



Adsorption properties and process performances relationship

Application to the screening of adsorbents for xylene isomers separation

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Thesis to obtain the Master of Science Degree in

Chemical Engineering

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October 2014

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Acknowledgements

First of all, I would like to thank to the department of Catalysis and Separation, without their support, sympathy and assistance this work would not be accomplished. For that, I would like to express my gratitude.

To Catherine Laroche and Julien Grandjean for their knowledge and guidance during my internship, it was due to their assistance and support that I was able to learn so much in so little time. I would also like to express my gratitude to Eduardo Filipe, his tranquility and friendliness was a precious help in the days that I must needed,

I would also want to express my deepest gratitude to Filipa Ribeiro, not only because of her help during all my internship in IFP but also for always believing in me during my last years in college.

I would also like to thank to everyone who accompanied me during these six months, namely Marisa, Leonel, Pedro, Matthieu, Yoldes and Remi for being there for me in every second of this experience. The period of time was short but I will always remember them. I would like to thank especially to my housemate, his company and champion attitude is something that I am going to value forever.

To Renato and Ruben, because what began as a professional relationship become one of the most important relationships in my life. I would like to express my deepest gratitude to Leonor, not only for being one of the best persons that I know, but also for being the person that believed in me in the moment that I must needed help.

To Francisco, Inês, Mariana, Diogo and Ana, the friends with whom I spent specials moments in my life and that I know I can always trust in my entire life. A special thanks to Chico, Rafael and Rita, not because they are my friends, but because they are my second family and I could not ask for better people to continue sharing my life with.

I dedicate my biggest gratitude to my family, especially to my parents Antónia and Luís, my brother Tiago and my two other parents Teresa and Luís. I couldn't ask for a better environment to grow, everything I am is due to their support, wisdom and love, thank you for everything. I would also like to thank Zita, I know she wanted more than anyone to share these moments with me and the rest of the family.

Finally, I would like to thank to Carolina, words are not enough to describe her importance in my life. Her presence, support, belief and humor make me a better person. Thank you for all your support.

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Resumo

Este trabalho tem como objectivo estudar o comportamento de diferentes adsorventes preparados experimentalmente no processo de separação de *para*-xileno utilizando condições representativas do processo industrial de modo a fornecer informações sobre o desempenho destes sólidos quando implementados no processo.

Para uma primeira análise destes adsorventes, é realizada uma classificação com base nas suas selectividades obtidas experimentalmente, o que permite observar, entre outras coisas, os compostos com maior afinidade para cada sólido e correspondente força de adsorção do desadsorvente.

As selectividade críticas dos adsorventes *para*-selectivos em dois pontos experimentais são analisados e comparadas com as obtidas para um adsorvente referência de modo a averiguar quais os sólidos que apresentam o maior potencial para serem implementados industrialmente. Uma primeira previsão do desempenho do processo resultante da utilização destes sólidos é obtida através de uma abordagem teórica baseada apenas em considerações termodinâmicas.

Por último, são realizadas simulações para os adsorventes testados com as características termodinâmicas mais atraentes e para um sólido industrial. Para tal são utilizados de dois modelos termodinâmicos simplificados de modo a calcular as performances do processo obtidas com estes sólidos. Verificou-se que o uso dos adsorventes FAU 1 e FAU 2 resulta num desempenho superior ao obtido actualmente a nível industrial. Como tal, ambos os sólidos aparentam ser bons candidatos para substituir o adsorvente industrial utilizado hoje em dia, sendo FAU 1 o sólido que resulta nos valores mais atraentes de produtividade e consumo de desadsorvente.

Palavras-chave: *para*-xileno; adsorção; Faujasite; Leite móvel simulado; Optimização.

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Abstract

This work aims to study the adsorption behavior of different adsorbents prepared experimentally in the *para*-xylene separation process under conditions representative of the industrial process to provide insight into the performances of these materials when they are implemented in the process.

For a first analysis of these solids, it is performed a classification based on their experimental selectivities values, which allows to observe, among other things, the affinity of the adsorbents for the different isomers and the corresponding adsorption strength of the desorbent.

Critical selectivities of the *para*-selective adsorbents in two points of the process are then analyzed and compared to those obtained for a reference adsorbent to verify which solids present the highest potential to be implemented industrially. A first prediction of the process performances obtained with the use of these solids is obtained through a theoretical approach based only on thermodynamic considerations.

Simulations are performed for the tested adsorbents with the most appealing thermodynamic characteristics and also for an industrial solid with the use of two simplified thermodynamic models in order to calculate the process performances obtained for these adsorbents. It was found that the use of the tested adsorbents FAU 1 and FAU 2 result in better performances than those obtained currently in the industrial process. Thus, both solids appear to be good candidates to replace the industrial adsorbent used nowadays, being FAU 1 the solid which results in the most satisfying values of productivity and desorbent consumption.

Keywords: *para*-xylene; adsorption; Faujasite; Simulated Moving Bed; Optimization.

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Nomenclature and abbreviations

Abbreviations

- CDS – Carbonated Soft Drinks
- D – Desorbent injection
- DMT – Dimethyl Terephthalate
- DS – Adsorption strength of the desorbent
- E – Extract outlet
- EB – Ethylbenzene
- F – Feed injection
- FAU – Faujasite
- LDF – Linear driving force
- LOI – Loss Of Ignition
- MX – *meta*-xylene
- NC – Number of components
- OX – *ortho*-xylene
- PDEB – *para*-diethylbenzene
- PET – Polyethylene terephthalate
- PTA – Purified Terephthalate Acid
- PVC – Polyvinyl chloride
- PX – *para*-xylene
- R – Raffinate outlet
- SMB – Simulated Moving Bed
- TMB – True Moving Bed

Nomenclature

- A – SMB column cross-section area (m^2)
- b_i – Langmuir adsorption equilibrium constant (m^3/kg)
- b_0 – Pre-exponential factor
- C_i – Liquid phase concentration of component i (kg/m^3)
- $C_{i,j}^{\text{in}}$ – Liquid phase concentration of component i at the inlet of zone j (kg/m^3)
- $C_{i,j}^{\text{out}}$ – Liquid phase concentration of component i at the outlet of zone j (kg/m^3)
- D_{Lj} – Axial dispersion coefficient in zone j (m^2/s)
- K_a – Dimensionless Henry's Law adsorption equilibrium constant
- L_c – Column length (m)

- P_E – Purity of the extract (%)
- PR – Productivity (kg PX/h m³)
- q_i – Adsorbed phase concentration of component i (kg/kg)
- q_i^* – Adsorbed phase saturation of component i (kg/kg)
- $q_{i,j}$ – Adsorbed phase concentration of component i in zone j (kg/kg)
- Q_j – Liquid phase flow rate in zone j of the SMB (m³/s)
- Q_j^* – Liquid phase flow rate in zone j of the SMB (m³/s)
- Q_s – Solid phase flow rate in zone j (m³/s)
- R – Gas constant (J.K⁻¹.mol⁻¹)
- R_E – Recovery of the extract (%)
- sk – Strong-key component
- t – time (s)
- T – Temperature (K)
- u_s – Solid phase interstitial velocity (m/s)
- v_j – Liquid phase interstitial velocity in zone j of the SMB (m/s)
- v_j^* – Liquid phase interstitial velocity in zone j of the TMB (m/s)
- V_T – Total volume of the adsorber (m³)
- wk – Weak-key component
- $ww+1$ – Weak component
- ww – Weakest component
- X – Adsorbed phase
- Y – Liquid phase
- z – Axial coordinate (m)

Subscripts and superscripts

- i – Adsorbable components ($i=PX, MX, OX, MOX, EB, PDEB$)
- j – Number of zone ($j=1, 2, 3, 4$)

Greek letters and symbols

- α – Selectivity
- ε – Porosity
- $-\Delta H$ – Limiting heat of adsorption at low coverage (J/mol)
- ρ_P – Apparent particle density (kg/m³)
- Ω – Reduced flow rate
- γ_j – Ratio between the liquid and solid interstitial velocities in zone j

1. Introduction

The demand of mixed xylenes, the second most important aromatic products in terms of world consumption, has suffered a significant growth over the years due to the constant increase of *para*-xylene consumption, result of the expansion in the polyethylene terephthalate (PET) market, driven by the demand in polyesters fibers and by the increasing application in carbonated soft drinks (CDS) packaging as well as rising consumption of packaged, frozen and other processed foods.

The sources used for xylene production (catalytic reformat, pyrolysis gasoline and toluene disproportionation/transalkylation) contain a mixture where *para*-xylene is found along with the remaining isomers and ethylbenzene, making it necessary to purify this compound through a separation process. Due to the proximity of boiling points of these aromatic compounds, it is not possible to separate them by conventional distillation. As such, three different methods to separate *para*-xylene from the remaining compounds are used industrially: Crystallization, adsorption and a hybrid crystallization/adsorption process.

Since commercialized, the adsorption process of Simulated Moving Bed (SMB) chromatography became the world's most used technology for *para*-xylene recovery. The SMB is a continuous countercurrent process which exploits the differences in affinity of a molecular sieve for the different xylenes. The countercurrent flow of solid and liquid phases is simulated by the periodic shifting of the inlet and outlet streams. In this process, the adsorbents used are usually zeolite of X or Y type containing exchangeable cations, which give specific adsorption properties to the material. The three principal industrial processes for *para*-xylene separation based on this technology are IFP's Eluxyl, UOP's Parex and Toray's Aromax.

The purpose of this work is to analyze the adsorption behavior of the different adsorbents prepared experimentally under conditions representative of industrial processes to provide insight into the performances of these materials when they are implemented in the process. For a first analysis of these solids, it is performed a classification based on their experimental values of selectivity.

Critical selectivities of the *para*-selective adsorbents are then analyzed and compared to those obtained for a reference adsorbent as to verify which solids have the highest potential to be implemented industrially. A first prediction of the process performances obtained for these solids is then calculated using a theoretical approach. Two simplified thermodynamic models with the objective of predicting the selectivities of the adsorbents along the SMB column are created.

Finally, simulations are performed for the industrial and tested adsorbents with highest potential to validate the simplified thermodynamic models and also to verify if the use of the adsorbents tested experimentally result in performances that justify their industrial implementation.

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2. Bibliographical study

This chapter presents the economic and technical background of *para*-xylene production. As such, the properties, applications and market analysis of the xylene isomers are presented. *para*-xylene production and separation processes are described in this chapter, with greater detail for the adsorption separation process through the Simulated Moving Bed technology. The basic notions on the thermodynamics of xylene adsorption on zeolites are also presented. Lastly, the modeling and optimization of a Simulated Moving Bed unit for the *para*-xylene separation is covered.

2.1 – Physical properties of C₈ aromatics

The aromatic compounds with the general formula C₈H₁₀ consists of a mixture of isomers with a boiling point range of 135-145°C, which are three isomeric dimethylbenzenes (*ortho*, *meta* and *para*), known as xylenes, and ethylbenzene (1). Their molecular structures are shown in Figure 1.

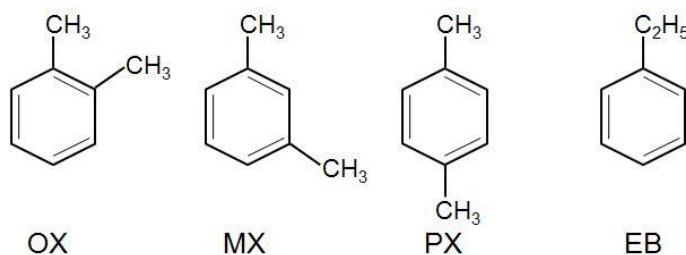


Figure 1 – Molecular structure of the different C₈H₁₀ aromatics

Due to their similar molecular structures, xylene isomers and ethylbenzene present many similar physical properties. The proximity of the boiling points of the mixed xylenes does not allow the separation of the isomers by conventional distillation, except for *ortho*-xylene, due to the 5°C difference between its boiling point and the next closest boiling isomer. Instead, the difference between the adsorption characteristics and freezing points are used commercially for the separation of these compounds (2), as it will be described further. It is also important to mention that these isomeric xylenes and ethylbenzene form azeotropic mixtures with water and different organic compounds (1).

The main physical properties of these compounds are presented in Table 1.

Table 1 - Physical properties for C₈ Aromatic compounds (2)

Property	<i>Ortho</i> -xylene	<i>Meta</i> -xylene	<i>Para</i> -xylene	Ethylbenzene
Molecular weight	116,2			
Boiling point (°C)	144,4	139,1	138,4	136,2
Freezing point (°C)	-25,2	-47,9	13,3	-95,0
Density at 25°C (kg/m ³)	861,0	864,2	880,2	867,1

2.2 – Applications and global market

Mixed xylenes are the second most important aromatic products in terms of world consumption for chemical manufacture, ranking only behind benzene and ahead of toluene (2). The production of *para*-xylene represents the major use of this mixture with 78% of total world consumption in 2011. The remaining percentage refers to the production of *ortho*-xylene, *meta*-xylene and for solvent applications, as can be seen in Figure 2.

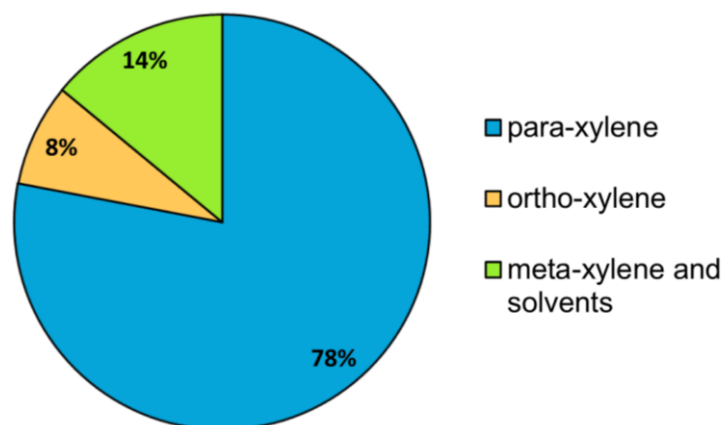


Figure 2 - Mixed xylenes demand structure (2011) (3)

Most of the separated isomers are oxidized to their corresponding carboxylic acid or anhydride (terephthalic acid for *para*-xylene, phthalic anhydride for *ortho*-xylene and isophthalic acid for *meta*-xylene). Terephthalic acid is used primarily to produce polyethylene terephthalate used in synthetic fibers, beverage bottles and food containers by polycondensation with ethylene glycol. Phthalic anhydride is used mainly in the production of PVC plasticizer and isophthalic acid as a copolymerizing monomer in the production of soft drink bottles (4).

As previously mentioned, *para*-xylene is the most widely used isomer. Around 97% of this compound is consumed in the polyester chain, via one of two intermediates, purified terephthalic acid (PTA) or dimethyl terephthalate (DMT), mainly in the production of polyethylene terephthalate (PET) – for fiber (65%), and for PET bottle resin (27%) and the remaining 8% for film and plastic end uses (5), (6). A small amount of this compound is used as a solvent and for the production of herbicides and *di*-*para*-xylene (5). The *para*-xylene applications structure can be seen in Figure 3.

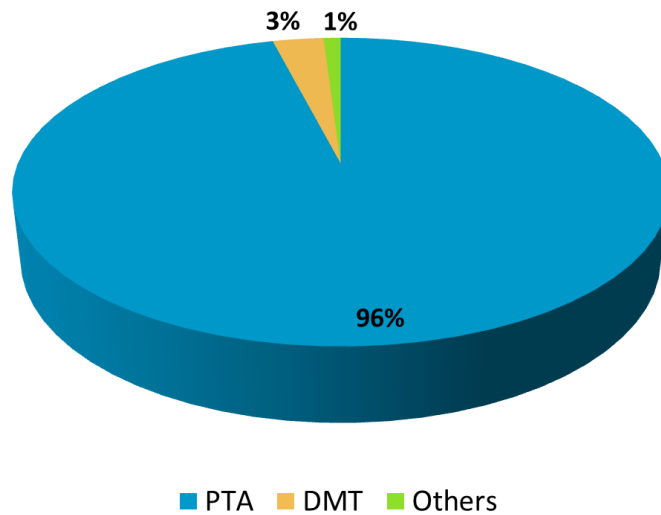


Figure 3 - *para*-xylene applications structure (2009) (6)

The value chain of *para*-xylene, from the original raw material to the final product can be observed in Figure 4.



Figure 4 - Value chain of *para*-xylene

Through the applications structure and the value chain of *para*-xylene it is possible to observe that the production of this compound is highly correlated with the market of polyesters through the use of PTA and DMT as intermediates.

The evolution of the worldwide *para*-xylene capacities, from 2011 to 2017 can be seen in Figure 5

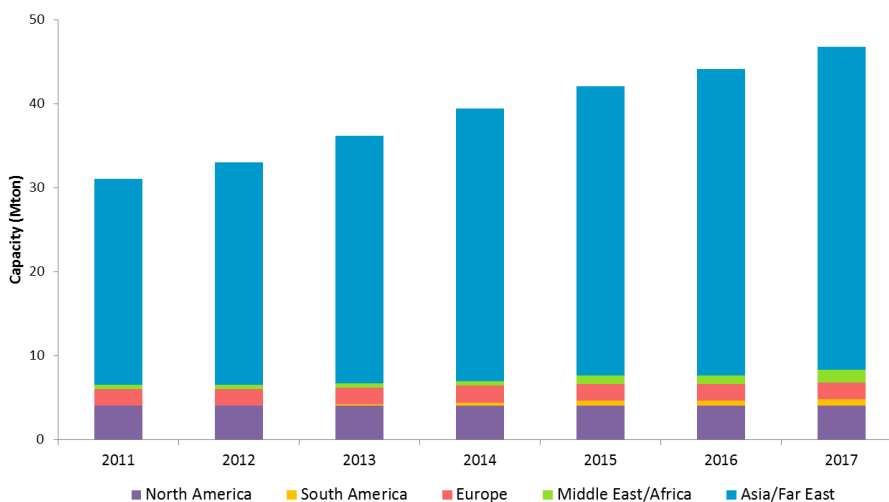


Figure 5 - Evolution of the worldwide *para*-xylene capacities from 2011 to 2017 (7)

The worldwide capacity of *para*-xylene in 2013 was of 36 million tons, with an annual forecast growth of 7% up to 2017 (7). The Asian market is the biggest responsible for this increase. Due to its large population, growing demand for polyester fiber and polyester resins, and rapidly growing polyester industry, this continent is now the highest producer and consumer of *para*-xylene.

In the next three years, almost 80% of new production capacities added worldwide are expected to be located in Asia. Even with this tremendous growth of capacity, this continent will continue to be a major importer of *para*-xylene (4). Other regions, such as Middle East, will have a faster capacity growth until 2017, but from a much smaller base.

2.3 Raw materials

The only natural source of xylenes is petroleum (2). The concentration of the isomers in the mentioned source depends on the extraction location and the geological age of the crude. Since the concentrations of mixed xylenes in petroleum is never higher than 1,5%, it is not economically feasible to separate these products directly from crude oil. Instead, naphtha is first subjected to either catalytic or thermal treatment with the objective of increasing the content of these aromatic compounds. After these conversion processes, it is then possible to separate the xylene isomers in an economical feasible way (1).

The two most widely used raw materials used for the production of mixed xylenes are *reformate* and *pyrolysis gasoline*, as can be seen in Figure 6.

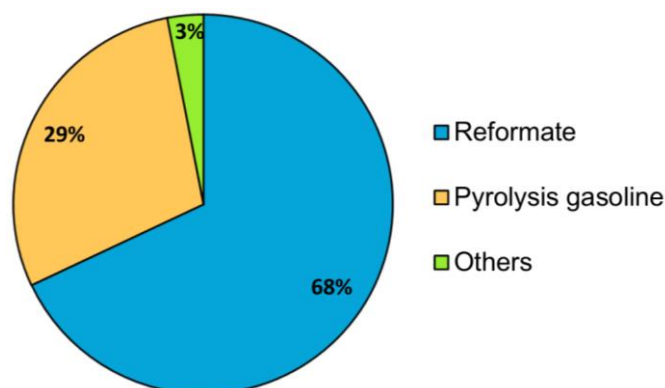


Figure 6 - World mixed xylenes sources (2009) (8)

In the catalytic reforming process, low octane naphtha cut is converted into high-octane aromatics, including benzene, toluene and the mixed xylenes through the contact with a catalyst at elevated temperature and pressure (9). The amount of xylenes found in the catalytic reformate depends on the fraction and type of crude oil, operation conditions and the catalyst used (2).

Pyrolysis gasoline, a mixture rich in aromatic compounds, is the by-product of ethylene and propylene production by thermal cracking of naphtha. After an initial hydrogenation, *pyrolysis gasoline* is sent to a second stage hydrogenation in which olefins are saturated, organic sulfur forms hydrogen sulfur, combined nitrogen is converted to ammonia and oxygenated compounds are reduced to hydrocarbons and water (2). The aromatic content of *pyrolysis gasoline* is extremely affected by the raw materials and the operation conditions used (1).

The aromatic composition in these two raw materials for the production of mixed xylenes is considerably different. While *pyrolysis gasoline* has a higher benzene content, *reformate* contains a higher percentage of xylenes. The average compositions of these two raw materials for the production of mixed xylenes are presented in Table 2.

Table 2 - Typical Composition (wt. %) of reformate and pyrolysis gasoline (8)

Component	Reformate	Pyrolysis gasoline
Benzene	3	30
Toluene	13	20
Xylenes	18	4
Ethylbenzene	5	3
C ₉ ⁺ aromatics	16	3
Total aromatics	55	60
Naphthenes	Low	High
Olefins	High	High
Paraffins	High	Low
Sulfur	< 1 ppm wt.	Up to 1000 ppm wt.

Another way of producing additional mixed xylenes is made through the reactions of disproportionation and transalkylation of toluene and heavy aromatics, components that can be found in either raw materials and possesses no market value (9).

The disproportionation reaction (Figure 7) results in the formation of mixed xylenes and benzene in the proportion of 1:1 from two molecules of toluene:

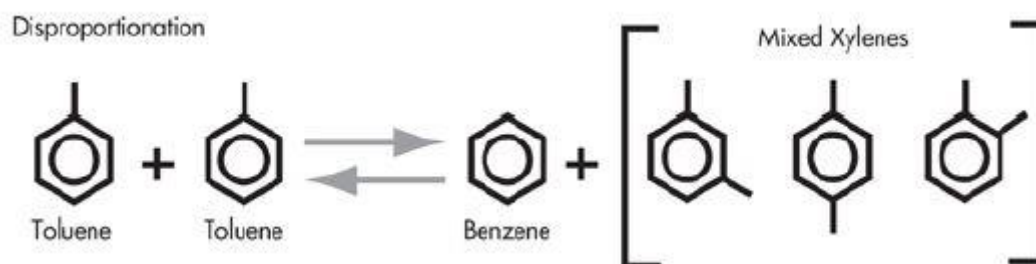


Figure 7 - Disproportionation of Toluene (10)

Transalkylation reaction (Figure 8) is the conversion of toluene and heavy aromatics (C₉ aromatics) to mixed xylenes through the migration of methyl groups between these methyl-substituted aromatics (9):

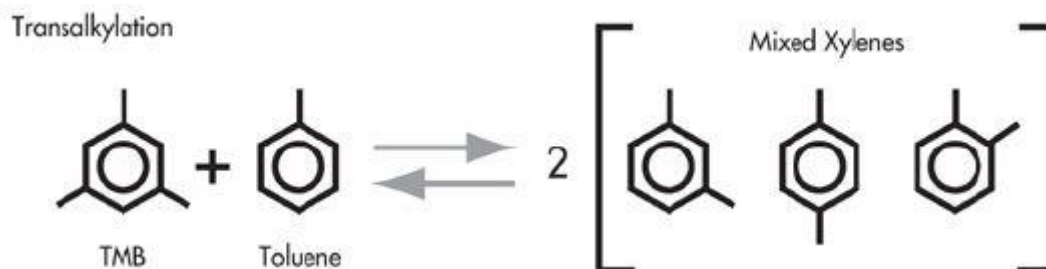


Figure 8 - Transalkylation of Toluene (10)

With the exception of xylene obtained by disproportionation of toluene, the isomeric xylenes and ethylbenzene are always produced as a mixture in all production processes. However, the relative proportions of the C₈ isomers often differ considerably (1).

2.4 Para-xylene production technology

The production of mixed xylenes is made in aromatics complexes, which results of a combination of process units that are used to convert *reformate* and/or *pyrolysis gasoline* into the following petrochemical products: benzene, toluene and xylenes (BTX) (9).

Aromatic complexes have many different configurations, depending on the desired petrochemical to be obtained. Figure 9 presents an aromatic complex configured for maximizing the production of *para*-xylene.

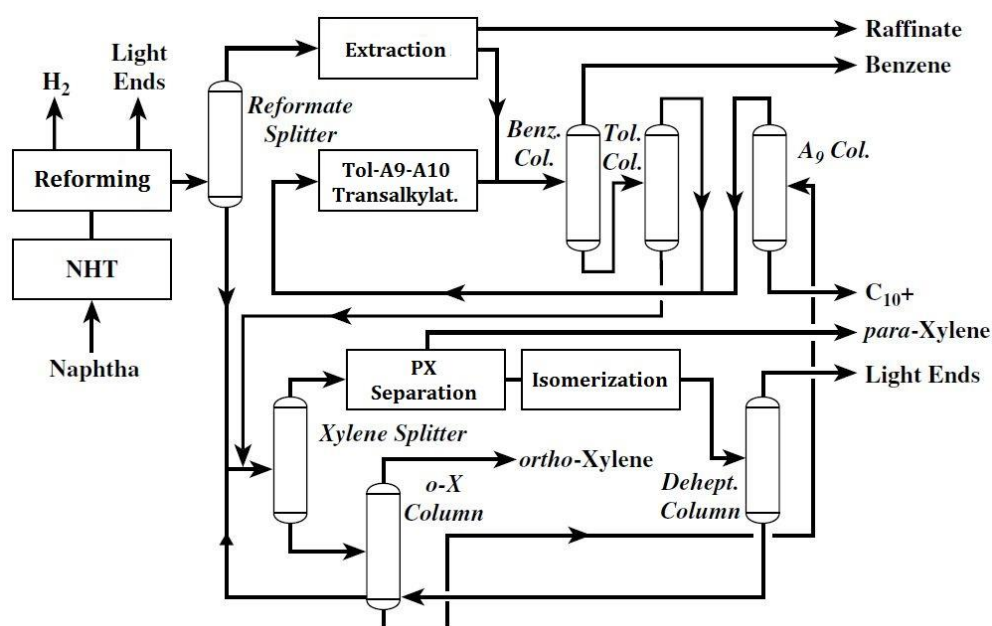


Figure 9 - Aromatics complex configuration for maximizing the productivity of *para*-xylene [Adapted from (9)]

An aromatic complex presents four distinct critical zones: Separation of light aromatics (benzene and toluene); toluene/heavy aromatics conversion; separation and isomerization of mixed xylenes.

Naphtha is used as the feedstock in this type of aromatic complex. Firstly it is fed to the reforming unit where is converted to a mixture rich in aromatics (*reformate*). *Pyrolysis gasoline* can also be added as feedstock to this mixture, which is then separated in light and heavy aromatics by classic distillation (1).

The extraction process is used in order to separate benzene and toluene from light hydrocarbons. While benzene is recovered as one of the main products of the complex, toluene is send to a disproportionation/transalkylation unit along with heavy aromatics in order to produce additional mixed xylenes and benzene.

In the separation/isomerization loop, mixed xylenes are first send to the separation unit which has the objective of isolating *para*-xylene from the mixed xylenes. The *para*-xylene depleted mixture is send to the isomerization unit where the thermodynamic equilibrium between the isomers is restored (see Table 3). This stream is then recycled to the *para*-xylene separation unit feed (9).

Table 3 – Thermodynamic equilibrium between C₈ aromatics at the isomerization unit temperature (9)

Thermodynamic equilibrium between C₈ aromatics (% wt.)			
<i>ortho</i> -xylene	<i>meta</i> -xylene	<i>para</i> -xylene	ethylbenzene
17	47	19	17

Currently, the market of licensors for process units in an aromatic complexes focuses on three major companies: Axens, Universal Oil Products (UOP) and Exxon Mobil Corporation (Exxon). While UOP license an integrated process for aromatics production, Axens and Exxon license individual processes and equipment, being that the overall process can be obtained through their alliance, ParamaX (11) (12) and (13).

2.5 – Separation of *para*-xylene

The separation of organic compounds in a refinery is made usually through fractional distillation, which is based on the difference between the components boiling points. However, as previously mentioned, it is not possible to conduct the separation between the xylene isomers through conventional distillation due to the close boiling points of these compounds (2). It is then necessary to use other physical characteristics of these isomers in order to carry out their separation.

There are essentially three methods used commercially to separate and produce high purity *para*-xylene (9):

- Crystallization;
- Adsorption – Through the Simulated Moving Bed (SMB) process;
- Hybrid Crystallization/Adsorption.

2.5.1 – Crystallization process

A low temperature fractional crystallization was the first and for several years the only commercial technology used for *para*-xylene separation from the remaining isomers. In this process, it is taken advantage of the higher freezing point of *para*-xylene in comparison with the other isomers. Thus, upon cooling, *para*-xylene isomer precipitates as a crystalline solid. With further cooling, the eutectic point is reached, resulting in the precipitation of the remaining isomers in a form of a crystalline solid. Commercially, this crystallization process is carried out at a temperature slightly above the one of the eutectic point. With temperatures above this point, *para*-xylene is still soluble in the liquid solution of the remaining isomers, which restricts *para*-xylene recovery to about 65% per pass (9).

The obtained crystals of *para*-xylene are usually produced in two or more stages of crystallization, separated by centrifuges. In the first stage, usually operated at the lowest temperature, it is obtained a cake with a purity of 80-90% (2). In the second stage, the crystals are reslurried with a high purity *para*-xylene stream obtained from a later stage of purification. Usually, a second stage of centrifugation is sufficient to obtain *para*-xylene purity higher than 99% (2). The solids crystals are typically separated from the mother liquor by filtration or centrifugation.

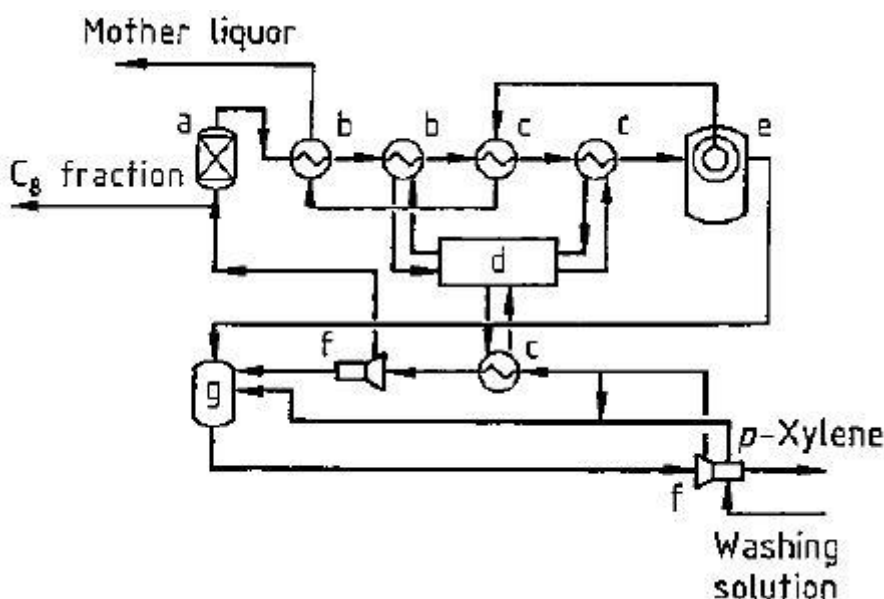


Figure 10 - *para*-xylene crystallization by indirect refrigeration. a) Drier; b) Pre-cooler; c) Scraped-surface crystallizer; d) Refrigeration plant; e) Filter; f) Centrifuge; g) Mixer (1)

A number of crystallization processes have been commercialized over the years. The more common are those developed by Chevron, Krupp, Amoco, ARCO, Phillips and Maruzen (14).

2.5.2 – Adsorption process

Since 1971, the year UOP commercialized the first adsorption process for xylene isomers separation, Simulated Moving Bed (SMB) chromatography became the world's most used technology for *para*-xylene recovery. The principal advantage of the continuous countercurrent separation technology is the ability to recover more than 97% percent of *para*-xylene in the feed per pass, while the crystallization process can't surpass a recovery of 65% due to the eutectic composition limit (9).

In this process, separation is accomplished by exploiting the differences in affinity of the adsorbent for *para*-xylene in comparison with the remaining isomers on faujasite-type zeolites. The adsorbed *para*-xylene is then removed from the adsorbent by displacement with a desorbent. The *para*-xylene 99% pure and a mixture constituted by the remaining isomers are withdrawn, respectively, by the extract and raffinate outlets (15).

The Simulated Moving Bed (SMB) is a continuous chromatographic countercurrent process that consists of a set of columns connected in series. The countercurrent flow between the solid and liquid phases is simulated by the periodic shift of the inlet and outlet streams in the direction of the fluid flow (14).

Ideally, an adsorption process would be implemented as a real countercurrent process between the liquid and solid flow rates. However, there are several difficulties associated with the process that made it impossible to implement commercially, such as mechanical erosion of the adsorbent and problems ensuring a truly uniform flows of both liquid and solid phases in large diameter beds (2). As such, UOP decided to commercialize a process that presented the same results by holding the beds stationary, but periodically moving the positions of the various liquid streams that enter and leave the process. Through this movement it is then possible to simulate the countercurrent movement of the two phases.

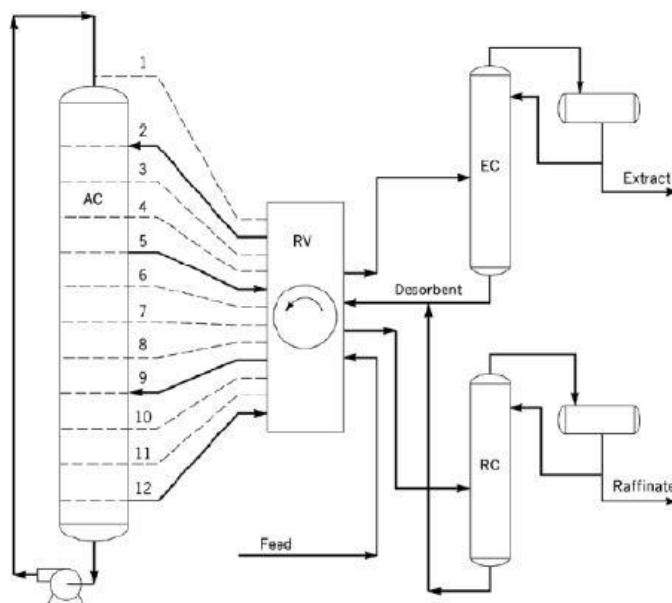


Figure 11 - Parex Process (AC-Adsorbent chamber; RV- Rotary Valve; EC - Extract Column; RC - Raffinate Column; Lines: 2 - Desorbent; 5 - Extract; 9 - Feed; 12 - Raffinate) (15)

The Parex process, the first simulated moving bed adsorption technology, was commercialized by UOP in 1971 (16). This process uses a rotary valve which periodically changes the positions of the inlet and outlet lines along the beds, as can be seen in Figure 11.

After the implementation of this process, other major companies commercialized their own Simulated Moving Bed technologies. In the early 1970s, Toray Industries developed the Aromax Process. In this technology, instead of a rotary valve, a sequence of specially designed on/off valves is used to move the inlet and outlet ports around the bed. With this process it is obtained *para*-xylene with a purity of 99,5% and a yield per pass higher than 90% (2).

In 1994, IFP commercialized the Eluxyl process. In this technology, individual on/off valves controlled by a microprocessor are used to simulate the movement of the adsorbent. The concentration profiles along the column are monitored by online Raman spectroscopy (14). With this process it is possible to obtain 99,9% *para*-xylene purity and a yield per pass of 97% (17).

The year of commercialization, number of units in operation and the respective capacities of Parex, Aromax and Eluxyl can be seen in Table 4.

Table 4 - Commercialization data of different SMB technology used for *para*-xylene separation

Technology	Year of commercialization	Number of units	Unit capacity (MTA of <i>para</i> -xylene)
UOP Parex (16)	1971	88	21,000-1,600,000
Toray Aromax (14)	1973	2	200,000
IFP Eluxyl (14), (18)	1995	20	180,000-750,000

2.5.3 – Hybrid Crystallization/Adsorption process

In 1994, the alliance between IFP and Chevron announced the development of a hybrid process of the Eluxyl process, which mixed the best features of adsorption and crystallization. In this process, a 90-95% pure *para*-xylene is produced through the Simulated Moving Bed and is then further purified in a single-stage crystallizer, being obtained in the end a *para*-xylene with a ultrahigh purity (99,9+%) (2). Due to a production of only 90-95% pure *para*-xylene in the Simulated Moving Bed, it is required a lower solvent to feed ration in comparison with the production of high purity *para*-xylene through the same process. However, economical studies indicate that this process configuration does not provide performances or cost advantages in comparison with the SMB process (9). So far, only three hybrid processes have been commercialized (14).

2.6 – Thermodynamics of xylene adsorption on zeolites

The primary requirement for an economic separation is an adsorbent with sufficiently high selectivity, capacity and lifetime. For practical processes, the choice of adsorbents is restricted to microporous adsorbents with pore diameters between a few Angstroms to a few tens of Angstroms (19). This choice is usually made between the traditional microporous adsorbents like silica gel, activated alumina and activated carbon and zeolites.

The process of *para*-xylene separation from the remaining isomers through selective adsorption uses X or Y zeolites modified by cation exchange (alkaline and alkaline-earth cations) (20).

2.6.1 – Zeolites

Zeolites are natural alumino-silicate minerals that are characterized by cage-like structures, high surface areas, and efficient cation-exchange capacities (21). Chemically, they are represented by the following empirical formula:



where y varies between 2 and 200, n is the cation valence and w represents the water contained in the voids of the zeolite (22). Structurally, zeolites are complex, crystalline inorganic polymers with a framework that consists of an assemblage of SiO_4 and AlO_4 joined together in various regular arrangements by the sharing of oxygen ions to form an open crystal frame containing pores of molecular dimensions into which molecules can penetrate. The micropore structure of a zeolite is defined by the crystal frame and therefore, it is precisely uniform with no distribution of pore size. This is the main characteristic of the zeolite that distinguishes it from the traditional microporous adsorbents.

Considering the zeolites frameworks, the primary structural units, SiO_4 or AlO_4 tetrahedra, are assembled into secondary building units, which are themselves polyhedral made up of several SiO_4 and AlO_4 tetrahedra.

Each aluminum atom in the framework introduces one negative charge on the framework that is balanced by an exchangeable cation. These cations are located at preferred sites within the framework and have an important role in determining the adsorptive properties (19).

In a zeolite, the Si/Al ratio may reach a minimum of 1, depending on the solid, however, this ratio has no upper limit. The adsorption properties present a transition between the aluminum-rich sieves, which have a high affinity for water and other polar molecules, and the silica-rich sieves, that are hydrophobic and have a preference affinity to *n*-paraffins rather than water. This transition from hydrophilic to hydrophobic zeolites occurs at a ratio value between 8 and 10 (19). Each set of framework structure, exchanged cation and Si/Al ratio results in a zeolite with different adsorptive properties.

There are numerous naturally occurring and synthetic zeolites, each with a unique structure. From this point on, this chapter is going to focus only on the most used zeolites for *para*-xylene separation, zeolites X and Y.

The framework structure of these zeolites, better known as Faujasite X and Y, present a cubic symmetry (23), as can be seen in Figure 12. It is built of sodalite cages linked together through hexagonal prisms. The large cavities created by this arrangement are named “supercage”. Each supercage is connected to four sodalite cages through a six membered-ring window. In total, there are eight supercages and eight sodalite cages per unit cell.

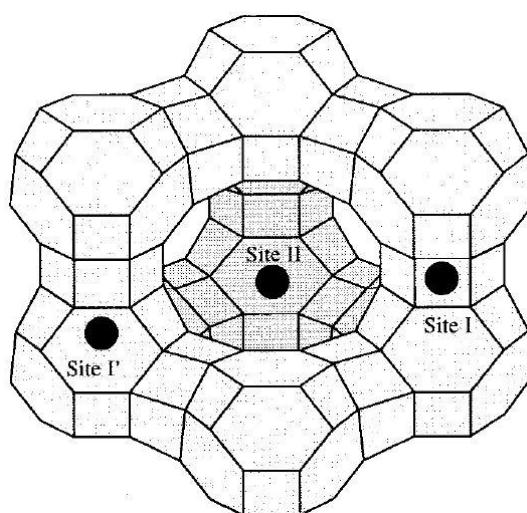


Figure 12 - Structure and cationic sites of the faujasite zeolites (23)

The separation of *para*-xylene is not a result of steric selectivity due to the size of the micropore, but a consequence of an energetic selectivity, which depends on the adsorption affinity of the adsorbent for each isomer found in the mixture (14). Therefore, the nature of the exchanged

cation, their size and location in the zeolite has a major influence in the interaction between the solid and the molecules.

Large aromatic molecules, such as xylene isomers, can only enter in supercages, while small molecules such as water can be adsorbed in both supercages and sodalite cages. The adsorption sites of both water and xylene molecules are mainly located near the exchanged cations. In experiences made for Faujasite BaX (23), it was verified that the barium cations are normally localized in three types of sites, identified in Figure 12. Site *I* is situated at the center of the hexagonal prism, site *I'* located in the sodalite cage in front of the six-ring window connected to the hexagonal prism and site *II* is found in the supercage in front of the six-ring connected to the sodalite cage. It was found that the adsorption sites for *para* and *meta*-xylene are located in site *II*, near to the Barium cation. Regarding *para*-xylene, it was also found an extra, less favorable non-cationic adsorption site, located in the plane of the 12-ring window (23).

The difference between Faujasite X and Y sieves lies in the Si/Al ratio that varies between 1 and 1,5 for X and between 1,5 and 3 for Y. This ratio influences the number of exchanged univalent cations found in the zeolite, which varies from 10 to 12 per cage in Faujasite X to as low as 6 for the silica rich Faujasite Y (19).

The zeolite pellets used for *para*-xylene separation are formed by a large number of microporous crystals bound with a binder (14). Most of the adsorption phenomena occur in these crystals. The void between these crystals creates a set of large pores called macropores that act as passage for the molecules to diffuse from the liquid phase into the interior of the pellet.

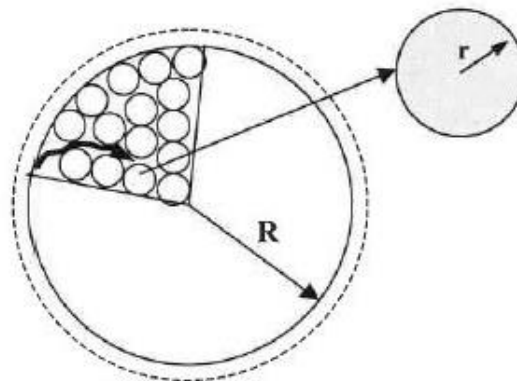


Figure 13 - Structure of the zeolite used in the *para*-xylene separation process (14)

2.6.2 – Selectivity

The selectivity of the adsorbent, which may depend on differences in sorption equilibrium, or, less commonly, on a difference in sorption kinetics, is a key factor in determining the viability of these types of process (24). The selectivity for an equilibrium-based process is measured by a separation factor which can be defined by the following expression:

$$\alpha_{A/B} = \frac{X_A/X_B}{Y_A/Y_B} \quad (2)$$

where X and Y are, respectively, the mole fractions of the components in the adsorbed and fluid phases at equilibrium.

The selective adsorption process is complex and the quality of the separation is dependent on various physical and chemical parameters such as:

- Nature and quantity of exchanged cations;
- Loading of the adsorbent;
- Composition of the mixture;
- Amount of preadsorbed water.

It was found that, for higher acid strength of zeolite (small cation, high Si/Al ratio, preadsorbed water), the zeolite affinity of *meta*-xylene increased (25). Regarding the composition of the mixture, since it varies along the SMB column it is predictable that the selectivities will also vary along the process.

The temperature of the process, an operational parameter, plays also an important role on the adsorption properties of the adsorbent. It was found that an increase of temperature results in the decrease of the total adsorption capacity (26).

2.6.3 – Adsorption isotherms

The adsorption of a substance from the liquid phase to the surface of the adsorbent, leads to a thermodynamically defined distribution of that substance between the phases when the system reaches the equilibrium (27). The most common way to define this distribution is to express the amount of substance adsorbed per unit weight of adsorbent, as a function of the equilibrium concentration of the substance in the remaining liquid phase. An expression of this type, referred as an adsorption isotherm, defines the functional equilibrium distribution of adsorption with the concentration of adsorbate in solution at constant temperature:

$$q_i = f(C_i) \quad (3)$$

Experimental isotherms are useful for describing the adsorption capacity to facilitate the evaluation of this process for a certain application, for selection of the most appropriate adsorbent and for preliminary determination of adsorbent quantity required (27). An additional potential use of the adsorption isotherms is for a theoretical evaluation and interpretation of the thermodynamic parameters.

In the specific *para*-xylene separation process, the isotherms are critical to evaluate the maximum quantities of xylenes adsorbed and to scale-up the experimental results into an industrial process.

Several isotherms have been developed to describe adsorption isotherm relationships. Any particular isotherm model may fit experimental data accurately under one set of conditions and fail completely under another (27). At very low concentrations, the molecules adsorbed have no influence on another. For these limiting conditions, it is possible to assume that the concentration in one phase is proportional to the concentration in the other (28):

$$q_i^* = K_a C_i \quad (4)$$

This expression is analogous to Henry's Law for gas-liquid systems. At a constant temperature, this expression becomes the simplest form of adsorption isotherms. Unfortunately, the conditions in which is possible to apply this isotherm are greatly reduced (19).

The simplest theoretical model for monolayer adsorption it is called Langmuir Isotherm. At higher liquid phase concentrations, the number of molecules adsorbed increases to a point at which the further adsorption is obstructed by the lack of space on the adsorbent surface. The rate of adsorption becomes proportional to the empty surface available and to the liquid concentration (28). At the same time as molecules are adsorbing, other molecules will be desorbing if they have sufficient activation energy. At a constant temperature, the rate of desorption will be proportional to the surface area occupied by adsorbate.

The basic assumptions on which the Langmuir isotherm is based are (19):

- Molecules are adsorbed at a fixed number of well-defined localized sites;
- Each site can hold only one adsorbate molecule;
- All sites are energetically equivalent;
- There is no interaction between molecules adsorbed on neighbor sites.

The Langmuir isotherm can be expressed with the following equation:

$$q_i^* = q_i \frac{b_i C_i}{1 + b_i C_i} \quad (5)$$

where q_i is the concentration of the adsorbed phase when the monolayer is complete and b_i is a thermodynamic equilibrium constant that can be calculated with the following expression:

$$b_i = b_0 \exp\left(\frac{-\Delta H_0}{RT}\right) \quad (6)$$

However, processes such as *para*-xylene separation involves mixtures with more than one component and therefore, it is necessary to extend the isotherms for a multicomponent system, in which the experimental measurement is quite difficult and time consuming due to the large number of variables involved (19).

The multicomponent Langmuir isotherm, the simplest theoretical multicomponent model, is expressed through the following equation:

$$q_i^* = q_i \frac{b_i C_i}{1 + \sum_{i=1}^{NC} b_i C_i} \quad (7)$$

Regarding the *para*-xylene separation process, it is assumed that all the compounds adsorbed presents an equal saturation loading capacity and that the adsorbent is constantly saturated, with a mixture of varying composition of xylenes and desorbent. With these assumptions, it is possible to apply the stoichiometric Langmuir Isotherm in this process through the following equation:

$$q_i = q \frac{K_i C_i}{\sum_{i=1}^{NC} K_i C_i} \quad (8)$$

The use of this isotherm allows the assumption that the selectivities between components remain constant along the process and are described through the ratio between the equilibrium constants of the compounds:

$$\alpha_{A/B} = \frac{q_A C_B}{q_B C_A} = \frac{b_A}{b_B} \quad (9)$$

2.7 – Simulated Moving Bed for *para*-xylene separation

Simulated Moving Bed chromatography, a continuous multi-column chromatographic process, has become the preferential technology for *para*-xylene separation from the remaining isomers.

Chromatography is normally operated in “elution mode”, being that the separation is achieved through the injection of pulses of the solute mixture into a stream of mobile phase flowing through a chromatographic column packed with a suitable stationary phase (29). Since the different solutes have a varying degrees of affinity to the stationary phase, they move with different velocities in the column. As such, the less retained compound will be the first to exit the column while the more retained one will exit later. Through a switching valve at the column outlet, it is possible to collect the compounds in different vessels, which allows the separation of the injected mixture. However, this process is not continuous and, as such, its productivity is limited.

Performing a chromatography process with a continuous countercurrent process, where the fluid and the solid phases run in opposite directions, allows a production process with a much more

attractive productivity. This type of process operation can be implemented through a True Moving Bed (TMB) unit with a four section configuration (29), where the mixture to be separated is fed between zones 2 and 3. The desorbent is introduced continuously into zone 1, while the extract and raffinate products are collected, respectively, at the outlets of zones 1 and 3. The feed mixture is separated in way that the less retained compound is carried by the fluid and leaves the process through the raffinate outlet while the other compound is retained through the solid phase and sent towards the extract outlet (29).

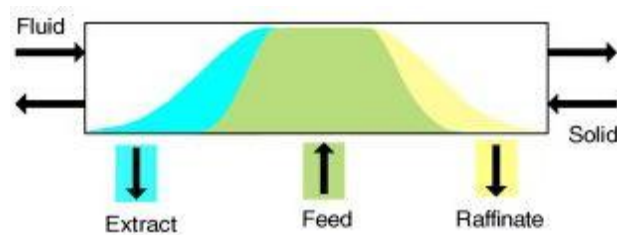


Figure 14 - Schematic for countercurrent chromatography (29)

The TMB process presents various advantages in comparison to the traditional chromatography operated in elution mode, there is no need to achieve complete resolution of the two solutes to obtain pure products and since this process is operated in a continuous mode, the feed is being constantly injected in the process, leading to the increase of productivity. The desorbent consumption in this process is also lower since this compound is being constantly recycled.

However, as previously mentioned, difficulties in ensuring homogeneous motion of the solid phase, mechanical erosion of the adsorbent and back-mixing made impossible to implement the True Moving Bed Process commercially (14). These problems have been overcome by the Simulated Moving Bed technology.

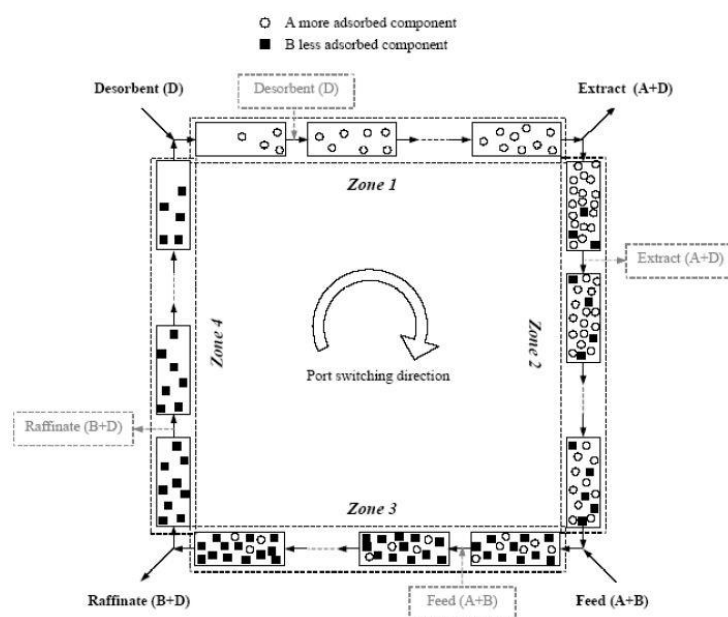


Figure 15 - Schematic diagram of the Simulated Moving Bed technology (15)

In the Simulated Moving Bed, the adsorbent is found in a finite number of interconnected conventional fixed bed chromatographic columns (15). The countercurrent movement of the solid phase is simulated through switching the inlet and outlet ports one column forward in the direction of the fluid flow at constant time intervals.

2.7.1 – Principle of Simulated Moving Bed Operation

The TMB process is a limiting case of a SMB process with an infinite number of columns and an infinitely small switching time of the inlet and outlet ports (15). Thus, the principle of Simulated Moving Bed operation can be described by reference to the equivalent True Moving Bed unit (14). In the TMB unit, two inlet and two outlet ports are fixed along the bed, dividing the process in four distinct zones. The liquid phase is recycled from the top to bottom of the unit and the solid phase is recycled from the bottom to the top of the unit. The solid flow rate is constant all over the process while there is a variation of the liquid flow rate due to the injection and withdrawal of the inlet and outlet streams.

For a more understandable explanation of the process, it is considered that the feed injected in the process is a mixture with two components: **A** (which corresponds to *para*-xylene) and **B** (which corresponds to the remaining isomers). Therefore, **A** is the more strongly adsorbed component while **B** is the one with lowest affinity for the adsorbent. The desorbent (**D**) used is a component that can displace the feed components from the adsorbent and the opposite also happens depending on the liquid and solid flow rates on a certain zone (14). The extract outlet, located between zones **1** and **2**, contains the more adsorbed component (**A**) mixed with desorbent while the raffinate outlet, located between zones **3** and **4**, contains the less adsorbed component **B** mixed with desorbent.

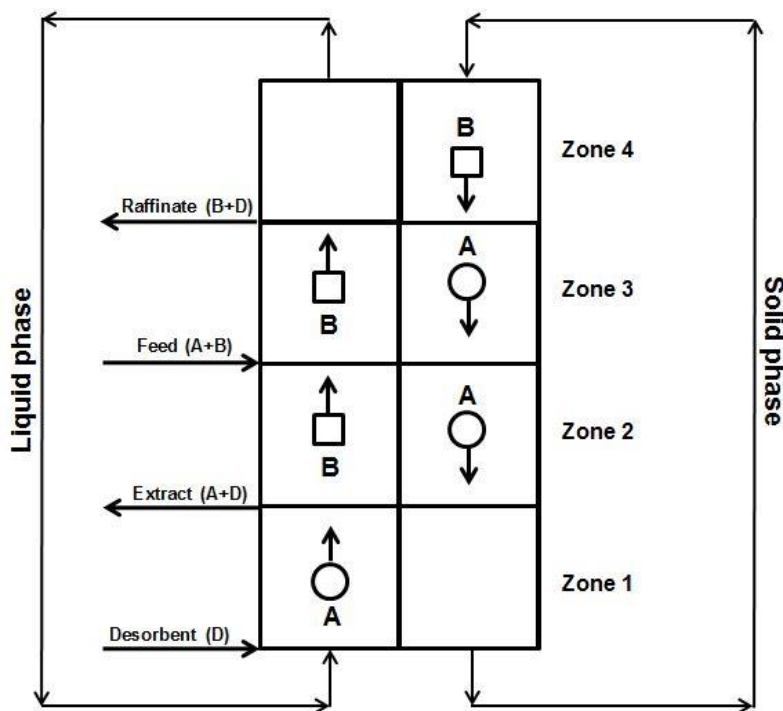


Figure 16 - Schematic diagram of the True Moving Bed (TMB) unit

In the TMB unit, two inlets and two outlet ports are fixed along the bed, dividing the process in four distinct zones in which distinct adsorption-desorption phenomena occur.

Zone 1 is situated between the desorbent and extract ports. The purpose of this zone is to desorb component **A** from the adsorbent to ensure that it leaves the process through the extract outlet. In this zone, the desorbent is highly concentrated in order to guarantee the desorption of **A**. For the occurrence of this desorption phenomena, it is necessary to have a low A/D selectivity. The adsorbent reaches the beginning of this zone completely free from both components and is recycled to zone 4 as clean adsorbent (14).

In zone 2, situated between the extract and the feed ports, it is necessary to ensure that the component with lower affinity, **B**, does not reach the extract node and contaminate this outlet (15). Thus, the objective in this zone is to guarantee the desorption of **B** from the adsorbent and that the component **A** is adsorbed and carried out with the solid phase. While the fluid phase coming from zone 1 contains only **A**, the solid phase coming in this zone from zone 3 contains both **A** and **B** adsorbed. As such, it is necessary to have a high A/B selectivity in this zone to ensure that **B** is gradually displaced from the adsorbent and replaced by **A**.

Zone 3 is situated between the feed and raffinate ports. The purpose of this zone is to prevent that **A**, the component with highest affinity, does not reach the end of this section and contaminates the raffinate outlet. It is then necessary to guarantee that this component is adsorbed from the liquid phase (14). Since the solid phase coming from zone 4 carries only **B**, it is necessary to have high A/B and A/D selectivities in this zone to ensure that **B** is gradually displaced from the adsorbent and replaced only by **A**.

In zone 4, situated between the raffinate and the desorbent ports, it is necessary to ensure the regeneration of the desorbent, ensuring that the liquid that reaches the end of this zone has only **D** and can be recycled to zone 1 as pure desorbent (14). For this purpose, it is necessary to have a high B/D selectivity in this zone in order to ensure that **B** is adsorbed in the solid phase to be sent to the raffinate port.

2.7.2 – Simulated Moving Bed modeling

The modeling of a SMB unit for *para*-xylene separation from mixed xylenes can be made through the True Moving Bed (TMB) and the Simulated Moving Bed (SMB) approaches (14). The first one considers that the simulated moving bed process is equivalent to the true moving system while the second represents the actual simulated moving bed configuration, taking into account the switch of the position of the inlet and outlet streams.

The main differences between these two approaches is that the stationary regime of the SMB is a cyclic steady state, in which in each zone there is an identical transient during the switching period (14). This cyclic state is reached after several cycles, however, the system state continues to vary over the time due to the periodic movement of the inlet and outlet ports along the columns. The relationships between the mathematical descriptions of both approaches are found in Table 5.

Table 5 - Equivalence relations between the SMB and TMB approaches for the modeling of an SMB unit (14)

Model	Parameter	Solid Phase	Liquid Phase
Simulated Moving Bed Approach	Velocity	0	v_j^*
	Flow rate	0	Q_j^*
True Moving Bed Approach	Velocity	$u_s = \frac{L_c}{\Delta t^*}$	$v_j = v_j^* - u_s$
	Flow rate	$Q_s = u_s A(1 - \varepsilon)$	$Q_j = Q_j^* - Q_s \frac{\varepsilon}{1 - \varepsilon}$

In a previous work by Minceva (14), it was confirmed that the performance of an industrial scale SMB units with 24 columns for *para*-xylene separation could be reasonably predicted with the equivalent True Moving Bed modeling strategy (15). As such, it is preferable to use this model instead of the SMB approach due to the different level of difficulty involved in the solution of the two models and the required computation time (30). Also, a True Moving Bed unit operates in steady state and so its stationary behavior can be described by a set of ordinary differential and algebraic equations.

The mathematical model created for the simulation of an equivalent TMB system takes into account axial dispersion flow for the liquid phase, plug flow for the solid phase and linear driving force (LDF) for the intraparticle mass transfer rate (15). The multicomponent adsorption equilibrium is described through the Langmuir Isotherm.

In this model formulation, it is necessary to make the following assumptions (30):

- Negligible thermal effects;
- Bed void fraction, radius and porosity of the particles constant along the columns;
- Constant flow rate in each zone;
- Negligible pressure drop along the column.

Since the TMB unit is divided into four zones through the inlet and outlet ports, it is possible to realize simple mass balances on the connecting nodes of the four zones, which are expressed through the following equations (30):

- Desorbent injection point:

$$Q_4 + Q_D = Q_1 \quad (10)$$

$$c_{i,4}^{out} Q_4 + c_{i,D} Q_D = c_{i,1}^{in} Q_1 \quad (11)$$

- Extract withdrawal point:

$$Q_1 - Q_E = Q_2 \quad (12)$$

$$c_{i,1}^{out} = c_{i,2}^{in} = c_{i,E} \quad (13)$$

- Feed injection point:

$$Q_2 + Q_F = Q_3 \quad (14)$$

$$c_{i,2}^{out} Q_2 + c_{i,F} Q_F = c_{i,3}^{in} Q_3 \quad (15)$$

- Raffinate withdrawal point:

$$Q_3 - Q_R = Q_4 \quad (16)$$

$$c_{i,3}^{out} = c_{i,4}^{in} = c_{i,R} \quad (17)$$

Through these mass balances, it is possible to obtain the fluid velocities and inlet concentrations in the different zones of the process.

The mass balance in a volume element of zone j and the particle mass balance are expressed through equations 18 and 19 (30):

$$\varepsilon \frac{\partial c_{i,j}}{\partial t} + (1 + \varepsilon) \rho_P \frac{\partial q_{i,j}}{\partial t} = \varepsilon D_{Lj} \frac{\partial^2 c_{i,j}}{\partial z^2} - \varepsilon v_j \frac{\partial c_{i,j}}{\partial z} + (1 - \varepsilon) u_s \rho_P \frac{\partial q_{i,j}}{\partial z} \quad (18)$$

$$\frac{\partial q_{i,j}}{\partial t} = u_s \frac{\partial q_{i,j}}{\partial z} + k_i (q_{i,j}^* - q_{i,j}) \quad (19)$$

- Initial conditions:

$$t = 0, \quad c_{i,j} = c_{Dj}^0 \text{ and } q_{i,j} = q_{i,j}^* c_{Dj}^* \quad (20)$$

- Boundary conditions:

$$z = 0, \quad c_{i,j}^{in} = c_{i,j} - \frac{D_{Lj}}{v_j} \frac{\partial c_{i,j}}{\partial z} \quad (21)$$

$$z = L_j, \quad \frac{dc_{i,j}}{dz} = 0 \text{ and } q_{i,j} = q_{i,j+1}^{in} \quad (22)$$

2.7.3 – Performance parameters

The modeling and optimization of a Simulated Moving Bed unit for the *para*-xylene separation process is evaluated by the performances parameters obtained, which can be divided in two different categories, the separation and process performance parameters.

Para-xylene, as the more strongly adsorbed component, is recovered in the extract outlet while the remaining components are recovered in the raffinate. Therefore, the only product stream of interest that has to satisfy the separation specifications is the extract outlet (31). As such, it is necessary to guarantee that this stream respects the constraints defined for the two separation parameters, the purity and recovery of *para-xylene*.

The purity of *para-xylene* is defined by the demand of this compound in the market (30). This performance parameter is expressed through the ratio between the concentration of *para-xylene* and the sum of the concentration of all xylenes in the extract outlet.

$$P_E (\%) = \frac{C_{PX,E}}{(C_{PX,E} + C_{MX,E} + C_{OX,E} + C_{EB,E})} \quad (23)$$

It is noteworthy that, despite the presence of PDEB in the extract stream, this compound is not taken into account for the calculation of the *para-xylene* purity. This is due to the fact that, after the SMB process, the extract stream is sent to a distillation column where the desorbent is completely separated from *para-xylene*.

The recovery is defined as the amount of the desired compound obtained in the extract stream relative to the injected in the feed inlet. The *para-xylene* recovery in the extract can be calculated through the following equation:

$$R_E (\%) = \frac{C_{PX,E} Q_E}{C_{PX,F} Q_F} \quad (24)$$

Once the separation parameters are determined, the choice of the specific optimal operating conditions can be performed on the basis of economic considerations (31). For the evaluation of this process two performance parameters are used: Productivity of the process and desorbent consumption.

The productivity of the process, the most important economic parameter of the process, is defined through the following equation:

$$PR = \frac{C_{T,F} Q_F}{(1-\varepsilon) \rho_s V_T} \quad (25)$$

In the *para-xylene* separation process, the desorbent has to perform two different tasks. In zone 1, it has the function of being adsorbed so as to facilitate the desorption of *para-xylene*. Therefore, for this particular task, it is advisable to use a desorbent with a high affinity for the adsorbent, that is, a strong desorbent. In zone 4, the desorbent has the function of being desorbed so as to facilitate the adsorption of the lighter components. As such, for this purpose, it is recommended to use a desorbent with low affinity for the adsorbent, that is, a weak desorbent (31).

Therefore, the use of an intermediate desorbent, such as the one used industrially (*para*-diethylbenzene) represents a good compromise between these two requirements. However, the choice of the desorbent to use in the process depends on the separation specifications defined. If one

pretend to obtain a larger recovery values in the extract stream it is advisable to use a strong desorbent, in the case of pretending a higher recovery in the raffinate stream it is more advisable to use a weak desorbent (31).

The desorbent consumption is expressed through the ratio between the desorbent and the xylenes inlet flow rates, calculated through the following expression:

$$\frac{S}{F} = \frac{Q_D}{Q_F} \quad (26)$$

2.7.4 – Optimization of the Simulated Moving Bed unit

The optimization of a Simulated Moving Bed unit considers the selection of the operating conditions and/or the geometric parameters that minimize/maximize a given objective function(s) (30). The optimization studies can be classified according to the number and type of objective functions.

Regarding the number of objective functions, the optimization problem can be classified in two categories, single or multiple-objective (30). The single objective optimization can include one objective or multiple objectives with different weight factor. Regarding the multiple objective optimization it is necessary to note that it may not be found a global optimum result respecting all objectives, instead, it is possible to obtain an entire set of optimal solutions that are equally good.

Regarding the type of objective functions, it is also possible to classify the optimization problem in two categories, process performance parameter (i.e. productivity, desorbent consumption) and separation cost (30). The utilization of a single objective optimization might result in different optimum conditions depending on the objective defined (i.e. minimization of desorbent consumption, maximization productivity). Therefore, the use of multi objective function optimization is advised, since it allows the simultaneous resolution of several objective targets. A secondary option is the use of a cost function, which gives the opportunity to join different process performance parameters (30).

An optimization process used for the *para*-xylene separation process is based on a two level optimization created by Minceva and Rodrigues (30), which uses the concept of “separation volume” methodology. The optimization procedure comprises two consecutive levels, being that in each it is considered a single objective function of a process performance parameter. In the first level, the productivity of the process is maximized for given flow rates in zones **1** and **4** and in the second level it is calculated the minimum desorbent consumption needed to achieve this productivity (30). The global solution of the optimization process results in the optimal operating conditions (flow rates in the four zones of the SMB unit) required to achieve the maximum productivity with a corresponding minimum desorbent requirement for the imposed purity and recovery constraints.

In the “separation volume” methodology, it is identified for a given pair of values of the flow rates in zones **1** and **4**, a specific triangular region in the (Q_2, Q_3) plane where the separation of the isomers is achieved (31). The vertex of the triangle obtained represents the optimal point of operation

regarding the process productivity, as it is the point where the difference between the flow rates in zones 2 and 3 is maximized, and therefore, the higher feed flow rate is obtained.

In the first level, the objective function selected to maximize is the process productivity. The objective is to find, for given values of the flow rates in zones 1 and 4, the set of values for the flow rates in zones 2 and 3 that result in the maximum feed flow rate and, consequently, in the maximum productivity. After the first level of optimization is accomplished, the optimum points for the pair of flow rates from the zones that influence the desorbent consumption, zones 1 and 4, are analyzed.

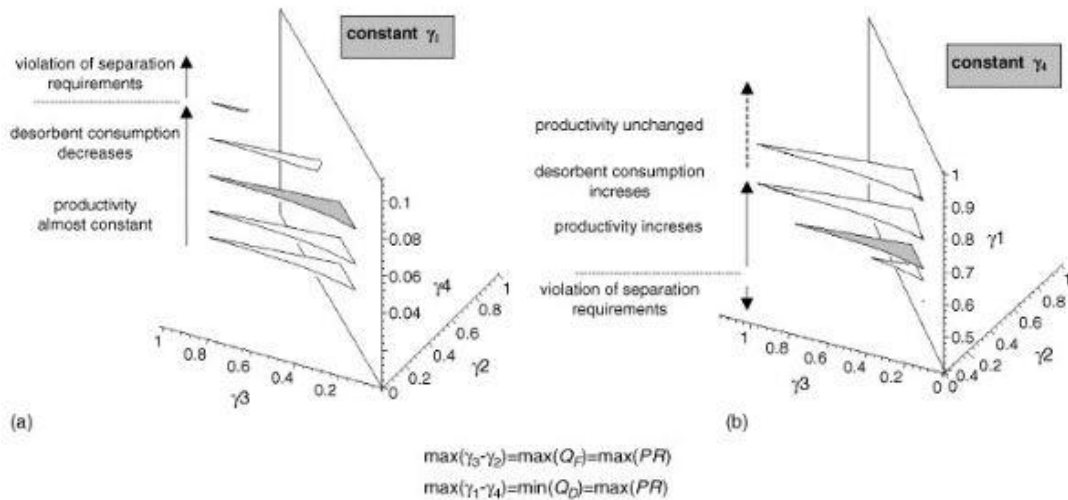


Figure 17 - (a) Influence of the flow rate in zone 4 (γ_4) on the separation region for fixed value of the remaining flow rates, (b) Influence of the flow rate in zone 1 (γ_1) on the separation region for fixed value of the remaining flow rates (30)

As it is possible to observe in Figure 17 (a), the separation regions remain constant until a given value of the flow rate in zone 4. From that point, the separation region starts to decrease dramatically with the increase of this flow rate. For a given flow rate in zone 1, it is of interest to work with the highest flow rate in zone 4 in the region of unchanged separation region size due to the smaller quantity of desorbent consumption spend in the process ($Q_D = Q_1 - Q_4$).

Through Figure 17 (b), it is possible to observe that, for a fixed value of flow rate in zone 4, the separation region increases with the increase of the flow rate in zone 1 up to a certain value (30). The further increase of the flow rate in that zone does not influence the size of the separation region. While the size of the separation region increases, the maximum point of the separation region tends also to increase, which results in a higher feed flow rate and consequently a higher productivity obtained. However, the separation region size does not increase more with the further increase of the flow rate in zone 1, as such, this will not affect the position of separation region maximum. Therefore, it is of interest to work with the minimum flow rate in zone 1 in which it is obtained the maximum separation region in order to obtain the maximum productivity for the process with the minimum desorbent consumption.

3. Work methodology

The aim of this chapter is to explain the methodology followed in the different parts of the present work. Firstly, the experimental procedure used for the adsorbent preparation and for the measurement of thermodynamic parameters is explained. The nomenclature and method used for the adsorbent classification is then presented. The theoretical approach used to obtain a first guess of the process performances of a given adsorbent is also explained. Lastly, the parameters chosen and the optimization strategy used for the process simulation are presented.

3.1 – Experimental section

The aim of this work is to evaluate the thermodynamic performances of new adsorbents in the *para*-xylene separation process through the Simulated Moving Bed technology. For this purpose, different Faujasite adsorbents were created and tested on a laboratory scale in IFPEn by coworkers. The experimental work made is divided in this chapter into two parts, the adsorbents preparation and the thermodynamic parameters measurement.

3.1.1 – Adsorbents preparation (design and making)

The preparation of ion-exchanged adsorbents is made by percolation, where a salt solution containing the desired cation(s) (KCl, CsCl, CaCl₂ or BaCl₂) is injected in a packed column filled with a zeolite previously hydrated. This method is used due to the advantage of not being limited by thermodynamics as the adsorbent is in constant contact with the solution injected.

The zeolites NaX and NaY with spherical shape are used as the original solids in this experimental work. Their structural characteristics are found in Table 6.

Table 6 - Structural characteristics of the original zeolites (32)

Type of solid	NaX	NaY
Ratio Si/Al	1,20	2,83
Microspore volume (cm ³ g ⁻¹)	0,282	0,271
LOI (%)	26	18

Experimental unit for ion exchange

The scheme of this experimental unit is illustrated in Figure 27 found in the Appendices. This unit is constituted by a quaternary pump that can distribute up to four mixtures (three salt solutions containing the cation to exchange and distilled water) to the oven where the adsorbents preparation is

made. This equipment can contain six columns, which allows the simultaneous preparation of different adsorbents. In this unit there is also a nitrogen flow meter, used to inject the compound in the columns in the drying and activation steps. All the equipment's found in this unit are operated automatically through the *iFLIX* software

Exchange cycle

The process of cations exchange takes places in five different steps:

- Hydration of the solid;
- Cation exchange;
- Washing of the columns;
- Drying of the adsorbent;
- Activation of the adsorbent.

After introducing the solid in the preparation columns, the temperature is increased up the temperature of the cation exchange step. After this parameter is stabilized, the salt solutions are injected in the column.

In order to remove the chloride created in the cation exchange step, the columns are washed with water. It is important to mention that, in this step, the columns remain at exchange cation step temperature. The water found in the column is then removed in the drying step through the injection of nitrogen. In this step, the temperature of the columns is constantly increased until achieving the desired drying temperature. With this operating condition and with the injection of a constant nitrogen flow it is possible to obtain an activated adsorbent with a residual amount of water

Finally, the temperature of the columns is then decreased at a constant rate of until reaching room temperature. At the end of the cycle, the adsorbent is removed and sent for the thermodynamic parameters measurement unit.

3.1.2 – Thermodynamic parameters measurement

After the preparation of the different adsorbents, it was necessary to measure their thermodynamic parameters in mixtures with similar compositions to the ones of critical points of the SMB column in order to characterize and evaluate the adsorbents regarding the thermodynamic performances. These tests were performed under the operating conditions of temperature and pressure of the industrial process.

Experimental units

It is important to mention that these experimental tests were made for two set of mixtures. While the first set, containing three different mixtures was tested for all the adsorbents created, the second was tested only for the two adsorbents that demonstrated the greatest potential for implementation at industrial level. Both tests were performed similarly but in different units with slight modifications. The differences between the two tests are explained in the experimental description found below.

The schemes of both experimental units used to measure the thermodynamic parameters are illustrated in Figure 28 and Figure 29 found in the Appendices. As it possible to observe in these figures, both units contain two pumps, used for the injection of the feed and the desorbent into the column(s), an oven to guarantee the required test temperature, a thermostatic bath to refrigerate the column effluent to room temperature and a fraction collector. The main difference between the units is that the one used for measuring the first set of mixture contains two columns (length of 25 cm) with independent circuits, which allow simultaneous breakthrough and reverse breakthrough tests, while the unit used for measuring the second set of mixture has only one column (length of 100 cm). These operate at the industrial temperature (175 °C or 160 °C according to the desorbent used) under a pressure between 6 and 20 bar. Both units have safety valves, check valves and fire alarms. The main characteristics of these two units are found in the following table.

Table 7 – Main characteristics of the units used for the thermodynamic parameters measurement

Characteristic	Unit 1	Unit 2
Number of columns	2	1
Column length (cm)	25	100
Mixtures used	1,2,3	A,B,C,D
Acquisition of data	Simplified reverse breakthrough	Simplified breakthrough + reverse breakthrough
Detection	GC	GC
Measurement of water content in the adsorbent	LOI	LOI

Tested mixtures and desorbent

The mixtures used for the experimental tests contain the xylene isomers to separate, the industrial desorbent (PDEB) and a tracer compound which is not adsorbed in the microspores of the adsorbent in the presence of aromatics. Therefore, the inclusion of the tracer in the mixture allows the calculation the non-selective volume of the column (voids between the zeolite grains within the column and the macropores) and consequently, the adsorbed volume.

$$V_{column} = V_{adsorbed} + V_{non-selective} \quad (27)$$

Two distinct tracers were used for the realization of the experimental tests, n-dodecane for the first set of mixtures and i-octane for the second set. It is important to note that both tracers do not influence the competitive adsorption of the xylene isomers.

Since PDEB is present in the mixtures tested with the objective of measuring the selectivities between the xylenes and the industrial desorbent, it is chosen to use toluene as the desorbent in this experimental work.

Table 8 - Properties of the components present in the mixtures used (2)

Components	Molecular Formula	Density at 25 °C (g/cm ³)	Boiling point (°C)
<i>Para</i> -xylene	C ₆ H ₄ (CH ₃) ₂	0,861	138,37
Ethylbenzene	C ₆ H ₄ (C ₂ H ₅)	0,867	136,19
<i>Meta</i> -xylene	C ₆ H ₄ (CH ₃) ₂	0,864	139,12
<i>Ortho</i> -xylene	C ₆ H ₄ (CH ₃) ₂	0,880	144,41
<i>Para</i> -diethylbenzene	C ₁₀ H ₁₄	0,862	183,95
iC ₈ /C ₁₂	C ₈ H ₁₈ /C ₁₂ H ₂₆	0,703/0,750	127,10/215,34
Toluene	C ₇ H ₈	0,866	110,64

The mixtures used for the measurement of the adsorption selectivities are prepared by measuring the desired amount of *para*-xylene (Sigma-Aldrich, purity>99%), ethylbenzene (Fluka, purity>99%), *meta*-xylene (Fluka, purity>99%), *ortho*-xylene (Fluka, purity>99%), *para*-diethylbenzene, octane (Fluka, purity>99%) and dodecane (Sigma-Aldrich, purity>99%) on an analytical balance.

Water content of the adsorbent

One of the parameters which influence most the adsorption properties of an adsorbent is the water content in the solid. As such, the rate of hydration of the zeolite was obtained through the LOI (Loss Of Ignition) measurement. This method allows the calculation of the water quantity through the following expression:

$$LOI (\%) = \frac{\Delta m(g)}{m_{initial}} \quad (28)$$

For this measurement, it is used an oven with a temperature of 950 °C for one hour, followed by a decrease of 5 °C/min until reaching the final temperature of 25 °C.

Filling of the column

The filling of the column is made in an analogous way to the one described in Chapter 3.1.1. The packed column is then inserted in the experimental unit, inside the oven.

Karl Fisher Test – Equilibre en eau (water equilibrium)

For each new adsorbent tested, it is necessary to calculate the amount of water found of the desorbent solution that is in equilibrium with the water within the adsorbent. This is made through the Karl Fisher test, which consists in the circulation of the solution in question through the solid in a close system at a temperature of 175 °C and a pressure of 7 bar. After the equilibrium is reached, samples are withdrawn for performing the test.

The Karl Fisher test uses the quantitative reaction of water with iodine and sulfur dioxide in the presence of a lower alcohol such as methanol and an organic base such as pyridine. This test is made through the coulometric titration method where, first, iodine is produced by electrolysis of the reagent containing the iodide ion, and then, the water content in a sample is determined by measuring the quantity of electricity that is required for the electrolysis, based on the quantitative reaction of iodine with the water.

Breakthrough tests

Before the experimental studies, it is necessary to fill completely the columns with toluene, the desorbent used in the experimental work. After ensuring that the temperature and pressure are stabilized and that the adsorbent is completely saturated with toluene, it is possible to proceed with the test.

The breakthrough curve test allows the study of the kinetic of adsorption, thermodynamic behavior and the capacity of separation of the adsorbable compounds. This is made through the injection of a mixture on a column that is saturated with desorbent and by the analysis over the time of the concentration of the different compounds in the column outlet. The components of the mixture injected are adsorbed on the zeolite, replacing the desorbent until the solid becomes completely saturated. Experimentally, this phenomena occurs when the concentration of the outlet becomes equal to the one of the mixture injected.

It is also made the reverse breakthrough curve test through the reverse operation, where the adsorbent is firstly saturated by the mixture containing the xylene isomers and after, the desorbent is injected, replacing the compounds from the solid in the course of time.

The methods used for the measurement of the thermodynamic parameters are different for both sets of mixtures. For the first set, it was calculated from a breakthrough curve obtained through a Raman online analysis and from simplified reverse breakthrough, while for second set of mixture it are obtained by simplified breakthrough and reverse breakthrough.

Based on the principle of polarizability of a molecule, the Raman spectroscopy is an analytical technique that studies the phenomena of vibrational transitions through the Raman scattering observed when an intense electromagnetic monochromatic radiation results in the excitation of a molecule to a virtual energy state before going back to a higher energy level than that of the initial

state of the molecule. The intensity of the scattered light, depending on the intensity of the incident laser beam, is proportional to the quantity of matter that diffuse. This method is used due to the possibility of tracking online the compounds at column outlet in a quantifiable way, without being necessary to collect samples for further processing.

The simplified breakthrough and reverse breakthrough are made by the collection of the effluent of the column in only one bottle and therefore, based on a single chromatographic analysis of the effluent obtained in the end of the experience. Thus, the adsorption equilibrium parameters are obtained in a faster way than for the complete breakthrough test in which is necessary to collect several samples.

3.2 – Adsorbents classification

Of the adsorbents prepared, only the ones that presented characteristics of interest for the *para*-xylene separation process are of interest to study in detail. As such, it is created a classification of the adsorbents using different criteria in order to evaluate the interest of the solids.

This classification is based on the nomenclature adapted by Mazzoti et al. (33) which considers that in a countercurrent adsorption process the mixtures can be divided in two different groups, the components which are collected in the extract outlet and the ones found in the raffinate. Regarding the isomers separation, it is pretended to separate the four aromatic compounds and the desorbent, obtaining only the isomer with highest affinity for the adsorbent in the extract outlet and the remaining in the raffinate. Therefore, in this particular process, the first group is only constituted by one component, titled as the strong key (*sk*), whereas the second group is constituted by three compounds, the weak key (*wk*) a weak (*ww+1*) and the weakest (*ww*) components. With this approach, it is possible to rank the components found in the feed mixture based on their affinity for the adsorbent:

$$K_{ww} < K_{ww+1} < K_{wk} < K_{sk} \quad (29)$$

To perform this classification, it was created a *macro* in the software *Visual Basic for Application* (VBA) that defined, for each adsorbent, which xylene corresponded to *sk*, *wk*, *ww+1* and *ww* components in a chosen mixture used in the thermodynamic parameters measurement. This association is obtained through the use of the selectivities between the xylenes and the desorbent with the objective of obtaining for each the adsorbent the following sequence:

$$\alpha_{sk/D} > \alpha_{wk/D} > \alpha_{ww+1/D} > \alpha_{ww/D} \quad (30)$$

In the adsorbent classification, each xylene is assigned to a specific number (PX-1; EB-2; MX-3 and OX-4), which allows to obtain, using the same *macro*, a simple four number classification for each solid considering a certain mixture. For example, if one considers an adsorbent typically used industrially, the selectivity order in the feed injection point is the following:

$$\alpha_{PX/PDEB} > \alpha_{EB/PDEB} > \alpha_{MX/PDEB} > \alpha_{OX/PDEB} \quad (31)$$

For this solid, PX is the *sk* component, EB the *wk*, MX the *ww+1* and OX the *ww*, which results in a **1234** classification for the feed injection point.

The adsorption strength of the desorbent also plays an important role in the xylene separation process, as explained in Chapter 2.7.3. As such, it was also created a *macro* in the software *Visual Basic for Application* (VBA) in order to classify the desorption strength based on the selectivities obtained between the different xylenes and the desorbent for a given mixture used experimentally. The adsorption strength of the desorbent is classified numerically as shown below:

- Weak desorbent ($1 < \alpha_{ww}$): 3
- Weak-intermediate ($\alpha_{ww} < 1 < \alpha_{wk}$): 2
- Intermediate ($\alpha_{wk} < 1 < \alpha_{sk}$): 1
- Strong ($\alpha_{sk} > 1$): 0

3.3 – Limit flow rate approach

The adsorbents performances are obtained through the use a *FORTRAN* simulator which requires significant calculations time. As such, before running the simulations, it is applied a simplified theoretical approach titled as Limit Flow Rate Approach (created previously in IFPEn) that allows the study of the thermodynamic impact in the process and as a first guess of the process performances. The advantage of this approach is that, using expressions of the flow rates of each zone of the process, it is possible to evaluate the influence of certain parameters on the process performance without the need of a simulator.

In this approach, the chosen variables that describe in the different zones, the behavior of the process, are titled as reduced flow rate and are expressed as a ratio between the liquid and the adsorbed phases flow rates. The limits of these flow rates in each zone (minimum for zones **1** and **2** and maximum for zones **3** and **4**) are determined based solely on thermodynamic considerations that are dependent on the feed composition, geometric characteristics (porosity) and physico-chemical properties (capacity, selectivities) of the adsorbent.

The expressions used for the calculation of these flow rates are based on inequations imposed in each zone of the process to guarantee that the compounds move in the pretended directions. The expressions obtained for the reduced flow rates in the four zones of the process are described below for an adsorbent used typically for the studied process (PX – *sk*, EB – *wk*, MX – *ww+1*, OX – *ww*). For this type of adsorbent it is possible to assume that *ortho*-xylene presents a similar behavior as *meta*-

xylene regarding the thermodynamic properties, which allows to work only with three xylenes: PX, EB and MOX.

3.3.1 – Reduced flow rate in zone 1

In order to obtain the desired yield of *para*-xylene in the extract point, it is necessary to adjust the flow rate in zone 1 to ensure that this component is driven by the liquid phase flow. As such, the following constraint must be respected in every point of zone 1:

$$Q_{z_1}^{tmb} C_{PX}^{z_1} > Q_s^{ads} q_{PX}^{z_1} + Q_s^{macro} C_{PX}^{z_1} \quad (32)$$

The point where $\Omega_1 \geq \Omega_1^{min}$ is the most restrictive. It can be located either in the desorbent injection point (in which the content of *para*-xylene is the lowest) or in the extract withdrawal point. With this assumption it is possible to affirm that the reduced flow rate limit in this zone is found either in the desorbent injection or in the extract withdrawal point, dependent on which present a higher value:

$$\Omega_1^{min} = \max[\Omega_D = f(\alpha_{PX/PDEB}^D); \Omega_E = f(\alpha_{PX/PDEB}^E)] \quad (33)$$

The influence of the PX/PDEB selectivities on the reduced flow rates in the desorbent injection and extract withdrawal points is illustrated in Figure 30 and Figure 31 found in the Appendices.

3.3.2 – Reduced flow rate in zone 2

To achieve the defined *para*-xylene purity in the extract point, it is necessary to adjust the flow rates in zones 2 and 3 so that the less adsorbed components move in the liquid flow direction. Being ethylbenzene the component with higher selectivity that must be driven by the liquid phase, the constraint in zone 2 is written in its function and must be respected in every point of the zone:

$$Q_{z_2}^{tmb} C_{EB}^{z_2} > Q_s^{ads} q_{EB}^{z_2} + Q_s^{macro} C_{EB}^{z_2} \quad (34)$$

The point where $\Omega_2 \geq \Omega_2^{min}$ is the most restrictive is the point where the concentration of *para*-xylene is the lowest, near the feed inlet. If the constraint is violated in this point, it will be observed in every point of zone 2 (assuming small variations of the selectivities in function of the composition). As such, this reduced flow rate is calculated in function of the different selectivities of the xylene isomers in the feed injection point:

$$\Omega_2^{min} = f(\alpha_{PX/EB}^F, \alpha_{PX/MOX}^F, \alpha_{PX/PDEB}^F) \quad (35)$$

The influence of the xylene selectivities on the reduced flow rate of zone 2 is illustrated in Figure 32, found in the Appendices.

3.3.3 – Reduced flow rate in zone 3

To obtain the desired yield of *para*-xylene, it is also necessary to adjust the flow rates in zones **2** and **3** to ensure that this component is driven by the solid flow (adsorbed and macro porous phases) towards the extract point. As such, it is mandatory to respect the following constraints in every point of zone **3**:

$$Q_{z_3}^{tmb} C_{PX}^{z_3} < Q_s^{ads} q_{PX}^{z_3} + Q_s^{macro} C_{PX}^{z_3} \quad (36)$$

The point where $\Omega_3 \leq \Omega_3^{max}$ is the most restrictive can be located either in the feed injection point (in which the content of *para*-xylene is the highest) or in the plateau (middle) of this zone. With this assumption it is possible to affirm that the reduced flow rate limit in this zone is found either in the feed injection point or in the plateau of this zone, dependent on which present a lower value:

$$\Omega_3^{max} = \min[\Omega_F = f(\alpha_{PX/EB}^F, \alpha_{PX/MOX}^F, \alpha_{PX/PDEB}^F); \Omega_P = f(\alpha_{PX/EB}^P, \alpha_{PX/MOX}^P, \alpha_{PX/PDEB}^P)] \quad (37)$$

The influence of the isomers selectivities on the reduced flow rates in the feed injection and plateau points is illustrated in Figure 33 and Figure 34, found in the Appendices.

3.3.4 – Reduced flow rate in zone 4

With the objective of obtaining the defined purity of *para*-xylene in the extract point, it is necessary to adjust the flow rate in zone **4** so the less adsorbed components move in the direction of the solid phase flow to the raffinate point. Since MOX are the components with lower affinity for the adsorbent, the constraint for the reduced flow in this zone is written in their function to ensure that it is satisfied. The following constraint must be respected in all points of zone **4**:

$$Q_{z_4}^{tmb} C_{MOX}^{z_4} < Q_s^{ads} q_{MOX}^{z_4} + Q_s^{macro} C_{MOX}^{z_4} \quad (38)$$

The point where $\Omega_4 \leq \Omega_4^{max}$ is the most restrictive is in the desorbent injection point, where the content of PDEB is the highest. If the constraint is violated in this point, it will be observed in every point of zone **4**. As such, this reduced flow rate is calculated in function of the MOX selectivity in the desorbent injection point:

$$\Omega_4^{min} = f(\alpha_{MOX/PDEB}^D) \quad (39)$$

The influence of the MOX/PDEB selectivity on the reduced flow rate of zone **4** is illustrated in Figure 35, found in the Appendices.

3.3.5 – Reduced feed and desorbent flow rates

The maximum reduced feed flow rate, an indicator of the process productivity, is obtained by the difference between the reduced flow rates of zones **3** and **2**:

$$\Omega_{feed}^{max} = \Omega_3^{max} - \Omega_2^{min} \quad (40)$$

The minimum reduced desorbent flow rate, an indicator of the desorbent consumption, is calculated by the difference between the reduced flow rates of zones 1 and 4:

$$\Omega_{desorbent}^{min} = \Omega_1^{min} - \Omega_4^{max} \quad (41)$$

3.4 – Simulation

The process performances of a given adsorbent in the *para*-xylene separation process are obtained through the use of a *FORTRAN* simulator created previously in IFPE. The simulations can be performed with different modeling approaches such as the Simulated Moving Bed and the True Moving Bed. For this work, all the simulations were performed using the last approach, in an Intel(R) Core (CPU 2,83 GHz, 4 GB RAM).

3.4.1 – Simulation parameters

In order to perform the simulations of the different adsorbents in this work, it is necessary to first define certain parameters related to the Simulated Moving Bed process and to the adsorbent.

The operating and geometrics parameters of the SMB unit are chosen in order to obtain similar conditions to those observed at the industrial level, with only the number of beds reduced from the typical used twenty four to fifteen so as to reduce the computation time of the simulations. The density of the liquid mixture in the four zones of the process is considered constant, independent of mixture composition and equal to the density of *para*-diethylbenzene, the component found in larger quantity in the majority of the beds. The kinetic and thermodynamic parameters were obtained through experimental work.

The chosen parameters use for the realization of the reference simulation can be observed in Table 18, Table 19, Table 20 and Table 21 of the Appendices.

3.4.2 – Thermodynamic models parameters

The simulator used for obtaining the process performances can work with different adsorption models, such as the generalized multi-component Langmuir isotherm. In the present work it is used three different models which consider that the selectivities of the xylene isomers vary with the composition of different compounds along the column. In the different thermodynamic models it is assumed that *ortho*-xylene and *meta*-xylene present the same selectivity values. Therefore, these models were obtained through the use of the PX/PDEB, EB/PDEB, MOX/PDEB selectivities measured experimentally. The coefficients obtained for the equations that allow to describe the variation of selectivities of the different xylenes are then inserted in the simulator as the thermodynamic model parameters.

The selectivities between the xylene isomers can be indirectly obtained using the following relationship:

$$\alpha_{A/B} = \frac{\alpha_{A/PDEB}}{\alpha_{B/PDEB}} \quad (42)$$

3.4.3 – Optimization process

As it was previously mentioned, the optimization procedure used in the present work is based on the two-level optimization process created by Minceva and Rodrigues (30). The optimization of the Simulated Moving Bed unit is made with the objective of maximizing the productivity of the process and minimizing the desorbent consumption with imposed constraints of *para*-xylene yield (97,0%) and purity (99,8%) in the extract outlet. In this optimization procedure, the liquid flow rates of the four zones of the unit are used as design variables.

In order to initialize the optimization process, it is necessary to obtain a first guess for the four flow rates of the process. In the present work, depending on the simulation performed, the initial values of the design variables used are obtained through a reference simulation or by the Limit Flow Rate approach.

In the first level of optimization, productivity of the SMB unit is defined as the objective function to be maximized. The objective is to find the values of the flow rates in zones **2** and **3** that result in the maximum productivity, which implies at the same time a maximum feed flow rate. The optimization procedure starts by fixing the values of flow rates in zones **1** and **4**. The flow rate of zone **2** is then decreased along with the increase of the flow rate in zone **3**, the productivity is at the maximum value when the constraints reach the imposed values.

In the second level of optimization, the objective function, desorbent consumption, is minimized for a given feed flow rate. The optimization procedure starts by fixing the value of flow rate in zone **1** and increasing the flow rate in zone **4** until the separation requirements begin to be violated, this result in the decrease of desorbent consumption without affecting the productivity. After the optimized flow rate of zone **4** is found, this variable is fixed and the flow rate in zone **1** is decreased. The second level of optimization is stopped externally by the user when the defined constraints cease to display the imposed values. The global solution of the optimization procedure that provides maximum SMB unit productivity with a minimum possible desorbent consumption is then achieved.

The flow sheet of the optimization procedure used is shown in Figure 18.

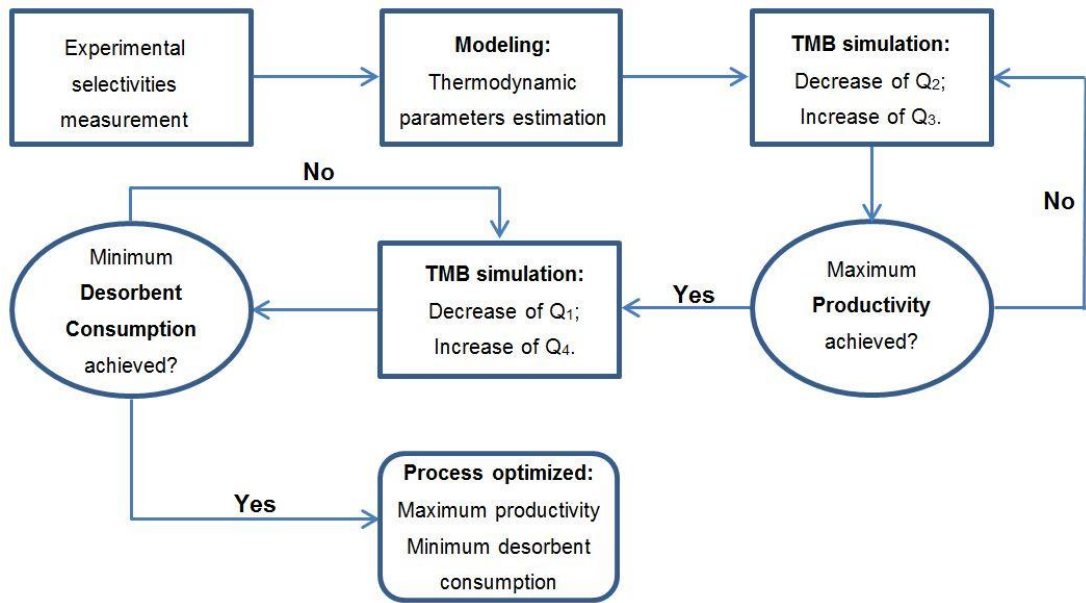


Figure 18 - Flow sheet of the optimization procedure

4. Results and discussion

In this chapter it is presented the results obtained over the work performed. First a classification of the adsorbents is carried to display, in a simplified form, the adsorbents of interest to the process studied. Thereafter it is selected the *para*-selective adsorbents of greater interest to study in detail based on their thermodynamic characteristics. Lastly, simulations are performed in order to assess whether the created thermodynamic models could be used to predict the process performances obtained with different adsorbents and also to verify if the use of the selected adsorbents result in superior performances to those obtained with the adsorbent currently commercialized for the *para*-xylene separation process.

4.1 – Classification of adsorbents

In order to evaluate the possibility of implementing new adsorbents in the *para*-xylene separation process at industrial level, experimental tests are performed for a total of 60 ion exchange faujasite-type zeolite adsorbents. As previously explained, these tests are made to measure different selectivities ($\alpha_{PX/PDEB}$, $\alpha_{EB/PDEB}$, $\alpha_{MX/PDEB}$, and $\alpha_{OX/PDEB}$) as a function of the mixed xylenes compositions.

It is chosen to perform these tests for three mixtures with different compositions. The first mixture, titled as desorbent point, is representative of zones **1** and **4** of the SMB unit, where the liquid phase is mainly composed of *para*-diethylbenzene, the second one has similar composition of a typical feed injection point and a third one with a quaternary concentration of the mixed xylenes without the presence of *para*-diethylbenzene. The compositions of the three mixtures are found in Table 22 in the Appendices.

While the first two mixtures are studied in order to evaluate the selectivities behavior of the xylenes in critical zones of the studied process, the quaternary mixture (mixture **3**) is used to discriminate the selectivities behavior in each adsorbent independently of the isomers concentration. The selectivities for these mixtures were obtained only through the simplified reverse breakthrough since the values obtained by the online Raman analysis of the breakthrough curve presented elevated associated errors.

Since it is not of interest to study in detail all of the adsorbents tested experimentally, it is created a classification using different criteria to verify which were of interest to study, as explained in chapter 3.2.

The numerical classification of the adsorbents is made for the feed injection point due to its importance for the proper functioning of the process, being necessary to ensure that only the *sk* component is adsorbed in preference to the remaining xylenes and is consequently driven towards the

extract outlet by the solid phase, while the remaining components are transported to the raffinate outlet by the liquid phase.

For a proper evaluation of the adsorbents to be used in the studied process, it is of great importance to guarantee the correct numerical classification of selectivities in the feed injection point. However, this parameter alone is not enough to evaluate the utilization of an adsorbent, it is also crucial to study the selectivities between the components in the different mixtures tested experimentally.

In the feed injection point (mixture **2**), it is important to ensure that sk/wk selectivity is the highest possible to guarantee a proper separation between the components with higher affinity for the solid. The $sk/ww+1$ and ss/ww also need to be as high as possible to ensure the separation of the sk over the remaining isomers. For this mixture it is also important to ensure that the sk/D selectivity is the highest possible to ensure that the desorbent found in the solid is replaced by this xylene.

The desorbent point (mixture **1**) is used to assess the separation performances in zones **1** and **4** of the process. As such, regarding zone **1**, it is necessary to ensure a sk/D selectivity as low as possible to guarantee that the sk component is desorbed from the solid and consequently transported by the liquid phase towards the extract outlet. Considering zone **4**, it is necessary to ensure a ww/D selectivity as high as possible to guarantee the adsorption of the weakest component and it is consequent transport by the solid phase towards the raffinate outlet.

The adsorption strength of the desorbent is classified in the desorbent point to verify whether the use of a given solid would facilitate the desorption of *para*-xylene through the replacement with the desorbent in zone **1**.

After the calculation of all parameters, the classification of the different adsorbents is made respecting the following order:

1. Numerical classification (Feed point) – From the lowest value (1234) to the highest (4321);
2. sk/wk selectivity (Feed point) – From the highest value to the lowest;
3. $sk/wk-1$ selectivity (Feed point) - From the highest value to the lowest;
4. sk/ww selectivity (Feed point) - From the highest value to the lowest;
5. sk/D selectivity (Desorbent point) – From the lowest value to the highest;
6. ww/D selectivity (Desorbent point) - From the highest value to the lowest;
7. sk/D selectivity (Feed point) - From the highest value to the lowest;

The adsorbents classification is shown in Table 9.

Through the analysis of this table, it is possible to conclude that 38 adsorbents are *para*-selective, 9 *ethylbenzene*-selective, 5 *meta*-selective and 8-*ortho* selective. A more detailed analysis allows to observe that there exist nine *para*-selective adsorbents with a numerical classification identical to the obtained industrially, **1234**. Concerning these solids, eight present a strong desorbent in the desorbent point, while FAU **9** presents an intermediate one.

From this point on, this report focuses only on the 38 *para*-selective adsorbents due to the following facts:

- *para*-xylene is the isomer with higher industrial interest
- Separation of *ethylbenzene* is not made by adsorption since it is not economically feasible
- Separation of *meta* and *ortho*-xylene is not made using *para*-diethylbenzene as the desorbent due to its weakness.

Concerning the 13 *meta* and *ortho* adsorbents, it may be interesting to study them in the future with a more suitable desorbent in order to analyze their potential.

Table 9 – Classification made for the adsorbents tested experimentally

Adsorbent	Feed injection Point						Desorbent Point	
	Num. Class	DS	$\alpha_{sk/wk}$	$\alpha_{sk/ww+1}$	$\alpha_{sk/ww}$	$\alpha_{sk/D}$	$\alpha_{sk/D}$	$\alpha_{ww/D}$
FAU 1	1234	0	2,48	3,73	3,87	1,46	0,68	0,15
FAU 2	1234	0	2,44	3,50	3,67	1,63	0,84	0,21
FAU 3	1234	0	2,32	3,18	3,27	1,52	0,88	0,27
FAU 4 (Ref)	1234	0	2,29	3,52	3,76	1,44	0,90	0,16
FAU 5	1234	0	2,27	3,61	3,64	1,10	0,51	0,13
FAU 6	1234	0	2,17	2,96	3,06	1,55	0,89	0,28
FAU 7	1234	0	2,16	3,22	3,22	1,15	0,67	0,28
FAU 8	1234	0	2,11	3,29	3,32	0,96	0,56	0,21
FAU 9	1234	1	2,02	3,17	3,35	1,35	1,12	0,31
FAU 10	1243	0	2,20	3,35	3,35	1,00	0,56	0,27
FAU 11	1243	0	1,91	3,50	3,74	0,66	0,82	0,21
FAU 12	1243	0	1,89	3,01	3,33	0,68	0,84	0,28
FAU 13	1243	0	1,82	3,02	3,11	0,90	0,77	0,21
FAU 14	1243	0	1,76	3,17	3,43	0,69	0,85	0,25
FAU 15	1243	0	1,62	2,83	3,07	0,79	0,75	0,23
FAU 16	1243	1	1,61	2,59	3,22	0,91	1,32	0,50
FAU 17	1243	0	1,59	2,31	2,63	0,79	0,97	0,34
FAU 18	1243	0	1,59	2,31	2,65	0,77	0,98	0,33
FAU 19	1243	0	1,44	2,21	2,40	0,74	0,97	0,34
FAU 20	1243	2	1,35	1,56	1,68	0,97	1,32	0,88
FAU 21	1243	3	1,19	1,48	1,59	1,75	2,06	1,29
FAU 22	1243	3	1,18	1,26	1,42	1,82	2,48	1,50
FAU 23	1243	3	1,18	1,26	1,42	1,82	2,08	1,54
FAU 24	1243	2	1,17	1,68	1,81	1,06	1,80	0,95
FAU 25	1243	2	1,15	1,78	2,05	1,10	1,83	0,95
FAU 26	1243	3	1,03	1,65	1,98	1,43	2,44	1,14
FAU 27	1243	2	1,02	1,44	1,56	1,21	1,70	0,94
FAU 28	1324	2	1,19	1,24	1,25	1,33	1,24	0,72
FAU 29	1324	2	1,02	1,03	1,05	0,79	1,51	0,99

FAU 30	1342	0	2,03	2,04	2,25	2,89	0,91	0,45
FAU 31	1423	1	1,61	1,65	1,86	1,27	1,45	0,85
FAU 32	1423	3	1,26	1,45	1,48	1,31	1,64	1,05
FAU 33	1423	3	1,25	1,48	1,50	1,34	1,75	1,15
FAU 34	1423	3	1,15	1,22	1,35	2,02	2,28	1,64
FAU 35	1432	3	1,42	1,66	1,81	1,68	1,76	1,04
FAU 36	1432	3	1,19	1,37	1,41	1,41	1,70	1,09
FAU 37	1432	3	1,11	1,44	1,49	1,41	2,19	1,57
FAU 38	1432	3	1,08	1,18	1,37	1,86	1,80	1,14
FAU 39	2143	2	1,23	1,27	1,80	1,67	1,59	0,89
FAU 40	2143	3	1,07	1,14	1,45	1,31	1,56	1,20
FAU 41	2143	2	1,06	1,34	1,47	0,91	1,54	0,72
FAU 42	2143	3	1,05	1,13	1,45	1,31	1,47	1,17
FAU 43	2143	2	1,05	1,36	1,74	1,05	1,12	0,65
FAU 44	2143	2	1,03	1,26	1,66	1,02	1,23	0,84
FAU 45	2143	2	1,02	1,25	1,66	1,00	1,25	0,85
FAU 46	2143	3	1,00	1,61	1,83	1,63	2,43	1,09
FAU 47	2413	3	1,38	1,61	2,12	3,00	2,49	1,20
FAU 48	3412	3	1,56	1,93	3,54	11,58	4,35	2,96
FAU 49	3412	3	1,39	2,88	7,08	14,46	17,82	4,54
FAU 50	3412	3	1,38	2,67	5,07	17,13	16,11	4,18
FAU 51	3412	3	1,28	1,54	2,07	1,93	2,31	1,78
FAU 52	3412	3	1,17	1,60	2,22	4,99	5,26	3,13
FAU 53	4132	3	1,27	1,34	1,61	2,20	2,78	2,16
FAU 54	4132	3	1,09	1,33	1,52	1,80	2,69	1,95
FAU 55	4213	3	1,17	1,24	1,24	2,75	2,56	2,21
FAU 56	4213	3	1,08	1,16	1,17	2,65	2,26	1,86
FAU 57	4213	3	1,07	1,16	1,18	2,51	2,31	1,96
FAU 58	4231	3	1,49	1,57	1,63	2,20	2,35	1,83
FAU 59	4312	3	1,04	2,08	2,97	5,68	7,60	2,60
FAU 60	4312	3	1,04	2,10	2,99	6,09	8,87	3,23

4.2 – *Para*-xylene selective adsorbents

In order to evaluate which *para*-selective adsorbents are of greatest interest to study in detail it is necessary to analyze their thermodynamic parameters that influence most the process performance.

4.3.1 – Thermodynamic parameters for performances

The utilization of an adsorbent for the *para*-xylene separation process at industrial level requires that the solid display certain thermodynamic parameters at different points in the SMB column. Experimentally, the two mixtures representative of the four zones of the SMB unit are the desorbent point (representative of zones **1** and **4**) and the feed injection (representative of zones **2** and **3**). To verify which of these *para*-selective adsorbents should be studied in further detail, it is necessary to compare their thermodynamic parameters with the ones of an adsorbent used industrially (titled as Faujasite **4**) in the mixtures mentioned above.

In order to facilitate the work and the comprehension of the results, it is assumed that, for the set of mixtures tested experimentally, *ortho*-xylene present a similar behavior as *meta*-xylene regarding the thermodynamic properties. As such, it is considered the average of the thermodynamic properties of these two compounds, which enables to work only with four compounds: PX, EB, MOX and PDEB.

To guarantee the proper performance of the process, it is necessary to ensure the separation between *para*-xylene and the remaining isomers in the feed injection point (mixture **2**). To this end, it is necessary that the adsorbents has, in this point of the process, high PX/EB and PX/MOX selectivities to guarantee that *para*-xylene is the only isomer adsorbed in these zones. It is then possible to state, in a first instance that, of the adsorbents tested, those who presents PX/EB and PX/MOX selectivities higher than the reference adsorbent (FAU **4**) are of interest to study in greater detail.

In order to analyze these thermodynamic parameters, the selectivities between the xylene isomers in the feed injection point obtained for the *para*-selective adsorbents are plotted in the figure shown below.

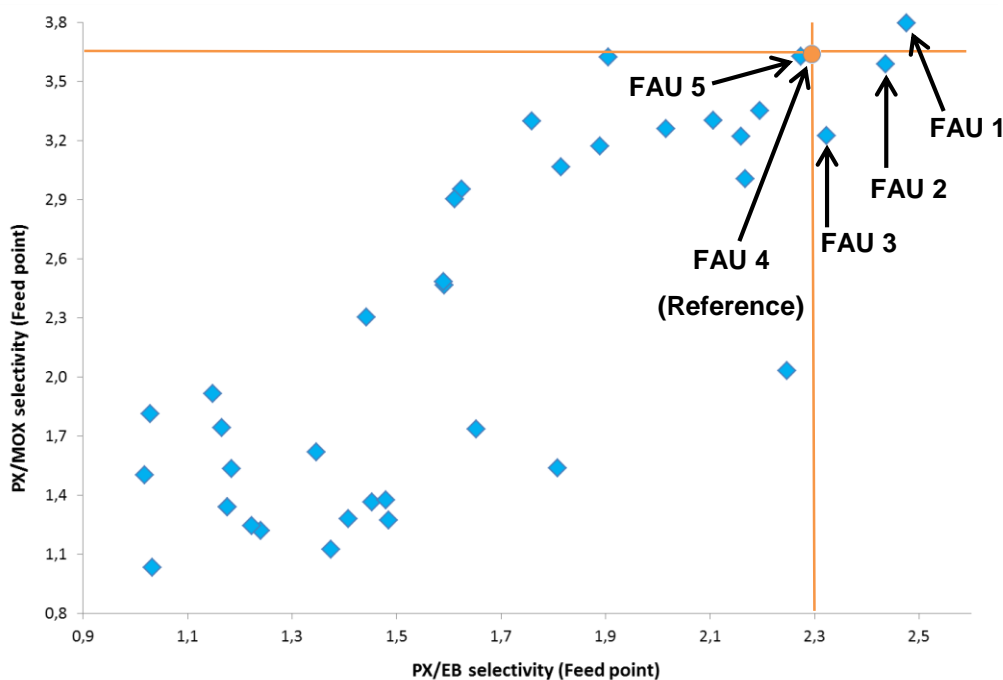


Figure 19 – Selectivities between the xylene isomers in the feed injection point obtained for the *para*-selective adsorbents

In Figure 19 it is possible to verify that only one of the adsorbents studied, FAU 1, presents a PX/EB and a PX/MOX selectivities higher than the reference adsorbent (FAU 4). However, since the selectivity between isomers that has greater impact on the xylene separation in this zone of the process is the PX/EB since these are the components with greater affinity for the solid, FAU 2 and FAU 3, despite having a PX/MOX selectivity lower than the one of the reference, appear to have appealing characteristics regarding the productivity of the process. Since FAU 5 presents similar selectivities values to FAU 4, it is also chosen to analyze the remaining thermodynamics characteristics of this adsorbent. No further study is conducted for the remaining *para*-selective adsorbents since their utilization would result in a poorer productivity than the obtained with the reference solid.

Regarding this point of the process, it is also necessary to ensure that *para*-xylene is adsorbed in detriment of *para*-diethylbenzene. As such, it is necessary that the adsorbents tested exhibit also a high PX/PDEB selectivity. It is then assumed that adsorbents which also present a value for this selectivity higher than the one of the reference (FAU 4) provide the desired separation of the components in zones 2 and 3 of the process.

In order to evaluate the separation of *para*-xylene from the isomers and the desorbent in the feed point, the PX/PDEB and PX/EB selectivities obtained for the solids FAU 1, FAU 2, FAU 3 and FAU 5 are plotted in Figure 20.

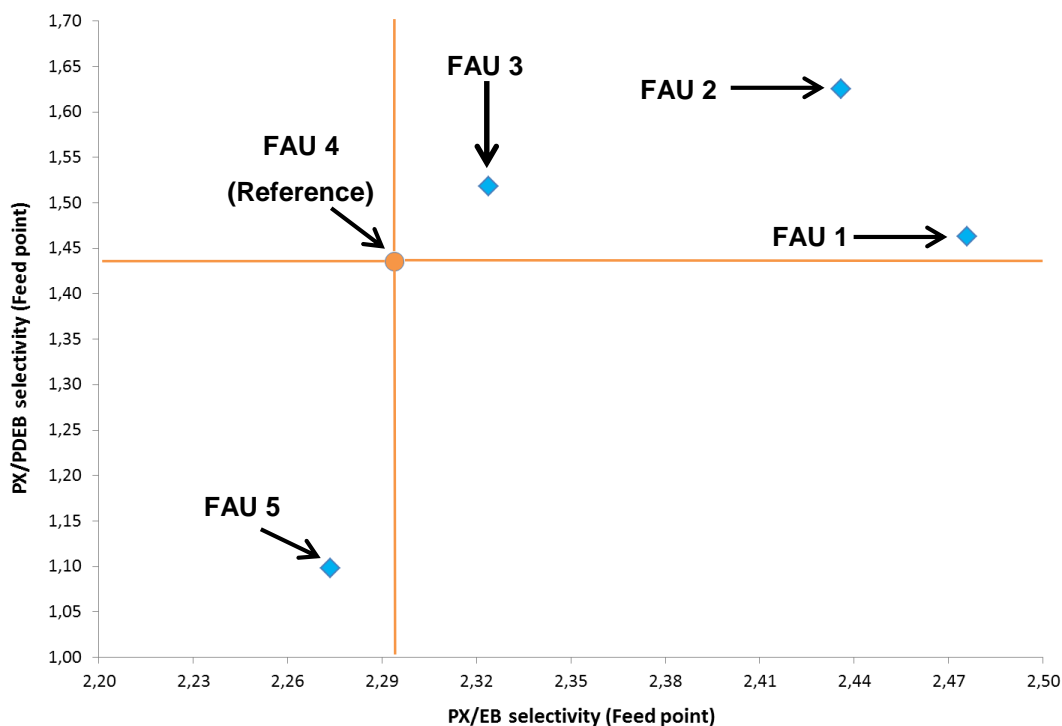


Figure 20 – PX/PDEB and PX/EB selectivities obtained for interesting *para*-selective adsorbents in the feed injection point

As can be observed in the figure above, three adsorbents exhibit higher PX/PDEB and PX/EB selectivities than the reference Faujasite: FAU 1, FAU 2 and FAU 3. Regarding the thermodynamic parameters in the feed injection point, it appears that FAU 1 is the best candidate of the adsorbents studied given that it presents, for the three critical thermodynamic parameters addressed, more satisfying values than the ones obtained for FAU 4. However, it is also considered that the utilization of FAU 2 and FAU 3 result in a gain of productivity since only the PX/MOX selectivity is lower than the obtained for the reference adsorbent. On the other hand, the use of FAU 5 is discarded once the values for all its critical selectivities are lower than those obtained with FAU 4.

Although the adsorbents mentioned appear to be the ones that deserved a more detailed study, it is still necessary to analyze their critical thermodynamic parameters in the desorbent point, mixture used for studying the behavior of the solids regarding zones 1 and 4 of the process.

To guarantee that *para*-xylene in zone 1 is desorbed from the solid through the replacement by the desorbent, it is necessary that the adsorbent exhibit a low PX/PDEB selectivity in this mixture. Regarding zone 4, it is necessary to ensure that the components with lowest affinity are adsorbed in the solid so that the liquid phase that reaches the end of this zone is only composed of desorbent. As such, it is necessary that the adsorbents tested also exhibit a high MOX/PDEB selectivity in the desorbent mixture.

It is then possible to affirm that the adsorbents that present higher MOX/PDEB and lower PX/PDEB selectivities than the reference would provide a gain in desorbent consumption. In order to

evaluate these two adsorption phenomena, the PX/PDEB and MOX/PDEB selectivities obtained for these solids are plotted in Figure 21.

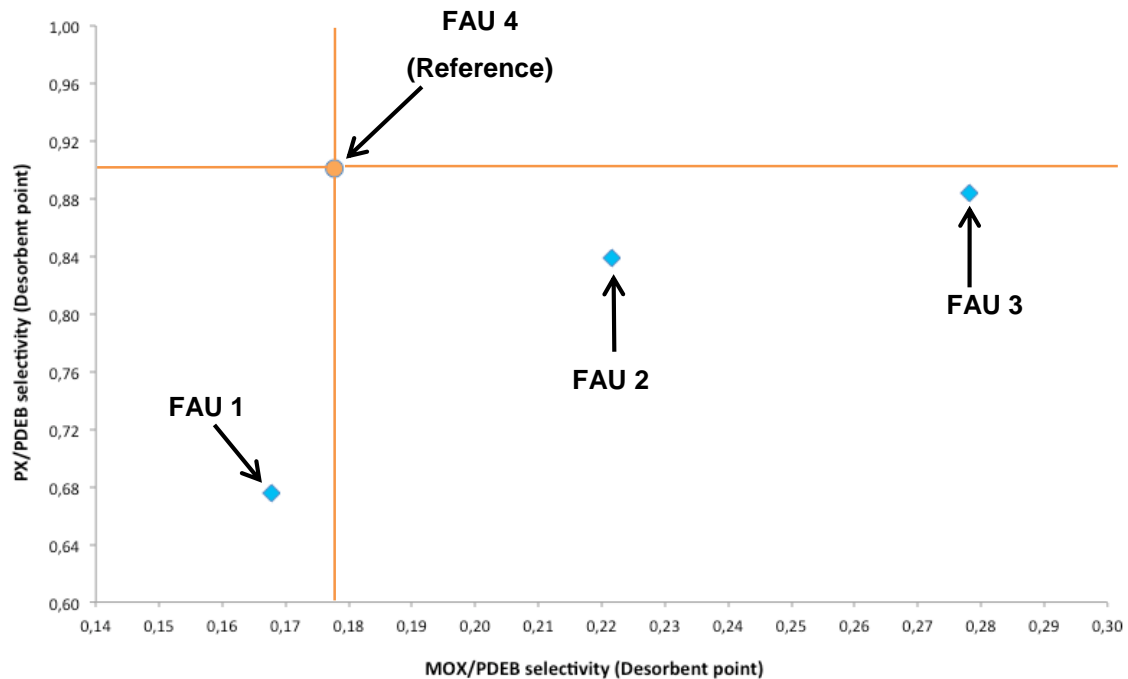


Figure 21 - PX/PDEB and MOX/PDEB selectivities obtained for the more interesting *para*-selective adsorbents in the desorbent point

It is possible to observe in Figure 21 that the three adsorbents exhibit PX/PDEB selectivities in the desorbent point lower than the reference solid, which indicates that their utilization would result in gain of desorbent consumption regarding zone 1. Considering the adsorption phenomena that occur in zone 4, it is possible to observe that FAU 2 and FAU 3 present higher MOX/PDEB selectivities than FAU 4, which consequently results in the pretended adsorption of the weakest components in this zone. However, the selectivity obtained for FAU 1 is lower than the one of FAU 4, meaning that regarding this zone, the use of this adsorbent would not result in a gain of desorbent consumption.

4.3.2 – Selection of adsorbents for further study: two parameter selectivity model

When considering all the thermodynamic parameters analyzed, PX/PDEB, PX/EB and PX/MOX selectivities in the feed injection point and PX/PDEB and MOX/PDEB for the desorbent point, no adsorbent presents all these selectivities with superior values than the reference solid. However, FAU 1, FAU 2 and FAU 3 present, for four of these parameters, values more attractive than the industrial adsorbent (FAU 4), which is an indicator that, concerning the thermodynamic characteristics, these solids deserve a more detailed study.

With regard to the industrial implementation of an adsorbent, it is necessary that its thermodynamic characteristics translate into a satisfactory process performance, otherwise there is no interest in its implementation. As such, to evaluate in a first instance the performances obtained for the different adsorbents, it is applied the Limit Flow Rate Approach. This theoretical approach allows the prediction, through the use of reduced flow rates, of the feed and desorbent flow rates of the process, indicators of productivity and desorbent consumption.

Since the experimental tests were conducted only with three mixtures, it is necessary to create a thermodynamic model that represent, in the most realistic way, the behavior of the xylenes selectivity along the entire SMB column.

Having only three mixtures tested experimentally, desorbent point (mixture **1**), feed injection point (mixture **2**) and a quaternary mixture without the presence of PDEB (mixture **3**), it is not possible to build a very complex and precise selectivity model. As such, it is opted to build a simplified model with two parameters, titled as **2P2M** model, where it is considered that the variation of the xylenes selectivities are dependent only of the PDEB composition along the column, as it is possible to observe through the following equation:

$$\alpha_{i/PDEB} = a_i x_{PDEB} + b_i \quad (43)$$

In order to build this model, it is applied a linear regression to the PX/PDEB, EB/PDEB and MOX/PDEB selectivities in function of *para*-diethylbenzene composition in the desorbent and feed injection mixtures. Although it is recognized the importance of the quaternary mixture in assessing the behavior of the isomers selectivities, it is decided to consider only these two mixtures for the model constructed so as to have the lowest associated error for the selectivities near these two critical points of the process.

The parameters obtained for FAU **1**, FAU **2**, FAU **3** and FAU **4** (reference) are found in Table 23 in the appendices.

After the construction of this model, it is applied the Limit Flow rate Approach in order to obtain Ω_F (indicator of productivity) and Ω_D / Ω_F (indicator of desorbent consumption) parameters for the three appealing adsorbents (FAU **1**, FAU **2** and FAU **3**) and the reference solid (FAU **4**).

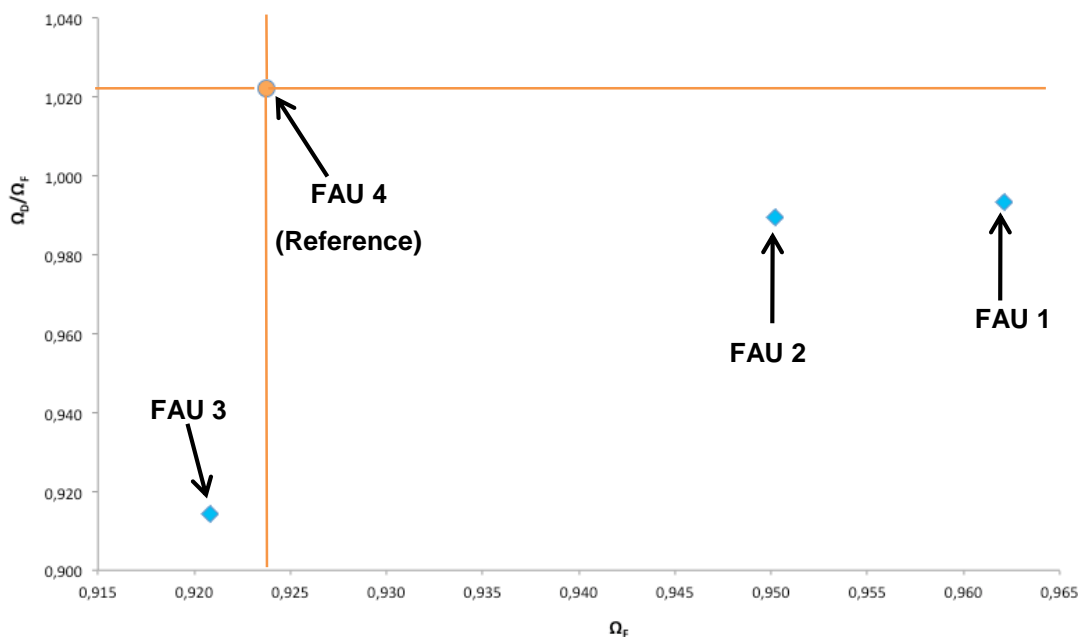


Figure 22 – Ω_F and Ω_D/Ω_F parameters obtained for appealing *para*-selective adsorbents

Figure 22 shows that, of the three appealing adsorbents, only FAU 1 and FAU 2 present more attractive values of Ω_F and Ω_D/Ω_F than the reference solid, while FAU 3, despite having the lowest desorbent consumption, presents a lower productivity than FAU 4. In this figure it is also possible to observe that, of the adsorbents studied, FAU 1 is the one that presents higher productivity, and since the desorbent consumption obtained for this solid and for FAU 2 are similar, it is concluded that in a first analysis with a theoretical approach, FAU 1 is, of all adsorbents studied, the one that presents the most appealing characteristics.

To emphasize the relationship between the selectivities and process performances, it is compared the different values obtained for FAU 1, FAU 2 and FAU 3 with FAU 4 in Table 10.

Table 10 – Deviations between the values of the best adsorbents and FAU 4 obtained for the critical selectivities and performance parameters

Adsorbents	Gain of selectivity in the desorbent point		Gain of selectivity in the feed injection point			Performance parameters (LFR)	
	$\alpha_{PX/PDEB}$	$\alpha_{MOX/PDEB}$	$\alpha_{PX/EB}$	$\alpha_{PX/MOX}$	$\alpha_{PX/PDEB}$	Ω_F	Ω_D/Ω_F
FAU 1	-25,0%	-5,6%	7,9%	4,4%	1,9%	4,2%	-2,8%
FAU 2	-6,9%	24,7%	6,2%	-1,5%	13,2%	2,9%	-3,2%
FAU 3	-1,9%	56,5%	1,2%	-11,4%	5,8%	-0,3%	-10,5%

As mentioned above, FAU 1, FAU 2 and FAU 3 exhibit, for the five critical thermodynamic parameters studied, only one with a less favorable value than FAU 4, the reference solid. In the case of FAU 1, this parameter corresponds to the MOX/PDEB selectivity in the desorbent point, which

affects the gain in desorbent consumption obtained for this solid. Regarding FAU 2 and FAU 3, the less appealing parameter corresponds to the PX/MOX selectivity in the feed injection point, which results in a lower productivity than the obtained with FAU 1.

As it is possible to observe in Table 10, these three adsorbents present a lower desorbent consumption when compared to FAU 4, however, only FAU 1 and FAU 2 present higher productivity than the reference case. As such, it is chosen to conduct more detailed studies only on these two adsorbents.

Through this table it is also possible to validate the Limit Flow Rate approach for the selection of the adsorbents with more appealing thermodynamic characteristics. Regarding the process productivity, it is possible to observe that FAU 1, the solid with the most appealing parameters in zones 2 and 3 (feed injection point), has the best performance regarding the parameter Ω_F . While FAU 3, the solid with the lowest thermodynamic parameters in the same mixture, is the one with the worst productivity. It is observed that the Limit Flow Rate approach presents also logical results regarding the desorbent consumption given that the use of the adsorbent with the most appealing thermodynamic parameters in zones 1 and 4, FAU 3, results in the lowest Ω_D/Ω_F ratio whereas FAU 1, the only adsorbent with lower MOX/PDEB selectivity than the reference, has the highest ratio of all the solids tested.

Once validated, the Limit Flow Rate approach becomes very useful for the selection of the adsorbent with the most interesting characteristics for the *para*-xylene separation process since it is a tool with a fast and simple utilization, being no longer needed the use of a simulator with elevated computation time for all the adsorbents tested experimentally.

It is then carried out a more detailed study on FAU 1 and FAU 2 to verify if these adsorbents had the characteristics that justify their industrial implementation.

4.3 – Four parameter thermodynamic model

For the more detailed study of FAU 1 and FAU 2, it was decided to conduct further experimental tests on these adsorbents with an additional set of mixtures, which consist of four points that corresponded to typical compositions of the feed injection (mixture **A**), extract withdrawal (mixture **B**), raffinate withdrawal (mixture **C**) and a mixture with equal composition of all the isomers and *para*-diethylbenzene. The selectivities for these mixtures are obtained by the average of the values obtained through the experimental simplified breakthrough and reverse breakthrough results. The compositions of this new set of mixtures are found in Table 25 in the appendices.

The study concerning the potential of FAU 1 and FAU 2 for the *para*-xylene separation process is done through the comparison between the performances obtained upon the utilization of these adsorbents with the ones of the adsorbent currently used industrially, titled as FAU 0. The

performance parameters are obtained through a simulator based on FORTRAN that was developed in *IFPE*n which requires the thermodynamic parameters of the used adsorbent as input.

The thermodynamic parameters for the adsorbents FAU **1** and FAU **2** had already been obtained for the model **2P2M**. However, a model built through a linear regression between only two points of the process and which considers that the behavior of the xylenes selectivities is only described by the variation of the composition of only one component (PDEB) may present significant errors in the description of the thermodynamic parameters of a such complex process.

As such, it is built a new model to estimate the thermodynamic parameters of the xylene isomers, this time through the use of the selectivities obtained for the new set of mixtures. For these set, several models were tested with a number of parameters varying between two and four. After the comparison of the values obtained through the different modeling and the experimental selectivities, it is decided to continue the study of FAU **1** and FAU **2** with a four parameters mode, titled as **4P4M** that considers that the behavior of the xylene selectivities is described by the compositions of *para*, *meta/ortho*-xylene and ethylbenzene through the following expression:

$$\alpha_{i/PDEB} = a_i + b_i x_{PX} + c_i x_{EB} + d_i x_{MOX} \quad (44)$$

To build this thermodynamic model it is necessary to apply the least square method. Being necessary to calculate first the squared error between the experimental selectivities and the ones obtained through the modeling. This calculation is made for the different selectivities in the four mixtures through the use of the following equation:

$$Error = \sum (\alpha_{Experimental} - \alpha_{modelling})^2 \quad (45)$$

This method is then applied through the minimization of the squared errors sum using the thermodynamic model parameters as design variables by the use of solver, a tool of the *Microsoft Excel* software. The parameters obtained for FAU **1** and FAU **2** with this model are found in Table 26 in the Appendices.

4.3.1 – FAU **0**

As previously mentioned, the objective of this work is to compare the process performances obtained while using FAU **1** or FAU **2** with the ones obtained by the use of FAU **0**, an adsorbent currently used in industrial units. To perform this comparison it is necessary to obtain firstly the thermodynamics parameters of the **2P2M** and **4P4M** thermodynamic models for the industrial solid.

It is not performed experimental measures of the thermodynamic parameters of FAU **0** for the set of mixtures used in the **2P2M** and **4P4M** models. However, a complete thermodynamic model, titled as Full model (**FM**), was already built in *IFPE*n for this adsorbent, based on a large number of selectivity measurements obtained for different compositions representative of a profile obtained on a

pilot plant. This model, described by a quadratic correlation, allows the calculation of the xylene isomers selectivity along the SMB column without associated errors.

Through the use of this quadratic correlation, the selectivities concerning the six mixtures used to build the models **2P2M** and **4P4M** are calculated for FAU **0**. Through these values it was then possible to obtain the thermodynamic parameters of these models for FAU **0** (Table 24 and Table 27 of the appendices).

4.4 – Simulation of adsorbents

TMB simulations are carried out in the present work with two distinct purposes. In a first instance, these are conducted for the industrial adsorbent FAU **0** with the three models in order to assess whether the utilization of the models **2P2M** and **4P4M** result in similar performances to those obtained with the more complete and realistic model (**FM**). After, simulations are performed for FAU **1** and FAU **2** in order to compare the performances obtained for these solids with the ones of the industrial adsorbent.

For the performance of all the simulations made, it is used a set of operational parameters as close as possible to the ones of a typical industrial *para*-xylene separation process. It is worth noting that the only sets of parameters changed for each simulation were the density of the solid and the thermodynamic parameters, which are dependent on the adsorbent and model used.

4.4.1 – Validation of the simplified models

As previously mentioned, before running simulations on the adsorbents tested experimentally with the simplified models, it is first necessary to conduct a set of simulations with the reference solid to assess the validation of these models. The use of this adsorbent result in performances only influenced by the thermodynamic models, since the selectivities used to obtain the thermodynamic parameters are calculated by the quadratic correlation of the **FM** model instead of being obtained experimentally.

The simulation performed with the solid FAU **0** using the **FM** model is defined as the reference case.

Reference simulation

In order to initialize the reference simulation, it is necessary to have an initial estimation of the four process zones flow rates. As such, the reduced flow rates obtained through the Limit Flow Rate approach for FAU **0** using the **FM** model were used as initial design variables after being converted into volumetric flow rates.

The utilization of these flow rates result in a poor performance, being obtained constraints with values far from the imposed industrially. Therefore, it is necessary to optimize this simulation through the strategy explained in chapter 3.4.3, with the objective of maximizing the productivity and minimizing the desorbent consumption of the process while respecting the constraints imposed for the yield (97,00%) and purity (99,80%) of *para*-xylene in the extract outlet, using only the flow rates of the different SMB zones as design variables.

The performance parameters obtained for the first and optimized simulations are shown in Table 11.

Table 11 –Performance parameters obtain for the initial and optimized simulations of FAU **0** using the **FM** model with a **3-6-4-2** configuration and a switching time of 82 s

Simulation	Initial	Optimized
Feed (cc/min)	43,94	63,16
Desorbent flow rate (cc/min)	44,71	58,39
Productivity (kg_{PX}/h/m³)	69,95	116,37
D/F	1,02	0,92
Purity (%)	97,87	99,80
Yield (%)	84,34	97,00

As it is possible to observe in this table, the use of flow rates obtained through the Limit Flow Rate approach result in a poor performance, both in respect of the constraints as to the performance parameters. Through the optimization process it is possible to increase the productivity in 66,4% and decrease the D/F ratio in 9,8%. It is possible to conclude that the use of the flow rates obtained through the theoretical approach as a first estimation of the design variables is not advised, which is expected since the LFR is a first approach that is not intended to give exact prediction of performances, but only for the comparing the performances obtained with different solids.

2P2M and 4P4M simulations

In the case of simulations performed for the models **2P2M** and **4P4M** for the same solid, it is used the flow rates obtained with the optimized simulation of the reference case as a first guess for the design variables. Ideally, the first simulation obtained for each models should result in a near optimized performance, however, it is necessary to adjust the design variables in order to obtain fully optimized simulation. The optimization process is performed according to the strategy previously explained.

The performance parameters obtained for optimized simulations using the two simplified models for the adsorbent FAU **0** are shown in Table 12.

Table 12 - Performance parameters obtain for the optimized simulations of FAU **0** using the different thermodynamic models with a **3-6-4-2** configuration and a switching time of 82 s

Model	FM	2P2M	4P4M
Feed (cc/min)	63,16	63,71	62,85
Desorbent flow rate (cc/min)	58,39	59,65	60,34
Productivity (kg _{Px} /h/m ³)	116,37	116,67	115,09
D/F	0,92	0,94	0,96
Purity (%)	99,80	99,80	99,80
Yield (%)	97,00	97,00	97,00

When comparing the parameters obtained for the optimized simulations with the models **2P2M** and **4P4M** it is possible to observe that the use of these models result in similar performances. The models validation is made by the comparison of the performances obtained for these models with the reference case. In order to facilitate the understanding of the analysis, the values obtained for the feed and desorbent flow rates, parameters used for this comparison, are normalized with the values obtained with the reference simulation.

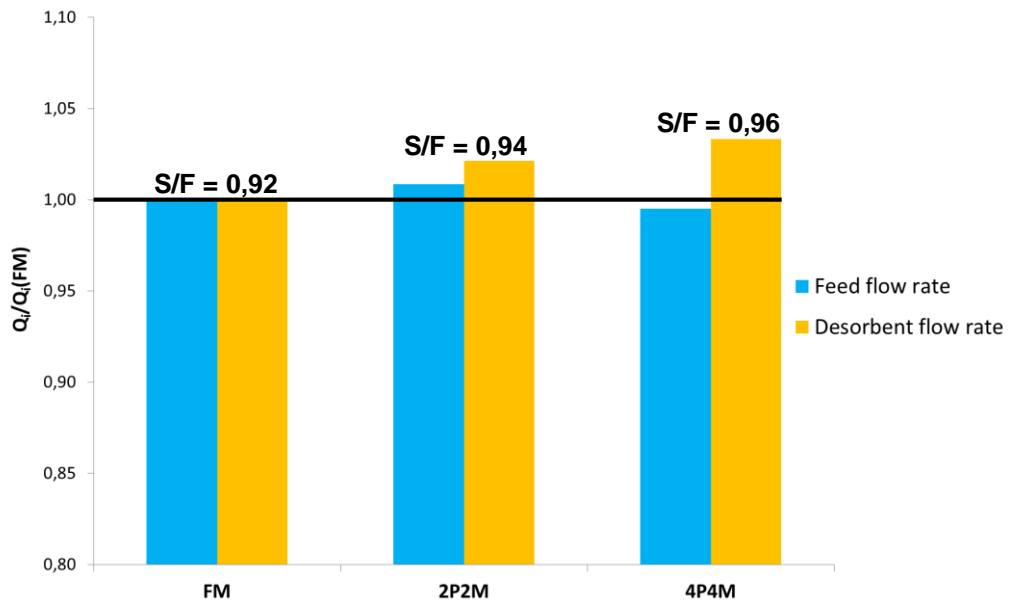


Figure 23 –Normalized feed and desorbent flow rates obtained for the optimized simulations of FAU **0** with the different models

As shown in Figure 23, the utilization of the **2P2M** and **4P4M** models for the solid FAU **0** result in similar performances to those obtained with the **FM** model. Considering the **2P2M** thermodynamic model, it is obtained a feed flow rate 0,9% higher than the obtained with the **FM** model, which indicates that this model is slightly non-conservative in regard to the productivity. With the use of this

model it is also obtained a desorbent flow rate 2,2% higher than the obtained for the reference case, indicating that this model is conservative in terms of desorbent consumption.

With the utilization of the **4P4M** model it is obtained a feed flow rate 0,5% lower than the obtained for the reference simulation, which indicates that the model is slightly conservative in regard to the productivity of the process. It is also obtained a desorbent flow rate 3,3% higher than the value obtained with the **FM** model, which allows the conclusion that this model is also conservative in respect to the desorbent consumption.

Since the use of the **2P2M** and **4P4M** results in almost identical performances to the obtained with the reference case, it is not possible to select the simplified model to be used in the simulations of the remaining solids solely analyzing the process performances. Given that the validity of a model is not exclusively related to the process performances obtained, the concentration profiles obtained for the simulations performed with these three models are compared.

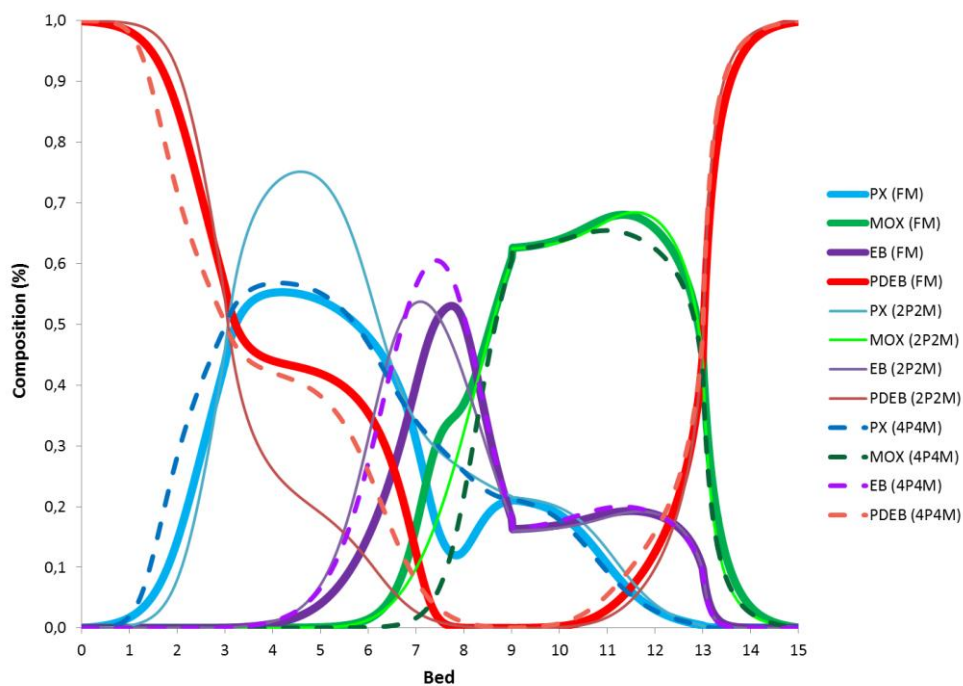


Figure 24 – Concentration profiles obtained for FAU 0 through simulations using different thermodynamic models

Through a first analysis of Figure 24, it is possible to affirm that, despite the similarities between the performances parameters obtained by the reference case, **2P2M** and **4P4M** models, their concentration profiles are quite distinct. Regarding the concentration profile obtained for the reference simulation, it is possible to verify that the only components present in zone 1 are, as expected, *para*-xylene and *para*-diethylbenzene, being the presence of the first in the liquid phase beginning to be noticed after the first bed. The remaining xylene isomers start to appear in the liquid phase after bed 5 as a result of desorption from the adsorbent. In the same concentration profile it is possible to observe

that in the raffinate outlet, situated in bed **13**, there is no *para*-xylene, as expected. Finally, it is also possible to observe that in zone **4** the weakest components are successfully adsorbed.

In the same figure, it is possible to observe that the **2P2M** model can correctly predict the behavior of the xylenes in zones **3** and **4**. However, in the first two zones of the process, the profiles obtained deviates significantly from the profiles of the reference case. Regarding the first zone, it is found that for the **2P2M** model, *para*-xylene is desorbed later than for the **FM** model. The major differences between these two models take place in the second zone of the process, where it is verified, between beds **3** and **6**, a much higher concentration of *para*-xylene for the **2P2M** model. For the remaining isomers it is possible to observe a displacement of concentration between beds **5** and **9**.

Regarding the **4P4M** model, there is a lower overall deviation as compared to the profile obtained with the **2P2M** model, however, this deviation occurs in three zones of the process. In the first zone of the process it is identified a greater desorption of *para*-xylene compared to the reference simulation. For zone **2**, this model do not fit the concentrations of the weakest components between beds **5** and **9**, having been obtained a higher concentration of ethylbenzene and a displacement of *meta/ortho*-xylene. Finally, it is also possible to verify that this model have difficulties to adjust to the concentrations of *para*-diethylbenzene and *meta/ortho*-xylene between beds **10** and **13** of the third process zone.

The use of the **2P2M** and **4P4M** thermodynamic models results in similar process performance to those obtained for the reference case, which indicates that these simplified models can be applied to the remaining solids studied in this work. Since both models present different flaws in the description of the concentration profiles, it is not possible to identify which model result in more realistic performances. Therefore, it is opted to perform the simulations of FAU **1** and FAU **2** with both thermodynamic models.

4.4.2 – Performances of FAU 1 and FAU 2: 2P2M model

Simulations for the solids FAU **1** and FAU **2** are then performed with the use of the **2P2M** thermodynamic model. These are executed analogously to those performed previously, being first necessary to insert the thermodynamic parameters of the model and the adsorbents properties. It is used the flow rates obtained for the reference simulation (FAU **0** with **FM** model) for initial values of the design variables. The process is optimized by strategy previously explained in order to obtain the imposed constraints while maximizing the process productivity and minimizing the desorbent consumption.

The performance parameters obtained for optimized simulations obtained for the adsorbents FAU **1** and FAU **2** using the thermodynamic model **2P2M** are shown in Table 13.

Table 13 - Performance parameters obtain for the different adsorbent using the **2P2M** simplified model with a **3-6-4-2** configuration and a switching time of 82 s

Adsorbent	FAU 0	FAU 1	FAU 2
Feed (cc/min)	63,71	71,73	69,53
Desorbent flow rate (cc/min)	59,65	51,41	53,26
Productivity (kg _{Px} /h/m ³)	116,67	131,34	127,36
D/F	0,94	0,72	0,77
Purity (%)	99,80	99,80	99,80
Yield (%)	97,00	97,00	97,00

The performances obtained for FAU 1 and FAU 2 are then compared with those obtained for FAU 0, the reference adsorbent, since there is only an interest in these solids if their use results in superior performances to the obtained with the adsorbent currently used industrially. For this purpose, the feed and desorbent flow rates obtained for FAU 1 and FAU 2 are normalized with the values obtained for FAU 0.

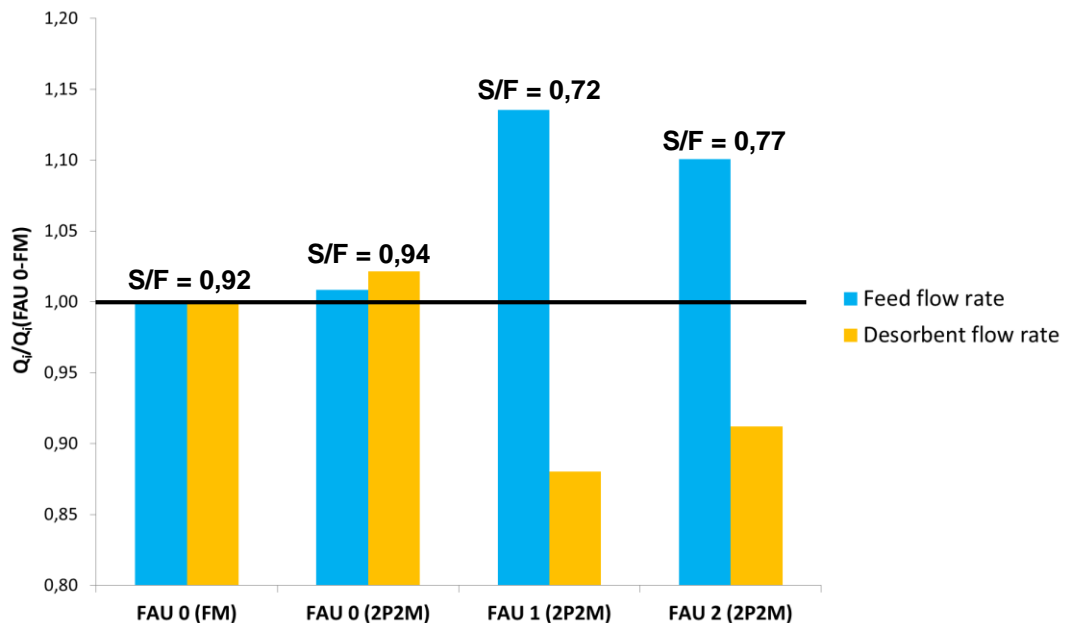


Figure 25 - Normalized feed and desorbent flow rates obtained for the optimized simulations of FAU 1 and FAU 2 with the **2P2M** thermodynamic model

As shown in Figure 25, the simulations of FAU 1 and FAU 2 with the **2P2M** model results in superior performances to those obtained with the reference adsorbent, FAU 0, which indicates that both solids are good candidates to replace the reference solid for the *para*-xylene separation process.

Considering FAU 1, it is obtained a feed flow rate 13,6% higher and a desorbent flow rate 12% lower than the obtained for the reference case. While the use of FAU 2 resulted in a feed flow rate 10,1% higher and a desorbent flow rate 8,8% lower than the values obtained with FAU 0. It is then

possible to state that both solids exhibited superior performances than the obtained for industrial adsorbent and that between the two solids, FAU 1 is the one that shows a superior performance.

4.4.3 – Performances of FAU 1 and FAU 2: 4P4M model

Lastly, simulations for the solids FAU 1 and FAU 2 are performed with the use of the **4P4M** thermodynamic model in order to verify if the results obtained with the **2P2M** model are reproducible. These simulations are executed analogously to those performed for the **2P2M** simplified model, being used the flow rates obtained for the reference simulation (FAU 0 with **FM** model) as a first approximation of the design variables. The process is optimized by the same strategy to obtain the imposed constraints while maximizing the process productivity and minimizing the desorbent consumption.

The performance parameters of the optimized simulations obtained for the adsorbents FAU 1 and FAU 2 using the thermodynamic model **4P4M** are shown in Table 14.

Table 14 - Performance parameters obtain for the different adsorbent using the **4P4M** simplified model with a **3-6-4-2** configuration and a switching time of 82 s

Adsorbent	FAU 0	FAU 1	FAU 2
Feed (cc/min)	62,85	40,23	56,92
Desorbent flow rate (cc/min)	60,34	52,25	56,88
Productivity (kg_{PX}/h/m³)	115,09	73,67	104,24
D/F	0,96	1,30	1,00
Purity (%)	99,80	99,80	99,80
Yield (%)	97,00	97,00	97,00

The performances obtained with FAU 1 and FAU 2 are then compared with the ones of the industrial adsorbent. For this purpose, the feed and desorbent flow rates obtained for FAU 1 and FAU 2 are normalized with the values obtained for FAU 0.

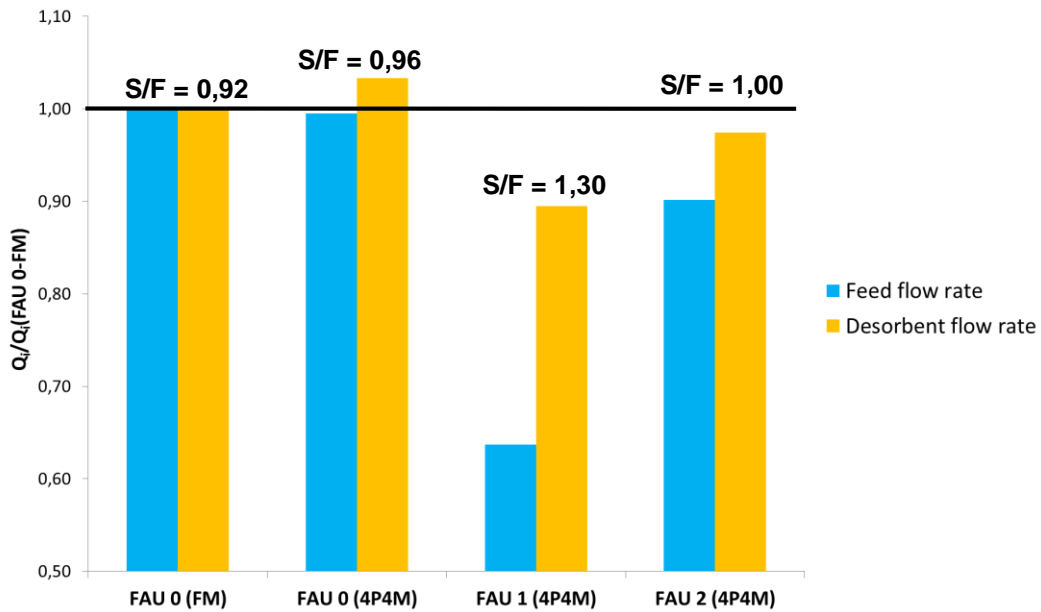


Figure 26 - Normalized feed and desorbent flow rates obtained for the optimized simulations of FAU 1 and FAU 2 with the **4P4M** thermodynamic model

As shown in Figure 26, the simulations of FAU 1 and FAU 2 with the **4P4M** model result in inferior performances to those obtained with the reference adsorbent, FAU 0, the opposite of what is indicated with the **2P2M** model. Considering FAU 1, it is obtained feed and desorbent flow rates 36,3% and 10,5% lower than the ones for the reference case. While the use of FAU 2 results in feed and desorbent flow rates 9,9% and 2,6% lower than the values obtained with FAU 0. It is possible to conclude that, despite showing lower desorbent flow rates than FAU 0, both adsorbents exhibit worse performances than the obtained for the industrial adsorbents. Lastly, between the two solids, FAU 2 presents a superior performance.

4.4.4 – Comparison between the results obtained with the simplified models

In order to evaluate the results obtained for the simulations performed for the three solids with different thermodynamics, the normalized feed and desorbent flow rates obtained for the different simulations are summarized in Table 15.

Table 15 - Summary of the normalized feed and desorbent flow rates obtained for the three adsorbents with different thermodynamic models

Adsorbent	Feed flow rate ($Q_i/Q_{reference}$)			Desorbent flow rate ($Q_i/Q_{reference}$)		
	FM	2P2M	4P4M	FM	2P2M	4P4M
FAU 0	1,00	1,01	1,00	1,00	1,02	1,03
FAU 1	-	1,14	0,64	-	0,88	0,89
FAU 2	-	1,10	0,90	-	0,91	0,97

Regarding the reference adsorbent, FAU **0**, it is observed that the performances obtained with both simplified thermodynamic models are similar to the one obtained for the reference simulation, which indicates that the use of these models for the simulations of remaining adsorbents would result in similar performances. However, as it is observed in this table, the results obtained for the tested adsorbents with the two models are quite distinct, mainly in regard to the feed flow rate, where it is obtained a gain of productivity with the **2P2M** model and a loss with the **4P4M**. Concerning the desorbent flow rate, in spite of obtaining slightly different values, it is obtained for both models a gain of desorbent consumption. Therefore, it is concluded that the difference between the performances obtained is not due to the thermodynamic models but to the selectivities used for the calculation of their parameters.

In order to confirm this hypothesis, new experimental measurements were conducted with a new FAU **1** for the feed injection point mixture used in the estimation of the parameters of the **4P4M** model. The selectivities obtained for the different measurements are found in Table 16.

Table 16 - Selectivities obtained for mixture **A** (feed injection) with FAU **1**

Measurement	$\alpha_{PX/PDEB}$	$\alpha_{EB/PDEB}$	$\alpha_{MX/PDEB}$	$\alpha_{OX/PDEB}$
Original	1,25	0,63	0,39	0,39
Repetition	1,49	0,61	0,41	0,41

It is then observed that the PX/PDEB selectivity obtained for the original measurement is significantly lower than the obtained for the repetition measurement made with a new FAU **1**, while the remaining selectivities between the isomers and the desorbent remained constant. The PX/PDEB selectivity obtained for the original measurement explains the lower feed flow rates obtained with the use of the **4P4M** model since this is a critical selectivity for the productivity of the process.

The difference between the PX/PDEB selectivities obtained for the two measurements is explained by the higher hydration of the FAU **1** solid used in the original measurement, which result from the multiple tests conducted on this original adsorbent. Given that between each test performed the unit is stopped and the temperature of the column where the adsorbent is found along with a given mixture is decreased to the room temperature, which favors the adsorption of water molecules in the solid. The co-adsorption of water is known to lead to the decrease of *para*-xylene adsorption, which explains the consequent decrease of PX/PDEB selectivity in the subsequent experimental tests. The repetition measurements were made with an FAU **1** with a similar water content to the one used at industrial level, which makes the selectivities obtained for this solid to be more close to those found in the industrial process.

The experimental selectivities obtained for mixture **2** (feed injection) and used to obtain the parameters of the **2P2M** thermodynamic model for FAU **1** are shown in Table 17.

Table 17 - Selectivities obtained for mixture **2** (feed injection) with FAU **1**

$\alpha_{PX/PDEB}$	$\alpha_{EB/PDEB}$	$\alpha_{MX/PDEB}$	$\alpha_{OX/PDEB}$
1,47	0,59	0,39	0,38

In respect to the **2P2M** thermodynamic model, the selectivities used for obtaining the parameters for the adsorbent FAU **1** are similar to those obtained for the repetition measurement of mixture **A**, which leads to the conclusion that the simulations performed with the **2P2M** model results in the most reliable performance between the two models. As such, it is possible to affirm that both FAU **1** and FAU **2** are good candidates to replace FAU **0** at industrial level and that between both solids, being the best performance obtained with the use of FAU **1**.

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5. Conclusions and perspectives

The objective of this study was to analyze the adsorption behavior of new adsorbents prepared experimentally in IFPEN under conditions representative of the industrial application to provide insight into the performance of these materials when they are implanted in the *para*-xylene separation process.

Since not all of the adsorbents prepared experimentally were of interest to the *para*-xylene separation process, it was conducted a classification of these solids based on the selectivities measured experimentally that allowed the conclusion that of all the adsorbents tested, 38 were *para*-selective, 9 *EB*-selective, 5 *meta*-selective and 8 *ortho*-selective.

It was then decided to analyze only the *para*-selective adsorbents since this work is focused solely on the *para*-xylene separation process. Through the comparison of critical selectivities obtained for the tested adsorbents and a reference (FAU 4) in two distinct points of the SMB process, it was found that the use of FAU 1, FAU 2, and FAU 3 could result in more satisfying performances than the obtained with the reference solid. To confirm this hypothesis, the Limit Flow Rate approach was applied for these adsorbents as to calculate a first prediction of their process performances. After the comparison of the results obtained with the ones of FAU 4, it was possible to conclude that two adsorbents, FAU 1 and FAU 2, appeared to be good candidates to replace the reference adsorbent at industrial level since their use resulted in gains of productivity and of desorbent consumption. The results obtained also allowed to validate this theoretical approach for the selection of the adsorbents with more appealing thermodynamic characteristics since the results obtained were consistent with the first selectivity analysis performed. Therefore, it is possible to affirm that this theoretical approach is a very useful tool regarding the adsorbents selection, since it allows a first prediction of the adsorbents performances in a very simple and fast way, contrary to use of the *FORTRAN* simulator which requires significant calculations time.

In order to calculate the selectivities of the different adsorbents along the SMB column, two simplified thermodynamic models were created, a first based on the selectivities measured for two experimental mixtures (feed injection and desorbent points) which considered that the variation of the xylenes selectivities was dependent only on the PDEB composition, titled as **2P2M**, and a second based on four experimental mixtures (feed injection, extract withdrawal, raffinate withdrawal and iso-quaternary points) which considered that the different selectivities varied with the PX, EB and MOX compositions, titled as **4P4M**.

Simulations were then carried out with two purposes, firstly these were performed for an industrial adsorbent, FAU 0, with three thermodynamic models to determine whether the utilization of the two simplified models (**2P2M** and **4P4M**) allowed to obtain similar results to those obtained with a more complete and realistic model, titled as **FM**. It was concluded that, in spite of obtaining distinct concentration profiles, the use of the two simplified models resulted in very similar performances to

those obtained with the **FM** model. Finally, simulations were performed for FAU **1** and FAU **2** with the use of both **2P2M** and **4P4M** models in order to compare the performances obtained for these solids with the ones of the industrial adsorbent. With the use of the **2P2M** model, it was obtained better performances for FAU **1** and FAU **2** than for the industrial adsorbent FAU **0**, in respect to both productivity and desorbent consumption, while the use of the **4P4M** model resulted in worst performances of FAU **1** and FAU **2** than for FAU **0** in respect to both parameters. Since both models were validated in simulations that are not affected by experimental errors and are only influenced by the thermodynamic models, it was concluded that the distinct performances obtained for the tested adsorbents were not due to the different models used, but due to the experimental selectivities used to obtain their parameters.

To confirm this hypothesis, new experimental selectivities measurements were conducted with a new FAU **1** for the feed injection mixture used in the estimation of the **4P4M** model parameters. When compared the selectivities values obtained for the original and repetition measurements, it was observed that the PX/PDEB selectivity obtained for the first measurement was significantly lower than the one obtained for the repetition while the other parameters remained constant. Therefore, it was concluded that the FAU **1** used for the estimation of **4P4M** parameters had a higher water content than the used industrially and as such, the use of this model would not be representative of the performances obtained industrially. Through the comparison between the selectivities used for the estimation of the **2P2M** model parameters and those obtained for the repetition measurement it was observed that their values were similar and therefore, it was possible to conclude that this model was obtained with more reliable selectivities.

Finally, it was possible to conclude that, since the performances obtained with the **2P2M** were the most reliable, the use of two tested adsorbents results in better performances than those obtained currently in the industrial process and therefore, these two adsorbents appear to be good candidates to replace FAU **0** at industrial level, being FAU **1** the adsorbent which results in the most satisfying values of productivity and desorbent consumption.

Concerning the continuation of the work done for this thesis, it is advisable to conduct new experimental selectivities measurements with a new FAU **1** for the feed injection mixture used in the estimation of the **4P4M** model parameters to confirm if the original solid test presented also elevated water content.

In order to obtain more realistic performances of the adsorbents FAU **1** and FAU **2**, new experimental tests should be conducted with mixtures representative of the two points where the **2P2M** model presents higher deviations from the concentration profile obtained for the reference thermodynamic mode: the point where EB composition is the highest (bed **8**) and a point representative of the first zone of the process.

Finally, the construction of a more complex model with the use of the selectivities obtained with the additional experimental points and the ones used for the **2P2M** model is advised, in order to confirm if FAU **1** and FAU **2** are good candidates to replace the industrial adsorbent used nowadays.

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