0.1739 \cdot D_i)} \quad (\text{A.7})$$

where N_T the number of trays and if is greater than 20, F_{NT} is 1. F_{TT} is a factor that acconts the type of tray and is equal to one for sieve tray. The factor F_{TM} depends on the column diameter and the material of construction, carbon steel.

After the purchase costs of the main process equipment is necessary estimate the utilities costs. Is necessary provide cooling water to the condenser and electricity for the reboiler. A price of 0.020\$/m³ for the cooling water and 0.10·kWh for the electricity were utilized to estimate the costs.

Thus, by knowing the value of its heat capacity and the temperature difference of the current, it is possible calculate the water flow (A.8) necessary to remove the thermal energy from the condenser. The annual cost (A.9) is based on the the Equation (A.8). The data necessary for the application of the mentioned Equations are presented in Table 16.

$$M = \frac{P_{UF}}{C_p \times \Delta T} \quad (\text{A.8})$$

$$\text{Annual cost CW} = \frac{M \cdot 3600}{\rho} \times t_{\text{operation}} \times \text{Cost}_{\text{CW}} \quad (\text{A.9})$$

Table 13 - Data for the cooling water annual cost estimation.

Cp_{water} / kJ·kg⁻¹·°C⁻¹	4.186
Te_{CW} / °C	20
Ts_{CW} / °C	30
Cost_{CW} / \$·m⁻³	0.02

As noted above, the hot utility used was medium pressure water vapor, which is heated by the combustion of natural gas. Thus, assuming a global efficiency of 90 % for the transfer of heat between the combustion of natural gas and water, the heat output from the combustion of natural gas was determined. Subsequently, given the annual operating time, the lower calorific value of the natural gas and its cost, annual cost of the hot utility can be obtained. The data required to perform the referred calculations are shown in Table 14.

$$P_{\text{GN}} = P_{\text{UQ}} / \eta \quad (\text{A.10})$$

$$\text{Annual cost HU} = \frac{P_{\text{GN}} \cdot 3600}{\text{PCI}_{\text{GN}}} \cdot t_{\text{operation}} \cdot \text{Cost}_{\text{GN}} \quad (\text{A.11})$$

Table 14 - Data needed to determine the steam cost.

PCI_{GN} (kJ·m⁻³)	33 488
Cost_{GN} / (\$·m⁻³)	0.45
Operation time (h)	8 000

Table 15 – Datasheet for the column with Feed stream (50%propylene/50%propane)

Feed stream (50% /50% propane-propylene)			
Flow / tons·h ⁻¹	50.194	Temperatura / K	288
		Pressure / bar	18
Characteristics			
Number of trays	202	Reflux ratio	16.1
Type of tray	Sieve	Light key	Propylene
Feed tray	144	Heavy key	Propane
Tray disntance / m	0.2501	Ratio D/F	0.51
Sizing			
Material	Carbon steel	higt / m	123.14
Diameter / m	4.85	Thickness / cm	6.09
W / kg	936 950	P ₀ / bar	1
S / psi	15 000	E	0.85
Product stream			
Top		bottom	
Flow /tons·h ⁻¹	25.05	Flow/ tons·h ⁻¹	25.144
Temperature / K	317.2	Temperature / K	308.9
PresSURE / bar	18	Pressure / bar	18
Purity / %	99.6	Purity / %	99.8

Appendix B - Scale up and cost for the VPSA unit

In the development of a project it is fundamental to analyse certain indicators in order to evaluate the feasibility of the project. Therefore, it was necessary to proceed with the survey of numerous costs, for example, the cost of investment, the cost of equipment, costs of operation, among others. Next, the methodology used to carry out the economic evaluation of this project is presented.

The capital cost Equations were provided by Turton calculate as the PVSA unit is incorporated in a chemical plant. To determine the size of the column, firstly is necessary calculate the volume of one column in m³ shown in Equation (B.1)

$$V_{bed,T} = \frac{F_{feed} \times y_{A,feed} \times Rec_A \times Prod_A}{\rho_p \times (1 - \varepsilon_b)} \quad (B.1)$$

Where $F_{feed,T}$ is the specified feed flow rate in mol·h⁻¹, $y_{A,feed}$ the propylene feed composition, Rec_A the propylene recovery and $Prod_A$ the propylene productivity.

The purchased cost of 1 column is given by Equation (B.2).

$$\log_{10} C_{p,col}^0 = 3.4974 + 0.4485 \times \log_{10} V_{bed,T} + 0.1074 \times (\log_{10} V_{bed,T})^2 \quad (B.2)$$

The bare module cost is given by Equation (B.3) and the grassroots cost is obtained by Equation (B.4).

$$C_{BM,col} = C_{p,col}^0 \times (2.25 + 1.82 \times F_{p,col}^0) \quad (B.3)$$

$$C_{GR,col} = (1.18 \times C_{BM,col} + 0.5 C_{p,col}^0 \times (2.25 + 1.82) \times N_T \times \frac{CEPCI}{397}) \quad (B.4)$$

From the two last Equations, $C_{BM,col}$ the bare module cost of one column, is the pressure factor and $C_{GR,col}$ is the grassroots cost of all the columns.

Each pump can only evacuate one column each time and is needed to have in consideration the waiting time between evacuations because the pump still on.

Purchased cost, bare module cost and grassroots cost of one the vacuum pump are determinate by the Equations (B.5), (B.6) and (B.7) respectively.

$$C_{Ev}^0 = 7185.9 + 6.428 \times F_{Ev} \quad (B.5)$$

$$C_{BM,ev} = C_{ev}^0 \times 3.4 \quad (B.6)$$

$$C_{GR,Ev} = 1.68 \times C_{BM,col} \times \frac{CEPCI}{397} \quad (B.7)$$

From the two last Equations, $C_{BM,Ev}$ is the bare module cost of one column, $C_{BM,ev}$ is the pressure factor and $C_{GR,col}$ is the grassroots cos of all the columns. The proylene recovery is less than 100% so is necessary study the lost propylene impact in the raffinate product. The annual LOC can be calculated accordingly Equation (B.8)

$$LOC_{Annual} = LOC_{cost} \times 220\,000 - Rec_A) \quad (B.8)$$