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New Processes and Adsorbents for *p*-Xylene Production

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by

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Abstract

p-Xylene (PX) is an essential intermediate in the industry, especially for the production of purified terephthalic acid (PTA) and dimethyl terephthalate (DMT), which are used for the production of polyester fibers, resins, and film. In 2016, the global *p*-xylene consumption accounted for 68.4% in Northeast Asia, most of which came from China. Asia continues to capture the market share of both global production and consumption. The worldwide *p*-xylene demand increases with an annual growth rate of 7.4 %. Maximizing the production of *p*-xylene is a troublesome task in the chemical engineering field due to the thermodynamic equilibrium of xylenes. The Simulated Moving Bed Reactor (SMBR) overcomes that problem by integrating the separation and isomerization in the same unit; in other words, the reaction and separation occur simultaneously. The SMBR has been studied as part of an aromatics complex, where a crystallization process was included for further purification of the high content PX ($\geq 70\%$) from the SMBR. Lower capital costs, energy consumption, and higher environmental and safety benefits are expected through the intensification of the process.

The combination of reaction and separation requires a tradeoff between the optimal operating conditions of both processes when performed separately. The optimum conditions for the SMBR are those where the temperature is high enough for the interconversion of xylenes without excessively reducing the adsorbent/adsorbate interactions. In this thesis, the SMBR was investigated at temperatures between 453 and 573 K, in the liquid phase. However, the information for both isomerization and separation at these conditions is very scarce, and the performance of adsorbents reported in the literature generally contained a certain amount of water. Thus, an experimental and parametric behavior study of xylene isomerization and the main side reactions that may occur in a SMBR for the production of *p*-xylene, was conducted

in the liquid phase over mono-functional acid beta zeolite with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (SAR) of 35 (BEA35). Additionally, the saturation capacity, the adsorption equilibrium constant, and the heat of adsorption of $\text{C}_6\text{-C}_8$ aromatics (*p*-xylene, *o*-xylene, *m*-xylene, ethylbenzene (EB), toluene, and benzene) were obtained over dry Ba-exchanged zeolite X through batch experiments.

Finally, the model of the SMBR was established based on the experimentally obtained parameters and investigated from the simulation and optimization point of view. The SMBR operation was modeled with the true moving bed reactor strategy with four different cases, respectively with EB involved or not in the feed, and toluene or benzene set as desorbent. Toluene showed better performance as desorbent and feed not involving EB worked more efficiently. The study and analysis of the energy saving improvement for the SMBR proved feasibility; energy can be reduced by 19% and profit increased by 4%. For the best case studied, an optimization based on costs resulted in yield of 127%, and productivity of 89 kg/h of PX per m^3 of solid at the operating temperature of 539 K with the configuration of 4-3-15-2.

Resumo

O *p*-xileno (PX) é um produto intermediário essencial na indústria, especialmente para a produção do ácido tereftálico purificado (PTA) e do tereftalato de dimetilo (DMT), que são usados para a produção de fibras de poliéster, resinas e películas. Em 2016, 68.4% do consumo global de *p*-xileno localizou-se no nordeste da Ásia, grande parte na China. A Ásia continua a ganhar cota na produção e no consumo global. A procura mundial de *p*-xileno aumenta com uma taxa de crescimento anual de 7.4%. Maximizar a produção de *p*-xileno é uma tarefa complicada no campo da engenharia química devido ao equilíbrio termodinâmico dos xilenos. O reator de leito móvel simulado (SMBR) supera esse problema integrando a separação e a isomerização na mesma unidade; por outras palavras, a reação e a separação ocorrem simultaneamente. O SMBR foi estudado como parte integrante de um complexo de aromáticos, onde também se incluiu um processo de cristalização para posterior purificação da corrente de saída do SMBR com alto conteúdo de PX ($\geq 70\%$). Custos de capital e consumo energético mais baixos, bem como maiores benefícios ambientais e de segurança, são esperados através da intensificação do processo.

A combinação de reação e separação requer um compromisso entre as condições ótimas de operação de ambos os processos, aquando realizados separadamente. De facto, as condições ótimas para o SMBR serão aquelas em que a temperatura é suficientemente alta para a conversão de xilenos sem reduzir excessivamente as interações adsorvente/adsorvato. Nesta tese, o SMBR foi investigado para temperaturas entre 453 e 573 K, em fase líquida. No entanto, a informação para isomerização e separação nestas condições é muito escassa, e o desempenho dos adsorventes reportados na literatura, é geralmente para adsorventes que contêm uma certa quantidade de água. Assim, um estudo experimental e paramétrico do comportamento da isomerização dos xilenos e das principais reações secundárias que podem ocorrer num SMBR

para a produção de *p*-xileno, foi conduzido em fase líquida sobre o zeólito beta na forma ácida com uma razão $\text{SiO}_2/\text{Al}_2\text{O}_3$ de 35 (BEA35). Adicionalmente, a capacidade de saturação, a constante de equilíbrio de adsorção e o calor de adsorção dos aromáticos $\text{C}_6\text{-C}_8$ (*p*-xileno, *o*-xileno, *m*-xileno, etilbenzeno, tolueno e benzeno) no zeólito X permutado com Ba foram obtidos através de experiências em adsorvedor fechado.

Finalmente, o modelo do SMBR foi estabelecido com base nos parâmetros obtidos experimentalmente e investigado do ponto de vista de simulação e otimização. A operação do SMBR foi modelada com a estratégia do reator de leito móvel verdadeiro em quatro cenários diferentes, com etilbenzeno envolvido ou não na alimentação, e tolueno ou benzeno usados como solvente. O tolueno apresentou melhor desempenho como solvente e o caso sem etilbenzeno apresentou um melhor desempenho. A análise da poupança no consumo energético do SMBR mostrou que este reactor é viável; de facto a energia pode ser reduzida em 19% e o lucro aumentado em 4%. Para o melhor cenário, uma otimização baseada em custos operacionais resultou numa produção de 127 % de PX e numa produtividade de 89 kg/h de PX por m^3 de sólido, com uma temperatura de operação de 539 K e com a configuração 4-3-15-2.

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Chapter 1 Introduction

This chapter presents the motivation, objectives, and outline of the research regarding the development of a process for *p*-xylene production, which couples the isomerization and separation processes in one unit. The main motivation is based on: the global *p*-xylene market has demonstrated a positive growth thanks to an increasing demand of polyester fibers for the textile industry; the chemical process becomes a target when it comes to energy efficiency, in the context of decreasing the environmental burden; leading to the process intensification by combining isomerization and adsorption. The main objective of the thesis is also described in this chapter. Additionally, the outline of the chapters that compose the thesis is briefly described.

1.1 Relevance and motivation

C₈ isomers are aromatic species with 8 carbon atoms in a molecule, including: *p*-xylene (PX), *m*-xylene (MX), *o*-xylene (OX), and ethylbenzene (EB). They are mainly obtained from catalytic reformat, and toluene disproportionation/transalkylation, small part from pyrolysis gasolines. PX is an important raw material for the production of purified terephthalic acid (PTA), which is the raw material of polyester fibers, resins, and films. The global PX market is expected to grow to USD 81.02 billion by 2022 with a compounded annual growth rate (CAGR) of 12.05%¹. Asia continues to increase its market share of global production and consumption. In 2016, 68.4% of the global PX consumption was in Northeast Asia, most of which was in China². China's PX imports were mainly from South Korea, Japan and Taiwan, accounting for 47.3%, 19.6% and 10.8% respectively³. A big gap exists in China's *p*-xylene market, and external dependence has increased up to 60% in 2017³.

On the other hand, to follow the environment guidelines that drive the world today, it is of major importance to develop processes with lower environmental impact and higher energy efficiency. Thus, there is a strong need to develop processes aiming to increase the PX yield, as well as optimize capital, energy, environmental and safety benefits.

The separation of C₈ isomers is mainly achieved through three processes: distillation, crystallization, and adsorption. Given that the C₈ aromatics show proximity in boiling points, it is difficult to separate through distillation, especially PX from MX. Crystallization technology was industrialized much earlier, however, the limitations on *p*-xylene recovery caused by eutectic formation with MX limited the yield and separation efficiency⁴. The development of the Simulated Moving Bed (SMB) technology was determinant for PX production and quickly became the main industrial process for the separation of C₈ aromatics. By switching the input and output ports periodically and synchronously, the counter-current

movement of adsorbate and adsorbent is simulated. Xylene isomerization is a process to re-establish the thermodynamic equilibrium of C₈ aromatics that has been previously depleted of OX (xylenes splitter) and PX (SMB). The Simulated Moving Bed Reactor (SMBR) has attracted attention as a promising process for PX production and separation. This unit combines separation and isomerization, reacting and separating simultaneously to overcome the thermodynamic equilibrium limitation. In this way, the PX yield may be increased; and optimized capital, energy, environmental and safety benefits can be achieved.

1.2 Objectives and outline

The main objective of this research is to build the SMBR model based on experimental data and to investigate the SMBR from the simulation and optimization point of view. It comprises: (i) An experimental and parametric behavior study of xylene isomerization through fixed bed experiments. (ii) Assessment of the main side reactions that possibly can exist in the SMBR unit. (iii) Adsorption experiments of C₆-C₈ aromatics (PX, OX, MX, EB, toluene (TOL), and benzene (Bz)) on an adsorbent commonly used in the industry. (iv) Modeling of the SMBR process including the experimentally determined parameters of both reaction and adsorption to find the optimal operating conditions to obtain the best performance of the unit. (v) Evaluation of the operating temperature and the role of energy consumption and energy savings in the process.

This manuscript is divided into seven main chapters to reach the aforesaid objectives.

Chapter 2 consists of a brief introduction on aromatics, including their applications, and a description of the world production and demand. Then, an overview of an aromatics complex is given. Special attention is given to SMB and SMBR processes, being the latter the major goal of the thesis.

The study of xylene isomerization in the liquid phase was conducted through fixed bed experiments and the results are presented in **Chapter 3**. Activation energies of xylene isomerization as well as the interconversion kinetics over two different catalysts were estimated. Better performance was obtained on BEA35 (monofunctional acid zeolite with a silica-alumina ratio of 35), which can be attributed to the higher amount of Brønsted acid sites. Also it is chosen as the catalyst adopted in the study of the SMBR.

In **Chapter 4**, EB disproportionation and EB-TOL transalkylation were confirmed as the main side reactions in SMBR; therefore, the activation energies and the kinetics of both side reactions over BEA35 were estimated.

In **Chapter 5**, the adsorption of C₆-C₈ aromatics were investigated through batch experiments at higher temperatures on a dry Ba-exchanged zeolite X, to assess the adsorption equilibrium properties in conditions that can be optimal for a SMBR. The saturation capacity, the adsorption equilibrium constants, and the heat of adsorption were obtained for each compound.

The model of the SMBR unit is described in **Chapter 6**, which considers a homogeneous mixing of adsorbent and catalyst in the columns. The system is modeled based on the true moving bed reactor (TMBR) approach for several arrangements of columns under different desorbent consumption constraints. Additionally, the operating temperature was investigated and the heat integration in the process is discussed.

Finally, **Chapter 7** presents the major conclusions of this thesis along with recommendations for future work.

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Chapter 2 State-of-the-Art

This chapter presents the state-of-the-art on *p*-xylene production; it starts with a brief introduction to aromatics applications, as well as the world supply and demand. Then, an overview of the aromatics complex is displayed followed by a detailed description of the *p*-xylene production and separation processes. Special attention is given to the SMBR, which is the main topic of the thesis. Types of technologies most employed and the principal suppliers worldwide of these processes are also discussed. The chapter ends with a quick look at the energy saving improvement related to *p*-xylene production in the industry.

2.1 BTX introduction

BTX including benzene, toluene, and xylene isomers are the primary raw materials for many petrochemicals. However, the demand for benzene, toluene, and xylene isomers varies widely. Benzene and *p*-xylene account for more than 80% in the total BTX consumption. The production of styrene, cyclohexane, and phenol accounts for almost 70% of overall benzene consumption. Over the last few years, benzene consumption in China had a yearly average increase of 9% from 2011 to 2016, while other countries showed a decrease in the demand, except a modest growth of about 0.5% exhibited by Middle East and North America¹. Global consumption growth has gradually slowed down, which is expected to prevail until 2021¹.

The consumption of the three xylene isomers is of extremely unbalanced proportion. PX is an important raw material for the purified terephthalic acid (PTA) production, which is usually used for the production of polyester fibers, resins, and films. It accounts for around 86% of the total consumption, in volume, far higher than the others². In the year 2024, China, with expected growth at a rate of 7% will drive the global *p*-xylene demand³. The growing tendency is mainly driven by the extensive development of the textile industry in China. On the other hand, the production capacity keeps a growth tendency at a yearly average of 5% because of the new plants' launched in Asia².

A large amount of toluene is used as additive or solvent. Given that benzene and *p*-xylene have higher demand, toluene is rather converted to these more valued aromatics through disproportionation and transalkylation.

2.2 Aromatics complex

In general, modern aromatics complexes for BTX production include five units: catalytic reforming, aromatics extraction, toluene disproportionation and transalkylation, xylenes isomerization, and xylenes separation. The main process units of a modern aromatics complex are shown in **Figure 2.1**.

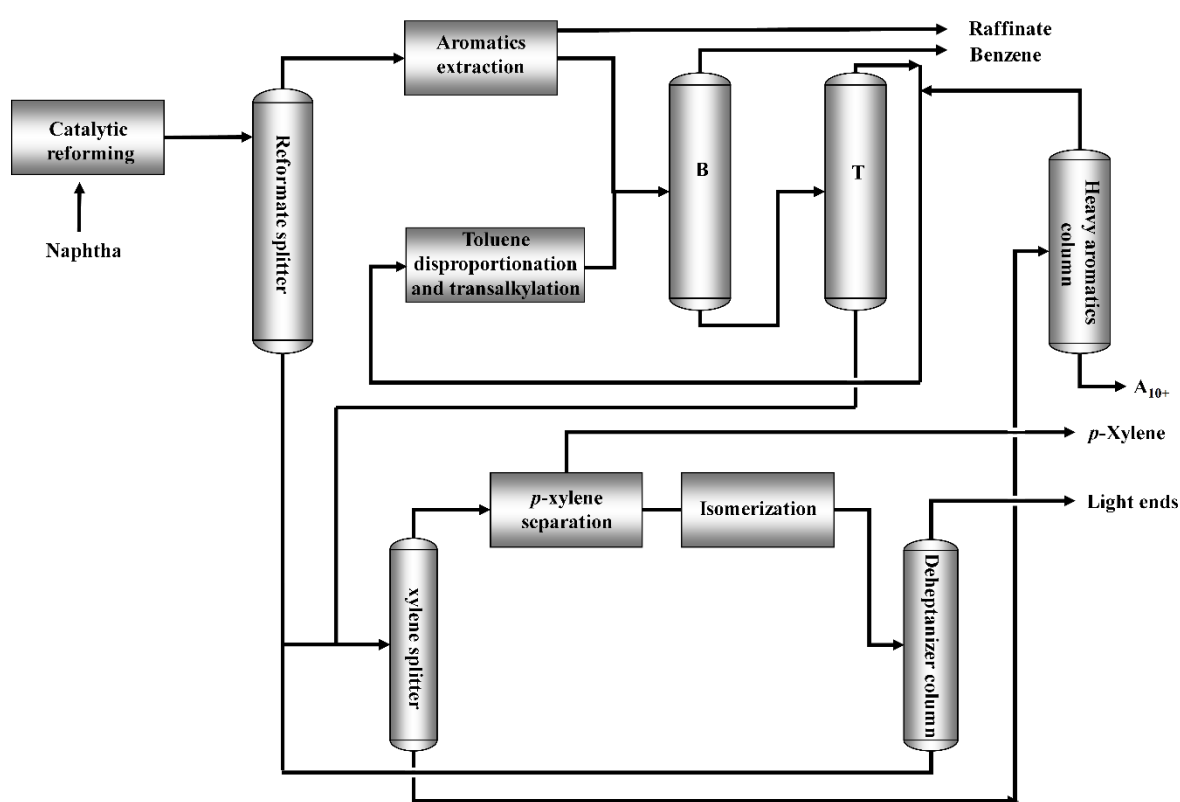


Figure 2.1 Main process units of a modern aromatics complex⁴

Catalytic reforming converts naphthenes and paraffins into aromatics; Besides BTX aromatics, the C_9^+ aromatics from catalytic reforming can also be converted to *p*-xylene through subsequent processes (disproportionation/transalkylation). Catalytic reforming and toluene disproportionation constitute respectively 80% and 15% of the total BTX supply for the PX production⁵. Pyrolysis gasoline is the by-product from steam cracking, which is used

for ethylene production. BTX source from pyrolysis gasoline presents the highest concentration of ethylbenzene, and a high proportion of benzene. The mostly used technologies for catalytic reforming are CCR platforming from UOP, and Aromizing from Axens⁶.

A series of distillation towers is used to separate mixed aromatics obtained from catalytic reforming, toluene disproportionation/transalkylation, and xylenes isomerization. The reduction of energy consumption of the fractionation unit is generally achieved through heat integration and optimization of distillation column sequence^{7, 8}. Through the fractionation units, the C₆~C₇ fraction is then sent to the aromatics extraction unit; the C₈ fraction is sent to the *p*-xylenes separation unit for PX separation; the C₉~C₁₀ fraction acts as the raw material for toluene disproportionation/transalkylation; and the C₁₀⁺ fraction is considered as a by-product.

Aromatics extraction is a process for separating aromatics from non-aromatic hydrocarbons. Liquid-liquid extraction is normally used for feeds with wide fraction. With the development of catalytic reforming processes, non-aromatics in C₈⁺ fraction is reduced and regular distillation for benzene and/or toluene can satisfy the requirement⁹. Thus, extractive distillation is more used in modern aromatics complexes. ED sulfolane from UOP adopted sulfolane as solvent¹⁰, and co-solvents are used in GT-BTX from GTC¹¹.

The separation of *p*-xylene from other C₈ isomers is based on the difference in certain properties. The properties of C₈ aromatics are presented in **Table 2.1**.

Table 2.1 Properties of C₈ aromatics

Properties	OX	MX	PX	EB
Density at 298 K, kg/m³	880.2	864.2	861.0	867.1
Boiling Point, K	417.42	412.1	411.35	409.19
Melting Point, K	247.82	225.13	286.26	178.02
Relative Basicity¹²	2	100	1	0.14

Due to the close boiling points of C₈ aromatics, separation through distillation is uneconomic. Mitsubishi Gas Chemical Co., Ltd. used to adopt MGCC process, which was based on the basicity of C₈ aromatics and was used for the separation of *m*-xylene¹². Crystallization was the dominating industrial technique employed to separate PX from its isomers in the early years. However, the adsorptive separation became dominant since its launch in the 1960s.

Xylene isomerization increases the production of PX by taking advantages of the thermodynamic equilibrium of the xylene mixture. It reestablishes the thermodynamic equilibrium after one or more isomers are depleted, to achieve the increase in PX yield. Disproportionation and transalkylation of toluene and C₉₊ aromatics turns the aromatics from low-value to high-value products. This process makes the most use of the methyl group and aromatic ring from the catalytic reforming.

The development of aromatics complexes is based on continuously improving the performance of existing solvents, catalysts or adsorbents; improvement of the single unit as well as the energy and process optimization of the whole aromatics complex sight.

2.3 *p*-Xylene production processes

Toluene disproportionation/transalkylation and xylene isomerization are the main processes used to increase the PX yield. Disproportionation and transalkylation of toluene and C₉₊ aromatics produces a xylene mixture with a low concentration in EB, and turns the aromatics from low-value to high-value products. This process makes the most use of the methyl group and aromatic ring from the catalytic reforming. Xylene isomerization increases the production of PX by taking advantages of the thermodynamic equilibrium of the xylene mixture. It reestablishes the thermodynamic equilibrium after one or more isomers are depleted, to achieve the increase in PX yield.

2.3.1 Xylene isomerizaion

Xylene isomerization aims to increase the xylene production, especially to increase the output of PX. The isomerization process can be divided into two categories according to the difference in the EB handling, i.e. EB dealkylation or EB isomerization. EB isomerization aims to turn ethylbenzene into additional xylenes, while in the EB dealkylation there is cleavage of the ethyl group and benzene can be produced as secondary product. Without the equilibrium limitation as in EB isomerization, EB dealkylation allows higher conversion of EB. However, this comes to the expense of lower PX yield, since a lot of EB turns into benzene. The process diagrams of both processes are quite similar, the critical difference lies in the adopted catalysts. The reactions occurring in the xylene isomerization process are presented in **Figure 2.2**.

The first generation process of xylene isomerization was launched in the 1950s, using an amorphous silica-alumina catalyst. The processes operated under high temperature without hydrogen, this made the catalyst easy to coke, and the process could not convert EB into xylene. The first generation processes that adopted amorphous silica-alumina catalyst includes ICI and Chevron method. Another process available during the same period of time was MGCC process proposed by Mitsubishi Gas Chemical Co., Ltd. The process was based on the basicity of C₈ aromatics, and the HF·BF₃ solvent was selectively used to form a complex with *m*-xylene. Since HF·BF₃ is also a catalyst for isomerization, the isomerization from *m*-xylene to *p*-xylene could be achieved by increasing the temperature to around 373 K¹².

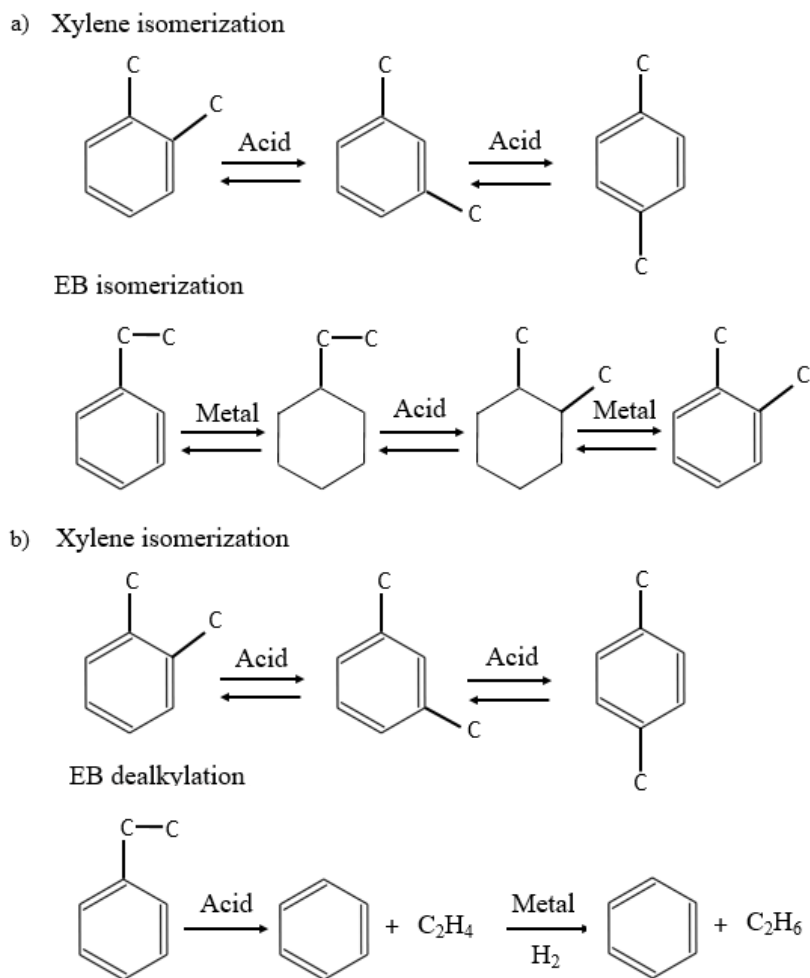


Figure 2.2 Reactions occurring in xylene isomerization process with a) ethylbenzene isomerization catalyst; b) ethylbenzene dealkylation catalyst

Until the 1960s, Octafining process from Engelhard Company (Now BASF catalyst LLC.) included platinum in amorphous silica-alumina catalyst, thus, it could convert EB into xylene. Since the 1970s, the development of zeolite-type acidic isomerization catalysts reduced the reaction temperature, increased the activity and improved the selectivity. Based on ZSM-5 zeolite, ExxonMobil developed various xylene isomerization processes to meet different isomerization requirements, such as MVPI (NiHZSM-5), MLPI (HZSM-5, without hydrogen), MHTI (HZSM-5), and MHAI processes¹³. Most representative xylene isomerization

technologies nowadays are Isomar from UOP and XyMax from ExxonMobil. Axens and Sinopec also have their technologies.

UOP's Isomar process

The UOP's Isomar process (shown in **Figure 2.3**) is applied for both EB isomerization and EB dealkylation. The most recent catalyst for EB isomerization (I-400, UZM type) was launched in 2005. It improved the processing ability to produce PX and simultaneously reduce the single-pass C₈ ring loss. The I-500 EB dealkylation catalyst converts EB into benzene co-product. It offers higher selectivity at a lower temperature. The selection of the catalyst partly depends on the feedstock. Since pyrolysis gasoline has a higher concentration of EB, the PX yield can be maximized with EB isomerization catalyst.

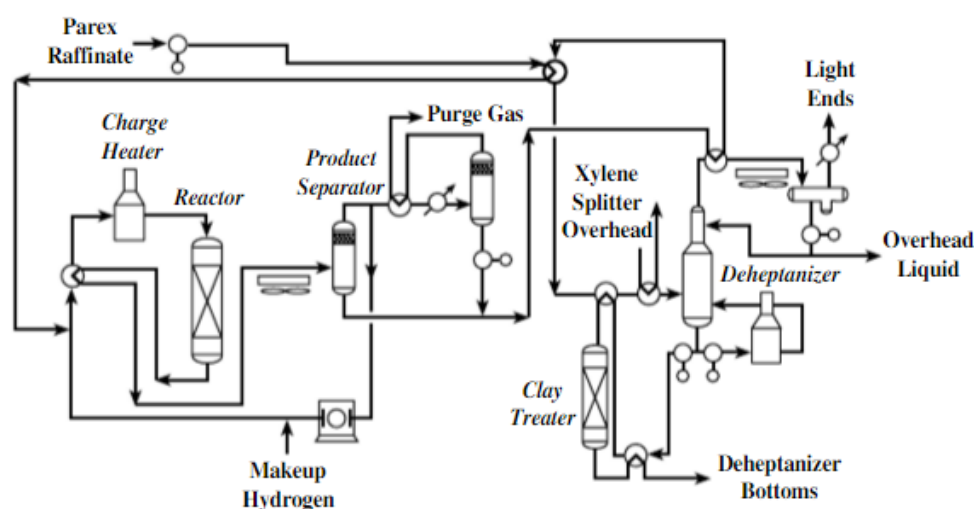


Figure 2.3 UOP's Isomar process diagram¹⁴

ExxonMobil's XyMax

The XyMax is characterized by a dual bed catalyst system (see **Figure 2.4**). A shape-selective catalyst EM-4500 (ZSM-5) is adopted. EB dealkylation happens in the upper bed layer and xylene isomerization happens in the lower bed layer, so as to ensure the high

activity and selectivity. When the EB conversion rate reaches 85%, the single-pass xylene loss is just only about 1%. In 2004, ExxonMobil introduced the improved XyMax-2 process and the corresponding catalyst, the operating temperature and pressure ranges are wider. Processes from other principal licensors that have been industrialized adopt a single catalyst bed. The EB conversion and xylene recovery may be lower than the dual bed catalyst system, but the reactor could be chosen between axial and radial.

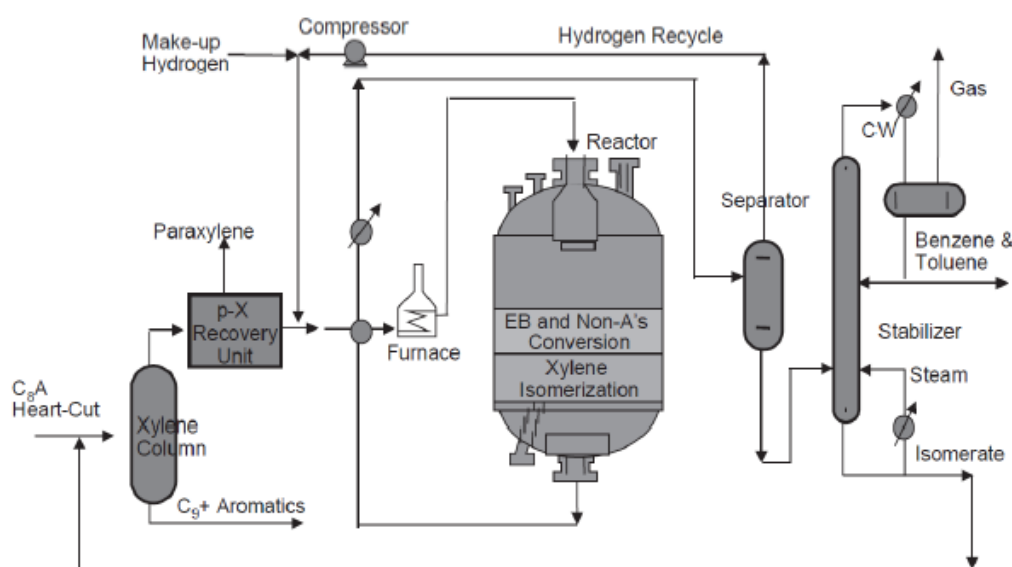


Figure 2.4 ExxonMobil's dual bed catalyst system¹⁵

Others

Axens launched Oparis series catalysts in 2001, which adopted molecular sieve with 10-member rings (EUO type). The unique feature of the catalyst allows optimal temperature for the processes of xylene isomerization and EB isomerization; since xylene isomerization is favored by temperature while EB isomerization is favored by milder temperature due to the naphthenic intermediate. The most recent EB dealkylation catalyst from Sinopec is SKI-210, while for EB isomerization is RIC-200, which was developed on 2010, and presents a EB conversion of 32.76%¹⁶. RIC-200 produces PX close to the equilibrium composition in about

95%, EB composition is close to the equilibrium around 60%, and the single-pass yield of C₈ aromatics is higher than 97.5%⁹.

2.3.2 Toluene disproportionation and transalkylation

Toluene is mostly used as a solvent or as component of the gasoline, while C₉ compounds are mainly used for gasoline. To satisfy the demand for benzene and PX, and make full use of toluene and C₉ aromatics, researchers started to pay attention to their conversion. Indeed, toluene disproportionation/transalkylation has been studied since the 1940s, and the first industrial process late appeared in the 1960s. The reactions that may occur in the toluene disproportionation/transalkylation process are presented in **Figure 2.5**.

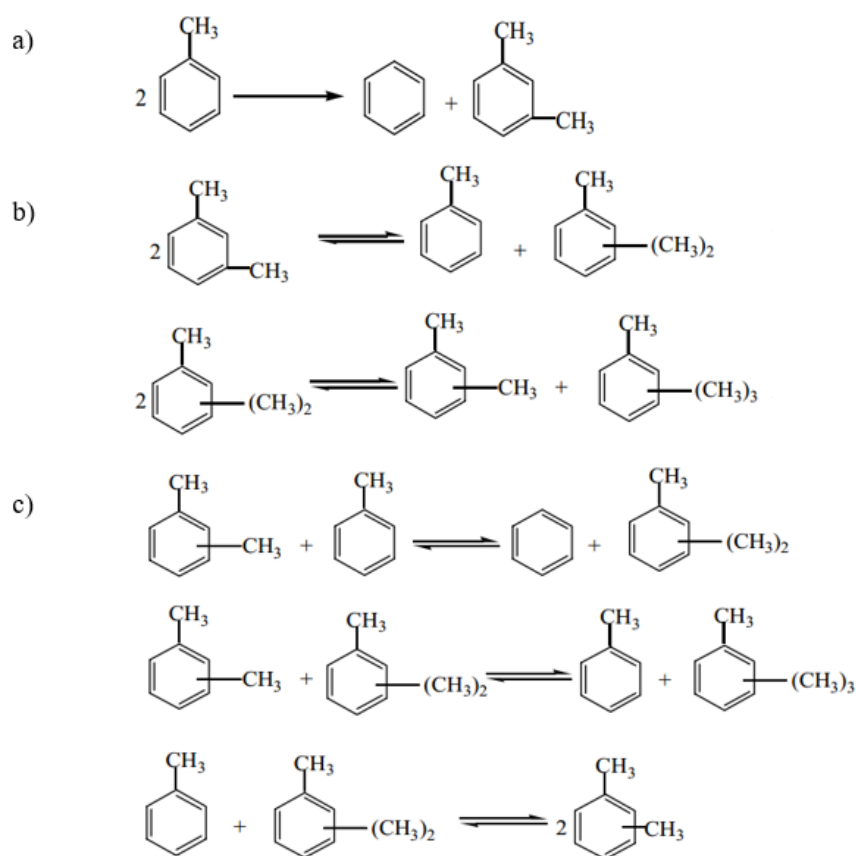


Figure 2.5. a) Toluene disproportionation main reaction; b) Side reaction: secondary disproportionation of xylene products; c) Side reaction: transalkylation reaction

Table 2.2 Toluene disproportionation and transalkylation processes and catalysts

Company	Process	Catalyst	Process Conditions
	Advantages		
UOP ¹⁷	Tatoray	TA-5 TA-20HP (2006) Rhenium metals included	Temperature: 675~725 K Pressure: 3.0 MPa hydrogen/hydrocarbon ratio: 6~10:1 Space velocity: 1.0 h ⁻¹
	TA-20HP is comparable to the previous TA-5 catalyst generation, except for the higher activity; the TA-20HP stability has been increased by 10 times. Tatoray process has fewer side reactions and higher conversion rate.		
UOP ¹⁸	TAC9		
	Feedstock with a high concentration of C ₉ and C ₁₀ ⁺ aromatics is allowed for TAC9. The catalyst was enhanced with the ability of dealkylation. It can remove the C ₂ ~C ₄ group and ensures the conversion of C ₁₀ ⁺ . The catalyst is also capable to turn the C ₉ compounds to methyl aromatics. Long catalyst life.		
ExxonMobil	TransPlus	EM-1100 EM-2300	Temperature: 675~745K Pressure: 2.2~3.5 MPa
	The feed can change from entirely C ₉ aromatics to a mixture of C ₉ aromatics, benzene, and toluene. The catalysts can be applied in much lower hydrogen/ hydrocarbon molar ratio (down to 1) and higher weight space velocity (3.5 h ⁻¹). The high rate of single-pass conversion and the stability of the catalyst also contribute to the low investment and operation costs of TransPlus process.		
Zeolyst ¹⁹	ATA	ATA-12 (2002)	
	The catalyst allows a wide variation of feed compositions, changing from the benzene-rich feedstock or pure toluene to pure C ₉ ⁺ aromatics. The catalyst improves the flexibility of the feed, allows a smooth processing of feed sources optimization.		

Arco-IFP ²⁰	Xylene-Plus (1968)	Y- zeolite containing rare earth metal	Temperature: 775K Pressure: atmospheric pressure Space velocity: 0.9 h ⁻¹
	Pure TOL or a TOL and C ₉ aromatics mixture can be used as feed, due to the 12-member ring in the large pore molecular sieve.		
GTC ²¹	GT-TransAlk		
	The process can deal with feed with a high concentration of C ₉ + compounds, and achieves high conversions. Since the cracking rate is low in this process, the consumption of hydrogen is decreased.		

Principal technology suppliers and related processes for toluene disproportionation/transalkylation include Tatoray technology and TAC9 technology from UOP, TransPlus technology from ExxonMobil, GT-TransAlk from GTC, and ATA technology from Zeolyst. The process diagrams of the principal licensors are the same; the main differences lay in the ability and the stability of the catalysts to deal with C₉+ aromatics. The processes and catalysts are listed in **Table 2.2**.

2.3.3 Ethylbenzene disproportionation

EB disproportionation is not a process aiming at the production of *p*-xylene. However, this reaction could be involved in the study of Simulated Moving Bed Reactor (SMBR). Thus, a brief summary on EB disproportionation process is presented below

The desired product of EB disproportionation is *p*-diethylbenzene (PDEB). Synthesis of PDEB by EB disproportionation is achieved through a shape selective catalyst, which restricts the size of the intermediates. In the 1980s, China's Taiwan styrene company developed a selective EB disproportionation process for the production of PDEB. The process launched in 1989, adopted ZSM-5 as catalyst modified with silica through chemical vapor deposition, with a capability of 1500 t/a²². The selectivity of PDEB is up to 96%. After further optimization, the

selectivity improved to 99%. Pan et al.²³ developed a method for synthesizing PDEB based on a HZSM-5 catalyst, modified with no less than 2 elements from boron, magnesium, aluminum, silicon, phosphorus, calcium, zinc, titanium, etc. The EB conversion rate is around 10% ~ 30% and PDEB selectivity is 95% ~ 99%. In general, the main research works in this field are focused on the zeolite modification^{24, 25}.

The industrialized process for PDEB production is mainly based on the synthesis method, adsorptive separation, and adsorptive separation-isomerization method. Most of the PDEB producers adopted adsorptive separation process, Such as UOP²⁶ The EB conversion in the synthesis process is only around 20%, the selectivity of diethylbenzene (DEB) in the product is around 60%, and the selectivity of PDEB is around 95%, resulting in a large amount of material recycle and high energy consumption.

2.4 *p*-Xylene separation processes

2.4.1 Crystallization

The crystallization method takes advantage of the difference in freezing point among different components. Namely, making a particular component drop out while others stay in the mixed liquor. Compared with other C₈ aromatics, *p*-Xylene presents a higher freezing point, which makes it possible to separate PX from others by deep cooling crystallization. However, the component that drops out first is determined by the initial composition of the solution (according to the concentration difference of the components when reaching a liquid-solid balance). High purity and recovery can be achieved by repeating the procedure of partial melting and crystallization. Before the development of adsorptive separation technology, crystallization was the only method used for PX separation. Since the mass concentration of

PX in the feed is generally 15-25%, a two-stage crystallization process was normally adopted. In the first stage, as much as possible PX is separated from xylenes at a low temperature (195-245 K). The solid phase is separated from the liquid through centrifugation. Mass concentration of PX in the solid phase is 65-90%, then the molten crystals are sent to the secondary crystallization stage to improve the purity. The temperature of the second stage is controlled at 255-275 K. Through the two stages crystallization process, the final product can reach a purity of 99%²⁷.

The most widely used crystallization processes are from BP licensed by Lummus (CB&I)²⁸, ARCO²⁹, and Chevron³⁰. The processes of Amoco and AROC are very similar. Ethylene and propane are respectively used as the cooling medium for the first and second stage. The product is washed by toluene and reaches a purity of 99.8%. Chevron process adopted CO₂ as a cooling medium, the crystals have a large particle size and are easy to separate. Given the disadvantages of low recovery of *p*-xylene and massive energy consumption of deep cooling, crystallization processes are slowly replaced by adsorptive separation processes.

2.4.2 Adsorptive separation

Adsorptive separation is mainly achieved through a fixed bed, moving bed, or SMB equipment. In fixed bed processes, the components to be separated flow through the fixed bed which is packed with an adsorbent. It takes advantage of the difference of the adsorbate concentration in the adsorbent particle and the bulk phase. In a moving bed process, the adsorbent is moving in a closed system, counter-currently to the liquid phase. Compared to the fixed bed, the moving bed process has a higher yield. Since the wearing of adsorbent particles in a moving bed leads to problems, such as equipment blockage and purity decrease; the requirement for the mechanical strength of the adsorbent is higher. The SMB combines the

advantages of a fixed bed and moving bed, it can effectively separate complex mixtures that have close boiling points, high molecular weight, or heat sensitive liquid mixtures. By switching the input and output ports periodically and synchronously, the counter-current movement of adsorbate and adsorbent is simulated. In this way, the SMB successfully avoids the drawbacks of the other two processes. Since the beginning of the 1960s, the SMB adsorptive separation technology emerged and was a significant breakthrough in C₈ aromatic separation. The separation efficiency was much improved, and the energy consumption was significantly reduced. More than 90% of the C₈ aromatics separation units then established were adsorption based³¹.

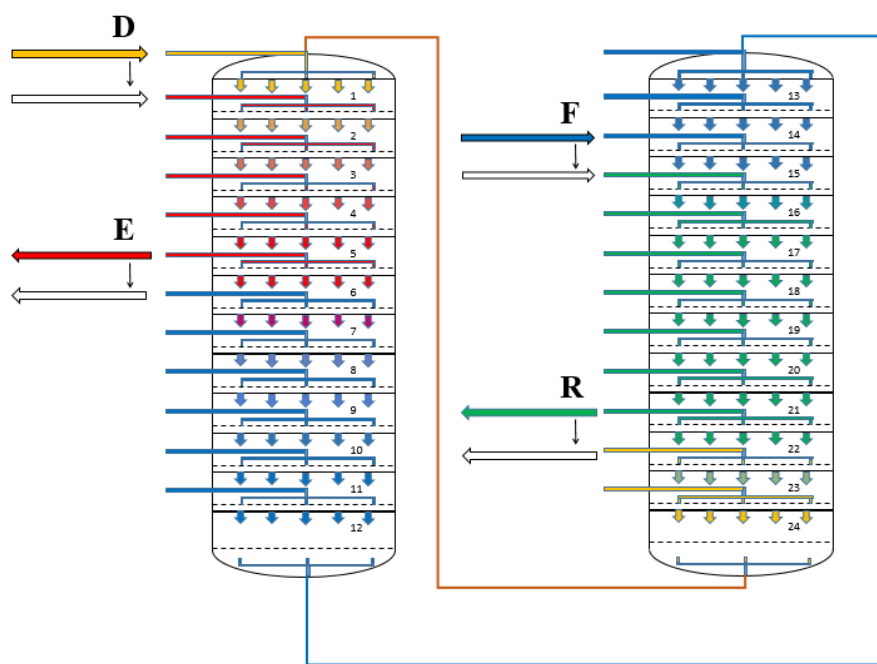


Figure 2.6 Simulated Moving Bed scheme³²

The scheme of the SMB is shown in **Figure 2.6**. In an industrial scale simulated moving bed for PX separation, 24 fixed beds are located in two individual columns. The circular flow between 2 columns is achieved through the pumps used for connection, which makes the two

independent columns work continuously for adsorptive separation. Four different streams respectively feed (F), extract (E), raffinate (R), and desorbent (D) divides the SMB into 4 basic zones. The consecutive fixed beds in the same column are connected by distribution plates, through which the streams can be injected or removed.

C₈ aromatics show different affinity towards the adsorbent. The adsorbent and adsorbate with higher affinity move in the same direction, while the adsorbate(s) with low affinity stays in the bulk phase and moves in the opposite direction. With appropriate selection of adsorbent and desorbent, the stream F is separated into two outlet streams, stream E and stream R. Thus, Zone II (between E and F nodes) and Zone III (placed between F and R nodes) are the separation zones. While, Zone I (located between D and E nodes) and Zone IV (located between R and D nodes) are respectively for the regeneration of adsorbent and desorbent.

Parex process

Parex process from UOP (shown in **Figure 2.7**) is the most representative *p*-xylene adsorption based process. In the Parex process the rotary valve is connected with all the distribution plates through transfer pipelines; the four streams are introduced or withdrawn through the pipelines. At any given time, only four of the bed lines actively carry the streams into and out of the adsorbent chambers. The periodic switch of the rotary valve makes the feedstock flow into different beds. In this way, the countercurrent contact of the two phases is simulated. PDEB is used as desorbent in the Parex process. X or Y type molecular sieves ion exchanged with barium or potassium are the most common adsorbents used in the Parex process. The purity of *p*-xylene product in this process can go to 99.9% and the recovery is above 97%; the concentration of *m*-xylene and ethylbenzene in the product is less than 500 µg/g, and the concentration of *o*-xylene is less than 300 µg/g³³.

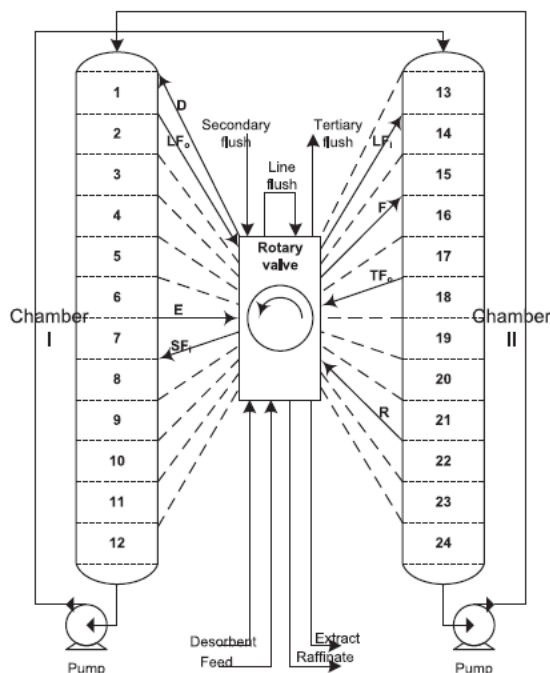


Figure 2.7 Parex process diagram³⁴

In 2004, UOP launched the adsorbent ADS-37, compared to the former adsorbent (ADS-27), ADS-37 has a 6% higher adsorption capacity⁹. In 2011, UOP came out with the latest adsorbent ADS-47; the adsorption capacity was further enhanced, as well as the mass transfer performance⁹. Additionally, the yield is also higher than with the previous adsorbent. LD Parex™ Aromatics Complex is available since 2015, ADS-50 (light desorbent system) only shows a slight difference from the previous adsorbent (ADS-47, heavy desorbent system). The adoption of light desorbent system makes the downstream separation more efficient. The capital investment was reduced by 15-17%, with a reduction of 20% in fractionation tray and equipment requirement³⁵.

Eluxyl process

Eluxyl process is the technology licensed by Institut Français du Pétrole (IFP) in France. Eluxyl process emerged in 1986. It has individual on/off value system, and advanced dynamic

control through the monitoring of concentration profiles by on-line Raman spectroscopy, as presented in **Figure 2.8**.

Axens also proposed the twin raffinate mode, which means the SMB process was operated with an additional outlet stream, and subdivided the zone between feed and raffinate into two zones. Appropriately adjusting the flowrate in the subzones, a mixture of MX/OX can be separated from ethylbenzene. To further separate the mixture of MX/OX, a crystallization unit or a second SMB unit could be adopted. The crystallization is able to produce MX or OX. The second SMB is capable for the production of MX, and less adsorbent and desorbent are needed due to the depletion of the ethylbenzene³⁶.

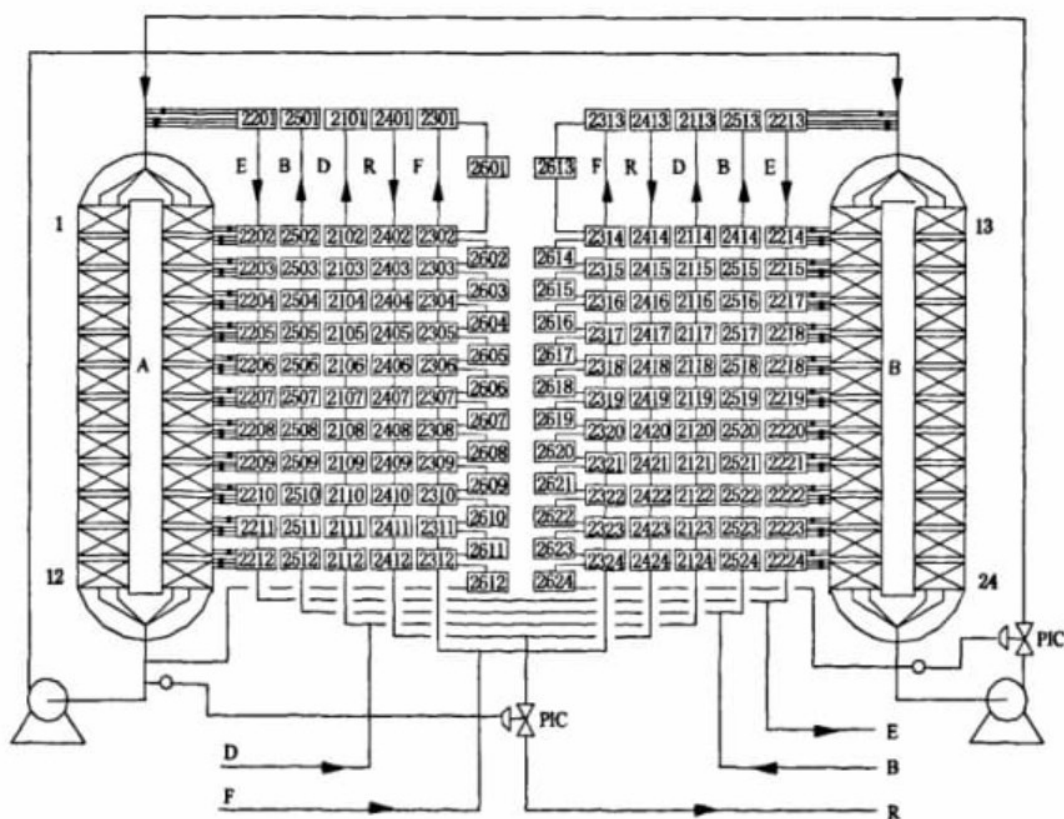


Figure 2.8 Eluxyl process diagram³⁷

Flushing strategies

As mentioned previously, the transfer pipelines are used to introduce or withdraw the streams. This may lead to contamination of the product. One possible solution for the problem is adopting separate transfer pipelines for different streams (such as in Eluxyl in **Figure 2.8**). Another way is to flush the residue that stays in the transfer pipelines with an additional stream, which is typically called flush-in or flush-out streams (such as in Parex in **Figure 2.7**).

Table 2.3 Flushing strategies of adsorptive separation processes

<i>p</i> -Xylene adsorptive separation process	Flushing method
UOP Parex	
Sinopec SorPX ³²	

Flushing materials respectively are: D represents desorbent; E represents extract; F represents feed; R represents raffinate; H_i represents flush-in; H_o represents flush-out; D_i represents desorbent flush-in; T represents flush-out; $C_{1,2,3,4}$ represents flush-in.

Parex from UOP has fixed the configuration of 5-9-7-3, the process implements the three times flushing of bed layer pipelines. Axens optimized the by-pass washing process, the pipelines are washed after each introduction or withdrawal, the configuration of Eluxyl is adjustable. According to the principle that “concentration of residues in the pipeline should keep close to the material concentration which is about to pass through the pipeline, concentration of the material is about to flush it should be kept close to the concentration in the bed”, SINOPEC came up with a new strategy of flushing³². The SINOPEC process (SorPX) optimally matched the flush position and composition, so as to achieve the goal of minimum disturbance to the concentration in the bed. Main flushing strategies are described in **Table 2.3**.

SMB development

The modeling of industrial-scale SMB for C₈ aromatic isomers has been mainly focused on the influence of operating parameters and dead volumes since 2000. Details like flushing and zoning strategies were also addressed. Major SMB modeling development focused on the strategies are presented in **Table 2.4**.

Table 2.4 SMB modeling development focused on strategies

Year	Application
2010	Mun ³⁸ studied the partial port-closing strategy to achieve high yield and high purity for 4-zone SMB binary separation. Partial raffinate-closing (PRC) or partial extract-closing (PEC) strategies were adopted to discard the stream in raffinate or extract port susceptible to being contaminated. The author concluded that both approaches enable much higher product concentration as well as higher productivity than the conventional operation. Port-closing length at 0.35 in PEC and 0.65 in PRC show a positive effect on product purities and productivity.
2011	Lee and Shin ³⁹ provided a method characterized by injecting two different feeds in different feed locations of the SMB to improve the PX recovery. The feeds are respectively high PX concentration mixture (85-95 wt %) from selective toluene disproportionation and low PX concentration mixture (20-24 wt %) from other processes (reformer, isomerization reactor and transalkylation of aromatics having 9 carbon atoms).
2012	Nowak et al. ⁴⁰ studied the separation of ternary mixtures by SMB to separate a target component with intermediate adsorption strength. In their study, the performance of pseudo SMB process, the SMB cascades, and the integrated 8-zones SMB processes were compared. The pseudo SMB shows bad performance in productivity. However, the pseudo SMB process performance can be significantly improved by adopting no less than two columns in each zone.

Table 2.5 SMB modeling development focused on model establishment

Year	Application
2002	Minceva and Rodrigues ⁴¹ investigated an industrial-scale SMB for <i>p</i> -xylene production from a simulation point of view. The authors concluded that the TMB and SMB models predict similar performances. The influence displayed by mass transfer resistance was also investigated. Noteworthy, the deactivation of the adsorbent was compensated by decreasing the switching time in their study.
2003	Minceva and Rodrigues ⁴² studied the influence of dead volume in the transfer line on SMB performance. The dead volume was considered within the mass balances in the stream nodes.
2007	Minceva and Rodrigues ⁴³ adopted the experimentally obtained data over ion exchanged faujasite zeolite in the modeling of the SMB. Xylene adsorption equilibria, as well as kinetics data, were adopted. The optimal operating conditions were investigated. The authors also concluded that the minimal possible bed porosity can help improve SMB productivity.
2008	Gomes et al. ⁴⁴ addressed the influence of adsorbent aging by adjusting the operation of simulated moving bed. The adsorbent aging causes problems such as loss of equilibrium adsorption capacity as well as the increase of mass transfer resistance. The authors compensate the consequences by increasing solid velocity and decreasing the internal flowrate. The switching time strategy (increasing solid velocity) proved to achieve higher productivity with the same purity requirements ⁴⁴ .
2015	Silva et al. ⁴⁵ conducted a simulation study on the industrial scale SMB, by incorporating the model with the three existing major types of dead volume, respectively located at circulation, bed, and bed head pipelines. Their results showed excellent agreement with that of an industrial unit.

As a first approach, the modeling development of SMB was based on the parameters from industrial experience or the literature. After the establishment of SMB, the influence of the operation conditions, dead volume, and mass transfer resistance were studied. However, the parameters from the literature are not adequate and sometimes contradictory. Thus, attention started to be paid to the experimentally obtained parameters. Batch or breakthrough experiments were conducted to study the parameters under the industrial SMB condition, to build a more reliable SMB model for the guide of process improvement. The development of SMB modeling focused on the model establishment is briefly introduced in **Table 2.5**.

2.5 Process Integration and Optimization

2.5.1 Simulated moving bed reactor

According to the literature in the last few years, the new trend for *p*-xylene production is the usage of several reactors under different conditions integrated for specific purposes. Intensification aims to optimize capital costs, energy consumption, environmental and safety benefits by radically reducing the physical size of the plant. Miller et al.⁴⁶ described a pressure swing adsorption reactor process integrated with SMB adsorption to produce *p*-xylene. The fixed bed is saturated with *p*-xylene and ethylbenzene at the end of the feed step, which are preferentially adsorbed. Then the feed is stopped, and the pressure is lowered to desorb the *p*-xylene and ethylbenzene. The effluent, which is rich in *p*-xylene and ethylbenzene, is fed into the liquid phase SMB unit to obtain high purity *p*-xylene. Zhang et al.⁴⁷ described a design to perform the isomerization reaction in a pressure swing adsorption reactor, to enhance the *p*-xylene concentration in the product. In this way, the process can overcome the limitation of the thermodynamic equilibrium.

Following the successful commercialization of the SMB technology and its potential to be used as an integrated reactor-separator. A proposed *p*-xylene production process, which comprises xylenes separation and xylenes isomerization, presents an interesting potential for process intensification.

The first development for $B \rightleftharpoons A$ type reaction concerned the isomerization of glucose into fructose; it was achieved by inserting reactors between the adsorption columns⁴⁸. For those systems with $B \rightleftharpoons A$ type reaction, reaction is not supposed to occur near the extract port where high purity is needed. Thus, reaction and separation alternately arranged were placed only in a specific zone. The conditions for reactors and separation units were chosen separately.

The previous idea was also used for a SMBR for PX production, as presented in **Figure 2.9**. Minceva et al.⁴⁹ studied the SMBR in the liquid phase using a feed free of ethylbenzene, with temperature ranging from 453 to 573 K. The proposed SMBR contains isomerization reactors only in zone III. The authors concluded that the performance of the process was significantly influenced by the switching time. For xylene feed identical to the Parex unit, shorter reactors and lower temperatures (453K) were recommended⁴⁹.

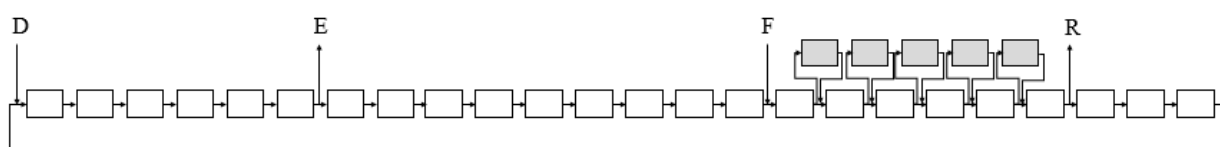


Figure 2.9 SMBR configuration for *p*-xylene production with five reactors and six adsorbers in zone III

Bergeot et al.⁵⁰ studied the SMBR process for PX production with HZSM-5 zeolite as a catalyst in the liquid phase. The adsorbers were operated at 448 K in the liquid phase. The configuration for the SMBR was 5-9-(7+6)-3, with seven adsorbers and six reactors alternately arranged in zone III. Ethylbenzene was included in the feed, and toluene was used as desorbent.

Higher EA (ratio of the *p*-xylene produced to the *p*-xylene at thermodynamic equilibrium, EA%) could be achieved, with higher temperature (575 K) and at low weight hourly speed velocities (WHSV 5 h^{-1}) in reactors.

In the first proposed designs, to get a high purity product, the reaction could not occur near the extract point, catalyst and adsorbent had to be in separated beds. However, in recent years, new designs coupling adsorptive separation with crystallization processes have been proposed, which reduces the requirement for the *p*-xylene purity leaving the SMB unit⁵¹. Gonçalves and Rodrigues⁵¹ adopted a SMBR design with mix adsorbent and catalyst, in dual layer beds, in the same unit for *p*-xylene production, the SMBR was connected with a single stage crystallization aiming at further purification of PX rich streams (**Figure 2.10**). In their work, configuration 2-6-14-2, with the higher number of columns in zone III, presented the best performance⁵¹. The authors further studied the optimal operating condition and found that the optimal particle diameter is 0.62 mm⁵². 15% of the first layer, which contains an adsorbent/catalyst homogeneous mixture (adsorbent/(adsorbent+catalyst)=0.4), and 85% of the second layer contains just adsorbent leads to the highest productivity⁵³.

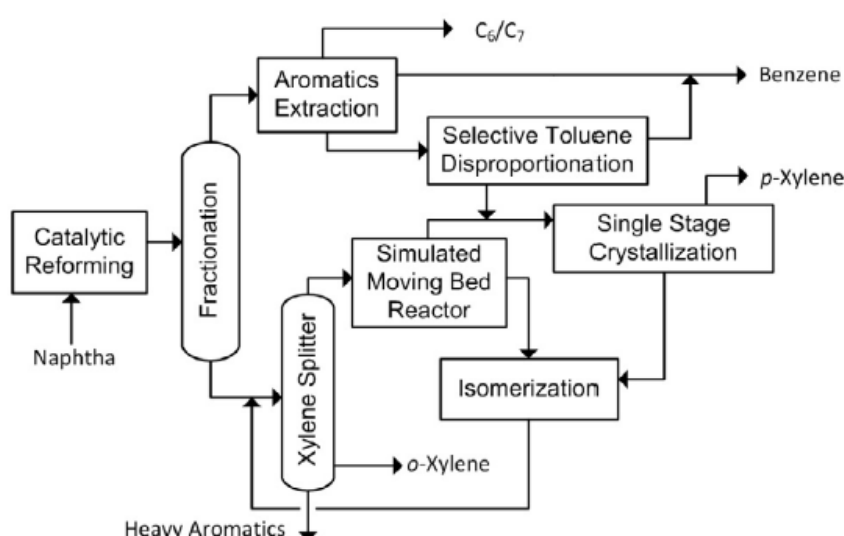


Figure 2.10 Proposed aromatics complex⁵¹

The SMBR model describes the periodical change of the inlet and outlet positions through a dynamic method; while TMBR is based on the true countercurrent flow of the adsorbent and adsorbate caused by the movement of the adsorbent. The SMBR can reach a cyclic steady state after a certain amount of time with the concentration still varying in a switching interval. As long as the averaged value of the SMBR in a cycle approaches the value from TMBR, the TMBR can be recognized as an efficient representation of the SMBR, which can simultaneously simplify the model and reduce the optimization time. The differences between the results obtained by the TMBR and the SMBR model only become significant when it is considered 8 or less columns^{54,55}.

2.5.2 Adsorption/crystallization

The crystallization technology, industrialized much earlier than adsorption based technologies, played an essential role in the *p*-xylene separation history. There are still many crystallization plants in use for high purity PX production. However, the formation of eutectic mixtures limited the yield and separation efficiency. The adsorptive separation and crystallization combined together have comprehensive advantages, especially in revamping old units.

Since 1980s, the Eysenk Rupp Kops Co. Ltd⁵⁶, CFP⁵⁷, UOP⁵⁸, IFP^{59, 12, 60}, Mobil Oil company⁶¹, etc, have launched a series of studies on adsorption-crystallization integrated method for separating *p*-xylene. After the raw materials for *p*-xylene production are removed from paraffins and naphthenes through distillation, they are then fed into an adsorptive separation device. In the adsorptive separation, with an adsorbent having strong affinity towards *p*-xylene, a *p*-xylene enriched fraction (I) and a *p*-xylene lean fraction (II) is obtained. The mass concentration of *p*-xylene in fraction I is about 20%~95% and normally less than 3%

in fraction II⁶². After the recovery of desorbent, fraction I is fed into the crystallization device. After the removal of the desorbent, fraction II is fed into the isomerization unit to re-establish the thermodynamic equilibrium of PX, OX, and MX and ethylbenzene, with a small amount of C₁ ~ C₅ fraction. The products of the isomerization unit are then sent back to the adsorptive separation unit after the C₁ ~ C₅ fraction is removed.

Crystallization units are usually composed of a single or two stages. The operating temperature of a single stage crystallization unit is usually 285-275 K⁶³. Swift et al.^{58, 64} used ethylene as the cooling medium for the first stage in a two-stage crystallization unit, the temperature of this stage is between 200-225 K, with a *p*-xylene recovery of 75-90 %. Propane acts as the cooling medium for the second stage, and the temperature is controlled between 265-275 K; the purity of *p*-xylene can reach to 99.8%.

Hotier et al.⁶⁰ adopted a process design that combines a two-stage crystallization unit with one adsorptive separation unit to get a *p*-xylene enriched fraction (I). The operating temperature of the first stage of the crystallization unit is 268-280 K, the solid product is washed with solvent and molten, to be fed to the second stage that operates at 250-268 K to re-crystallize. The solid product is separated from the mother liquor by a centrifuge. Part of the recovered mother liquor is recycled to the crystallization unit to regulate the concentration of the crystal slurry; another part is sent back to the unit for adsorptive separation. The isomerization of xylenes is realized with a feed containing MX and OX with the presence of hydrogen. A small amount of olefins and polymers could be produced, which are very detrimental for adsorptive separation efficiency, leading to deactivation of the adsorbent. Besides, during the process of *p*-xylene isomerization along with ethylbenzene isomerization, paraffin wax, naphthenes and other C₉+ fraction intermediates are also produced. Their volatilities are just between the desorbent and xylenes, and have significant impact on the separation efficiency. Thus, Hotier

et al.⁶⁰ added a clay treatment before the adsorptive separation unit. This step can effectively reduce the concentration of paraffin, naphthene, aldehyde, ketone, etc. as well as prolong the service life of adsorbent and desorbent, and improve the recovery of *p*-xylene.

For the technical upgrade of existing adsorption or crystallization units, adsorption-crystallization integrated method can improve the *p*-xylene concentration in the crystal slurry, reducing the energy consumption, improving the crystal processing capacity and separation efficiency. *p*-Xylene recovery can be higher than 90%, and the purity can reach more than 99.9%. Therefore, the transformation of existing processes by integration of adsorption with crystallization can be an effective solution.

2.5.3 Energy integration and process optimization

Frequently, the obligatory investments aiming to increase productivity in the chemical industry is not always accompanied by the increase of energy efficiency. Process energy saving focuses largely on process design based on energy or heat integration. The energy consumption over the total process flowsheet can provide important indicators for the evaluation of the process.

Lummus Process Technologies is the licensor of BP's *p*-xylene technology. BP's crystallization process is a unique process employing multi-stage crystallization for PX recovery. The innovative configuration, paired with high feed impurity tolerance and low overall unit energy consumption, makes the Lummus Technology/BP PX crystallization technology an energy-efficient PX recovery method. Despite the higher power consumption in the crystallization unit than adsorptive separation technology, lower energy consumption in xylene splitter is obtained. Overall, the technology supplier claimed lower xylene splitter reflux

ratio, lower total column traffic, and lower xylene splitter pressure (about 1/3); less energy usage and lower investment is declared by Lummus⁶⁵.

UOP introduced Energy Efficient Aromatics Complex (EEAC) in 2010. As a novel, proprietary heat integration flow scheme, it dramatically reduced energy consumption across the PX complex by 20-40%. Since the late 1970s, virtually all new Parex designs have used heavy desorbent (HD); HD systems had an energy advantage over light desorbent (LD) systems with the adsorbent technology available at the time. By 2010, improvements in adsorbent technology have enabled designs with LD to have equivalent energy consumption as those with HD. With the LD Parex aromatics complex, desorbent recycle loop is reduced by 32%.

In addition to the improvement in energy performance, the role of aromatics complex optimization is also emphasized. Compared to the traditional heavy desorbent system, using LD not only enables separation efficiencies, it provides an opportunity to reduce the cost and improve the energy efficiency⁶⁶. It also switches the heat integration center from raffinate column to xylene column, delete the desorbent rerun column, and facilitate the integration of isomerization distillation and xylene separation sector to remove the deheptanizer tower; so as to achieve the optimal flow scheme of aromatics complex⁶⁷.

2.6 Nomenclature

Abbreviations

BTX, benzene, toluene, and xylenes

DEB, diethylbenzene

D, desorbent

E, extract

EB, ethylbenzene

EEAC, Energy Efficient Aromatics Complex

F, feed

HD, heavy desorbent

IFP, Institut Français du Pétrole (French Institute of Petroleum)

LD, light desorbent

MHAI, Mobil High Activity Isomerization

MHTI, Mobil High Temperature Isomerization

MLPI, Mobil Low Pressure Isomerization

MVPI, Mobil Vapor Phase Isomerization

MX, *m*-xylene

OX, *o*-xylene

PDEB, *p*-diethylbenzene

PET, polyethylene terephthalate

PEC, partial extract-closing

PRC, Partial raffinate-closing

PTA, purified terephthalic acid

PX, *p*-xylene

R, raffinate

SMB, Simulated Moving Bed

SMBR, Simulated Moving Bed Reactor

TMB, True Moving Bed

TMBR, True Moving Bed Reactor

TOL, toluene

UOP, Universal Oil Products

WHSV, Weight Hourly Speed Velocities

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Chapter 3 Xylene Isomerization over Beta Zeolites in the Liquid Phase

An experimental study of xylene isomers interconversion (isomerization) kinetics was conducted in this chapter to gain a more in-depth insight into the field. Two Beta zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 35 (BEA35) and 38 (BEA38) were used as catalysts for the performed experiments. The isomerization reactions were carried out under the following conditions: 513, 493, 473, and 453 K at 2.1 MPa in the liquid phase. Four different models were used to estimate the kinetic constants of xylene isomerization, two of them were based on the xylene isomerization thermodynamic equilibrium from the literature. Finally, activation energies over the two catalysts were estimated through the Arrhenius equation.

This chapter is based on Shi, Q.; Gonçalves, J. C.; Ferreira, A. F. P.; Plaza, M. G.; Rodrigues, A. E. Xylene Isomerization over Beta Zeolites in Liquid Phase. *Ind. Eng. Chem. Res.* 2018, 57, 5568-5579.

3.1 Introduction

Xylene isomerization mainly occurs through methyl shift in benzenium ion intermediates, which are protonated by the Brønsted acid sites of the catalyst¹. Disproportionation and dealkylation of xylenes are also catalyzed by the same Brønsted acid sites^{2, 3}. The xylene isomerization occurs through bimolecular mechanism when ample space around the acid sites exists, however on Beta catalysts (BEA-type zeolites), due to pores steric hindrance, the reaction mostly undergoes through the monomolecular mechanism⁴. The molecular size of *p*-xylene is smaller than the other two isomers, the steric constraint of *m*- and *o*-xylene leads to shape selectivity towards the smaller isomer during the reaction. Toluene disproportionation, as well as ethylbenzene disproportionation, may undergo through different pathways regarding the crystal sizes of the catalysts, and on large pore zeolites like BEA catalyst most likely via diphenylethane intermediates⁵. Additionally, for dealkylation reaction, the energy needed to remove a methyl group is much higher than intramolecular methyl transfer; therefore, higher temperatures are required for this type of reaction.

Two reaction schemes are mostly used in the literature to describe xylene isomerization, triangular reaction scheme, and linear reaction scheme. For triangular reaction scheme, xylenes convert through mutual interconversion, allowing 1,3-methyl shift mechanism. Whereas for linear reaction scheme, *o*-xylene can only convert to *p*-xylene via *m*-xylene as intermediate through 1,2-methyl shift mechanism^{6, 7}.

Cappellazzo et al.⁸ studied the kinetics of xylene isomerization on ZSM-5 (MFI-type zeolite) in the liquid phase at a temperature range of 523-573 K. They found that kinetic constants of reaction between *o*- and *p*-xylene are much smaller than others, which indicates the reaction between them is more complicated. The mechanism for xylene isomerization was also studied

by Kang et al.⁹ using molecular simulation techniques. They concluded that compared with the 1,2-methyl shift, the 1,3-methyl shift mechanism is more complicated and has a higher transition state energy. Gonçalves and Rodrigues¹⁰ stated that the apparent direct conversion between *o*- and *p*-xylene starts to appear only at high temperatures in the liquid phase over BEA- and MOR-type zeolites.

p-Xylene diffuses faster to the bulk phase, as had been proved by Olson¹¹, while *o*- and *m*-xylene are retained for longer times in the crystals which may cause the multistep reaction of *o*- and *m*-xylene. Consequently, it seems like the direct formation of *p*-xylene from *o*-xylene when the diffusion effect outweighs the kinetics. All these considerations indicate the prevailing of the linear reaction scheme at lower temperatures.

Xylene isomerization experiments are typically performed at high temperature in the gas phase over ZSM-5^{8, 12} since it presents high activity and shape selectivity. ZSM-4 (MAZ-type zeolite) and Ni exchanged Ni/H-ZSM-5 both have high isomerization activity. ZSM-4 can be used for the isomerization at low temperatures and in the liquid phase; the products distribution approach to the thermodynamic equilibrium and by-products account for only 0.5% of the mass fraction. However, it will leave the ethylbenzene unchanged^{13, 14}, while on Ni/H-ZSM-5, under a hydrogenating environment, ethylbenzene isomerization has a conversion of 34.9%.

The medium pore size catalyst like ZSM-5 does not cause appreciable transalkylation and shows selectivity for the *para*-isomer even without metal cation exchange due to steric constraints¹⁵. Nevertheless, for a potential catalyst to be used in Simulated Moving Bed Reactor (SMBR), the higher conversion is the main requirement, since the adsorbent itself provides the selectivity for *p*-xylene¹⁶. The *p*-xylene diffusion coefficient in ZSM-5 is three orders of magnitude higher than *m*- and *o*-xylene diffusion coefficients⁸. Considering the diffusion constraint for *m*- and *o*-xylene on medium pore zeolite, such as ZSM-5, a large pore zeolite

might be a better option for the xylene isomers interconversion. Indeed, the study of Gonçalves and Rodrigues¹⁰ on the *o*-xylene isomerization, at 493 K, in the liquid phase was performed with BEA and MOR zeolites, which can be considered to have large pores. Zeolite Beta exhibited higher conversion due to its appropriate acidity, and the isomers can all diffuse into the channels of the zeolite without steric constraints.

The disproportionation of xylenes which leads to by-products, such as trimethylbenzene and toluene, will decrease the desired yield. The study of Olson et al.¹⁶ observed that the disproportionation/isomerization selectivity is related to the concentration of acid sites but shows no correlation with the SiO₂/Al₂O₃ ratio (SAR). The higher concentration of acid sites on the catalysts, like for synthetic Faujasite and HY (FAU-type zeolites), is more favorable to the disproportionation reaction than ZSM-5, which typically has fewer acid sites.

Maximizing the production of a given xylene isomer in complex reaction systems is a troublesome task in the chemical reaction engineering field. As previously mentioned, the *p*-xylene obtained from xylene isomerization is limited by the thermodynamic equilibrium. Thus, SMBR that integrates isomerization and separation in a single unit was investigated in the thesis to overcome the limitation. Classical studies of xylene isomerization are more often conducted under industrial conditions: 655-755 K, 1-2.8 MPa (gas phase), in the presence of hydrogen over a bi-functional-type catalyst, where ZSM-5 is the most employed zeolite¹⁷. However, the operating conditions of the adsorption-based separation process in industry are different; it is at 445-460 K, 0.8-0.9 MPa, liquid phase, over a Ba exchanged FAU-type zeolite. Based on the aforementioned and considering that information available in the literature on xylene isomerization in liquid phase is very scarce, the purpose of this chapter is to conduct xylene isomerization experiments on beta zeolites within the temperature range of 453-513 K, which is a compromise between both temperature ranges, at 2.1 MPa, keeping the feedstock in liquid phase.

3.2 Experimental method

3.2.1 Materials

o-Xylene (OX), *m*-xylene (MX), *p*-xylene (PX), and *n*-heptane, all with purity higher than 99.0 %, are from ACROS ORGANICS, and were purchased to Enzymatic, Portugal. All reactants were used without further purification.

BEA35 was kindly supplied by Clariant in powder and in the acid form. BEA38 was purchased from Zeolyst in powder and in the ammonium form. BEA35, as received, without binder addition, was shaped into cylindrical pellets of 4 mm diameter and 2 mm height by uniaxial compression in a benchtop model tablet press (TDP 1.5) with a maximum impulsive force of 15 kN. BEA38 was shaped into pellets through an extrusion-spheronization process using Caleva Multi Lab – CML (Caleva, UK). The equipment included a mixer with a capacity to hold up to 80 mL, a screw extruder with a perforated die with 2 mm diameter openings, and a spheronizer with a rotating textured disc at the base. The zeolite was mixed with γ -alumina, purchased from ACS materials, to act as binder (30 wt%). The mixing process was conducted at 80 rpm for 30 min while adding 0.46 mL of ultra-pure water per grams of solid. Afterwards, the extrusion and spheronization process was carried out at 60 rpm and 650 rpm respectively. Finally, the pellets were calcined at 823 K for 4 hours.

3.2.2 X-ray diffraction

The structure and crystallinity of the two catalysts in pellet form were examined with a Philips X'Pert diffractometer, operating in reflection geometry using $\text{CuK}_{\alpha 1,2}$ radiation, ($\lambda_1 =$

1.540598Å and $\lambda_2 = 1.544426$ Å) at the Laboratório Central de Análises of University of Aveiro, Portugal.

3.2.3 Single particle crushing strength

The crushing strength was measured with a Dr. Schleuniger type 8M tablet hardness tester. The tablet hardness tester has a measuring range of 1-400 Newton, at Delft Solid Solutions B.V., Wateringen, The Netherlands. The pellets were placed in the instrument one by one, and the solid automatically laid in the most stable position. The tablet tester measured the strength of each pellet; in case of elongated particles they were crushed from the side, and thus the radial crushing strength was obtained. To obtain a representative crushing strength, about 50 particles were measured for each sample.

3.2.4 Textural characterization

The morphologic characterization was performed by Scanning Electron Microscopy (SEM), and Energy-Dispersive X-Ray Spectroscopy (EDS), operated at 15 kV (FEI QUANTA 400 FEG ESEM) at Centro de Materiais da Universidade do Porto (CEMUP). Mercury porosimetry analyses were performed at Laboratório de Caracterização e Certificação de Materiais Granulares (IPN - LabGran) to determine the density. Nitrogen sorption data were obtained at 77 K using a manometric adsorption system (Micrometrics ASAP 2000 analyzer), at Laboratório de Sólidos Porosos, Servicios Centrales de Apoyo a la Investigación (SCAI), Universidad de Málaga, Spain.

3.2.5 NH₃-temperature programmed desorption

Ammonia Temperature Programmed Desorption (ATPD) tests were conducted in a Micromeritics Auto Chem II Chemisorption Analyzer equipped with an OmniStarTM mass spectrometer from Pfeiffer vacuum. Prior to analysis, near 100 mg from each zeolite already in pellet form was dehydrated in 50 mL/min of helium flow at 773 K for 30 min, and then cooled to 373 K. The probe gas (5% NH₃, balance He) was subsequently adsorbed for 30 min using a flow rate of 50 mL/min. After purging at the same temperature with 50 mL/min of He flow for one hour, the temperature was raised at a rate of 10 K/min up to 823 K in 50 mL/min of He flow while monitoring the ammonia evolved from the sample. For calibration purposes, the analyzer baseline was measured in He flow and the mass-to-charge (*m/z*) signal 16 was measured in probe gas flow bypassing the sample before and after the ATPD test.

3.2.6 FTIR spectroscopy

Concentration of Lewis and Brønsted acid sites of each catalyst already in pellet form were determined using pyridine as probe molecule by FTIR spectroscopy (Thermo Nicolet Nexus 670). All samples were prepared as self-supporting wafers previously outgassed at 723 K. Adsorption of pyridine was conducted at 423 K followed by evacuation of excess pyridine under vacuum for 30 min. The temperatures of desorption were 423, 523, 623, and 723 K; each spectrum was recorded after 30 min of desorption using a resolution of 4 cm⁻¹ with 64 scans per spectrum.

3.2.7 Experimental set-up and procedure

The fixed bed experimental set-up is presented in **Figure 3.1**. Indeed, fixed bed experiment is an expedite way to determine the kinetics of the reaction. The experimental procedure is described as follows:

The catalyst was loaded into the fixed bed column and dried overnight at 473 K under a constant flow rate of nitrogen. Afterwards, the column was heated up to the desired reaction temperature (513, 493, 473, and 453 K respectively) at a constant pressure of 2.1 MPa under a continuous feed of heptane. Once the column reached the desired temperature, the feedstock switched from heptane to pure xylene. The feed flow rate was controlled by an HPLC pump and verified by measuring a given volume of the outlet stream for a certain time. The fluid passed through a serpentine coil inside the oven to guarantee pre-heating of the feed to the desired temperature. The fixed bed outlet stream passed through a filter, to remove possible existing catalyst fines, and then was cooled in a serpentine immersed in a water bath, at ambient temperature before the back-pressure regulator. Samples of the effluent were collected at atmospheric pressure and ambient temperature, at a predefined sampling rate. The analysis of the samples was performed by gas chromatography.

Catalyst regeneration was conducted every ten hours of operation to keep the same catalyst activity for all experiments. The regeneration process was conducted with a gas stream comprising 2-3% oxidizing gas in nitrogen. The procedure was validated by repeating an experiment carried out in the previous set and verifying that the conversion matched in both experiments.

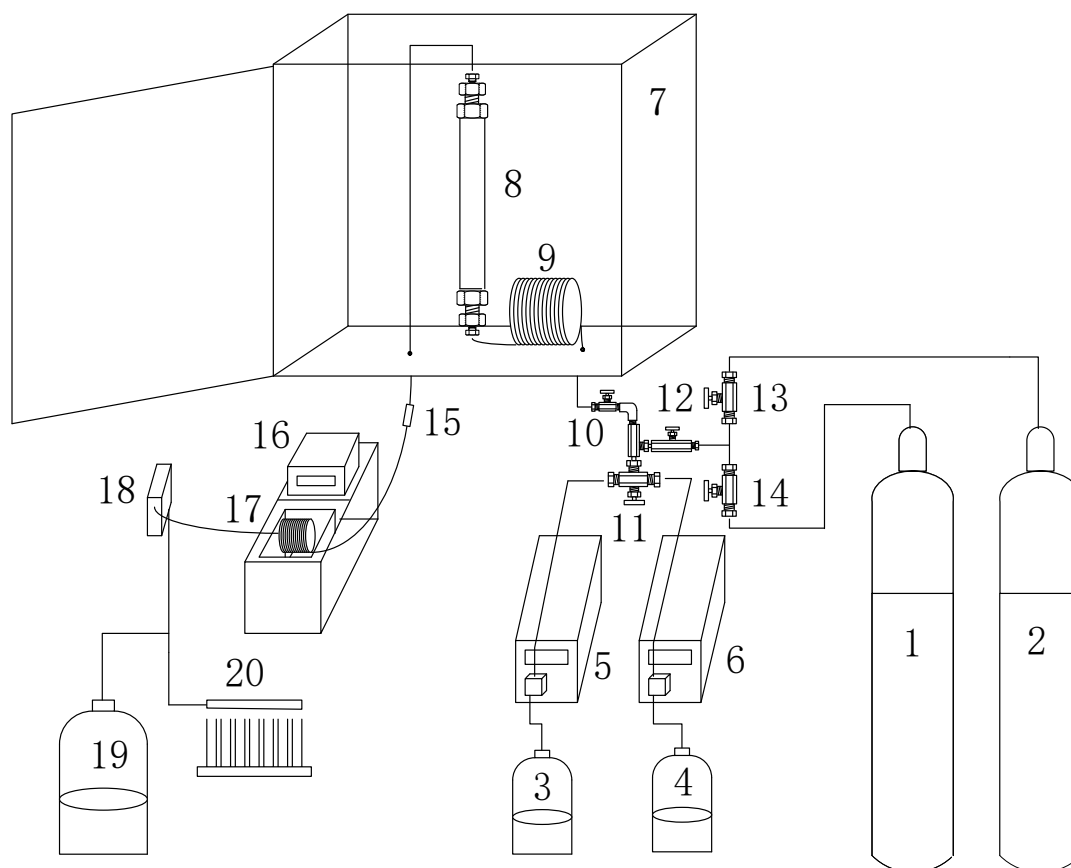


Figure 3.1 Fixed-bed experimental set-up. 1: Nitrogen gas cylinder; 2: Air gas cylinder; 3: Bottle for heptane; 4: Bottle for feed mixture; 5,6: Pumps; 7: Oven; 8: Column; 9: Serpentine; 10: On-off valve of column; 11: Switch valve of liquid feed; 12: On-off valve of gas; 13: On-off valve of air; 14: On-off valve of nitrogen; 15: In line filter; 16: Thermostatic bath; 17: Serpentine; 18: Back pressure regulator; 19: Waste bottle; 20: Fraction collector.

3.3 Kinetic models development

As mentioned above, the linear reaction scheme describes the reaction through 1,2-methyl shift mechanism, which means the conversion between *o*- and *p*-xylene can only occur through *m*-xylene as intermediate (**Figure 3.2a**). In the triangular reaction scheme, the reaction can also happen through 1,3-methyl shift mechanism with direct interconversion between *o*- and *p*-xylene (**Figure 3.2b**). Disproportionation and dealkylation reactions are not expected under the studied conditions.

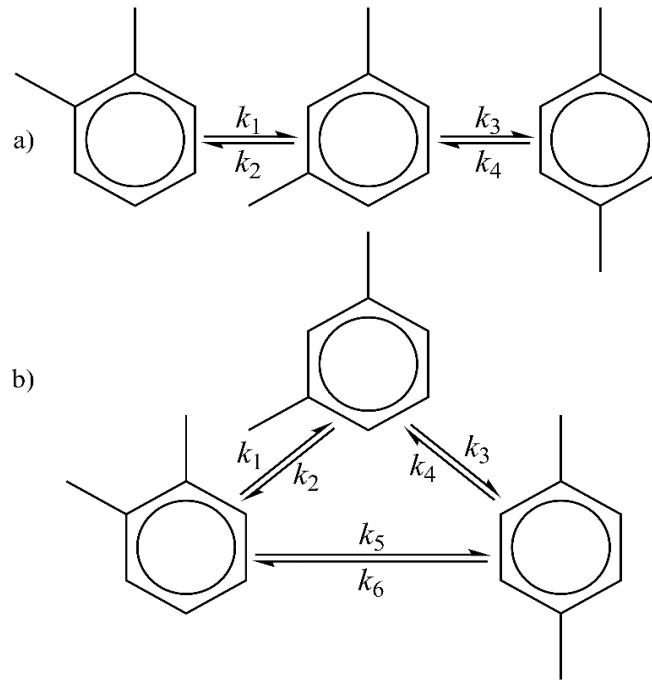


Figure 3.2 a) Linear reaction scheme b) Triangular reaction scheme for xylene isomerization

In the absence of internal and external mass-transfer resistance, the mass balance for species i in a plug-flow reactor under isothermal conditions is as follows:

$$u \frac{dC_i}{dz} = \frac{1-\varepsilon}{\varepsilon} \rho_p R_i \quad (3.1)$$

with the following boundary condition:

$$C_i|_{z=0} = C_{in} \quad (3.2)$$

where C_i is the molar concentration of component i , mol/L; ε is the bed porosity; ρ_p is the particle apparent density, g/L; u is the fluid interstitial velocity, m/s; and z is the axial coordinate.

The overall reaction rates through the 1,3-methyl shift mechanism (triangular scheme) are given by:

$$R_{OX} = k_2 C_{MX} + k_6 C_{PX} - k_5 C_{OX} - k_1 C_{OX} \quad (3.3)$$

$$R_{MX} = k_1 C_{OX} + k_4 C_{PX} - k_2 C_{MX} - k_3 C_{MX} \quad (3.4)$$

$$R_{PX} = k_5 C_{OX} + k_3 C_{MX} - k_6 C_{PX} - k_4 C_{PX} \quad (3.5)$$

The overall reaction rates through the 1,2-methyl shift mechanism (linear scheme) are given by:

$$R_{OX} = k_2 C_{MX} - k_1 C_{OX} \quad (3.6)$$

$$R_{MX} = k_1 C_{OX} + k_4 C_{PX} - k_2 C_{MX} - k_3 C_{MX} \quad (3.7)$$

$$R_{PX} = k_3 C_{MX} - k_4 C_{PX} \quad (3.8)$$

where $k_1, k_2, k_3, k_4, k_5, k_6$ are rate constants of each reaction defined in **Figure 3.2**, $\text{m}^3/\text{kg s}$; C_{OX}, C_{MX}, C_{PX} represent the concentrations of *o*-xylene, *m*-xylene and *p*-xylene, respectively, mol/L ; R_{PX}, R_{MX}, R_{OX} are the apparent reaction rates of *p*-xylene, *m*-xylene and *o*-xylene, respectively, mol/g s .

Linear and triangular schemes, as shown in **Figure 3.2**, are adopted to calculate the kinetic parameters. The thermodynamic equilibrium of xylene isomerization in the liquid phase proposed by Gonçalves and Rodrigues¹⁸ was used to guarantee thermodynamic consistency and, at the same time, to reduce the number of parameters to be estimated. The influence of the temperature on the kinetic constants was accounted for through the center-type Arrhenius equation.

$$k_j = k_{0,j} \exp \left[-\frac{E_{a,j}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (3.9)$$

$k_{0,j}$ is the kinetic constant at the centered temperature T_0 , (middle temperature of all the investigated temperatures); T is the temperature, K; R is the gas constant, J/mol K; and $E_{a,j}$ is the activation energy of reaction j . The parameters were estimated through the commercial software gPROMS v4.2.0 from Process Systems Enterprise with the maximum likelihood method with constant variance and tolerance of 10^{-5} .

Besides the two models (triangular and linear) considering the equilibrium from literature, as mentioned before, and hereafter referred as triangular-equilibrium from literature and linear-equilibrium from literature, two other models were also studied, where no constraints

related to the equilibrium constant were made, and all six kinetic constants were considered as parameters to be estimated, hereafter referred simply as triangular and linear.

3.4 Results and discussion

3.4.1 Catalyst textural characterization

The textural characterization results are presented in the Annex A. **Figure A1** presents the X-ray diffraction (XRD) of BEA35 and BEA38 compared to reported powder pattern by the International Zeolite Association; **Figures A2** and **A3** present the scanning electron microscopy (SEM) images of BEA35 and BEA38, respectively. The crushing strength data in newtons (N) is given in **Table A1**. Nitrogen adsorption equilibrium isotherms on BEA35 and BEA38 pellets at 77 K are shown in **Figure A4**.

3.4.2 Catalyst acid sites characterization

Figure 3.3 shows the profile of desorbed NH_3 against temperature for samples BEA35 and BEA38, where the amount of NH_3 desorbed has been normalized by the mass of sample, at the end of the TPD test, to facilitate the comparison. Both samples present alike NH_3 desorption profiles, with three overlapping peaks that correspond to sites with increasing activation energies of desorption. Normally, three kinds of desorbed ammonia peaks are observed at low (l), high (h1), and additional high (h2) temperatures, corresponding to weak, strong and very strong acid sites^{19, 20}.

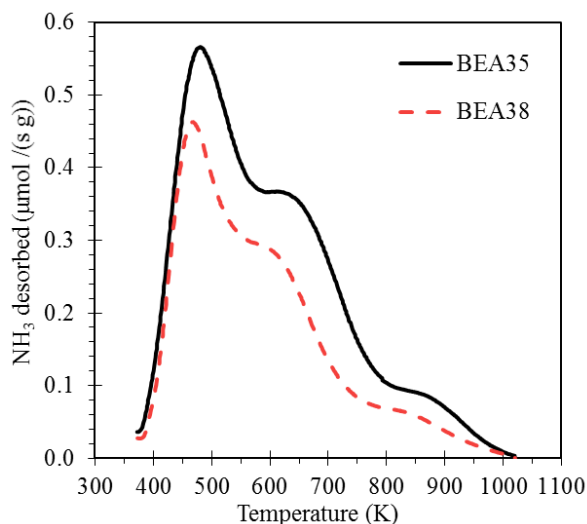


Figure 3.3 ATPD spectra of BEA35 and BEA38: NH_3 desorbed versus desorption temperature during heating at 10 K/min in 50 mL/min of helium flow

In zeolite BEA, the peaks may overlap²¹. Its tail-like spectrum might be due to a defective zeolite framework; this gives BEA a unique aluminum (Al) configuration^{21, 22}. Moreover, the additional peak at higher temperatures has been observed in commercial BEA zeolite; it was attributed to dislocation of framework Al leading to the formation of extra-framework aluminum (EFAl)²². EFAl are known to be very strong Lewis acid sites²³.

Also from **Figure 3.3**, BEA38 presents lesser NH_3 desorption than BEA35 in the entire temperature range evaluated, which means that BEA38 presents a lower concentration of acid sites per mass of sample. The shift observed in the NH_3 desorption profile of BEA38 to lower temperatures compared to that of BEA35 indicates the monotonic decrease of the strength of the acid sites as the SAR ratio increases²⁴. Moreover, the fact that BEA38 includes 30 wt% of binder may have also contributed to the said decrease of the acid sites compared to BEA35 which was pelletized without a binder.

The total amount of NH_3 desorbed from BEA35 and BEA38 is shown in **Table A2**. A Gaussian deconvolution of the NH_3 profiles into the three peaks, l, h1, and h2 was carried out to estimate their relative contribution. The goodness of fit can be seen in **Figure A5** and the corresponding concentration of the adsorption sites in Table A2.

Pyridine desorption analyzed by FTIR assessed the amount of Lewis and Brønsted acid sites. Their concentrations were calculated using the extinction coefficients from Emeis²⁵ and are displayed in **Table 3.1** at different desorption temperatures. The acid sites at high temperature correspond to strong acid sites.

Table 3.1 Concentration ($\mu\text{mol/g}$) of Lewis and Brønsted acid sites of the two catalysts at different desorption temperatures

Desorption Temperature (K)	BEA35		BEA38	
	Brønsted	Lewis	Brønsted	Lewis
423	253	164	109	191
523	206	149	84	157
623	130	146	48	134
723	30	148	9	108

The difference spectra in the pyridine and OH stretching regions for the two samples at different temperatures are depicted in **Figures 3.4**. In the pyridine region, the peaks at 1544 cm^{-1} and 1455 cm^{-1} correspond to the Brønsted and Lewis acid sites, respectively; those peaks were used to determine the acid concentration presented in **Table 3.1**. The band at 1490 cm^{-1} results from both contributions²⁶ It can be seen that BEA35 presented the highest amount of Brønsted acid sites, over which the isomerization of xylenes occurs. Therefore, it can be concluded that BEA35 must exhibit better performance compared to the other catalyst in xylene

isomerization. It is important to note that BEA38 included 30 wt% of γ -alumina as binder, which may dilute the amount of Brønsted acid sites in the final catalyst.

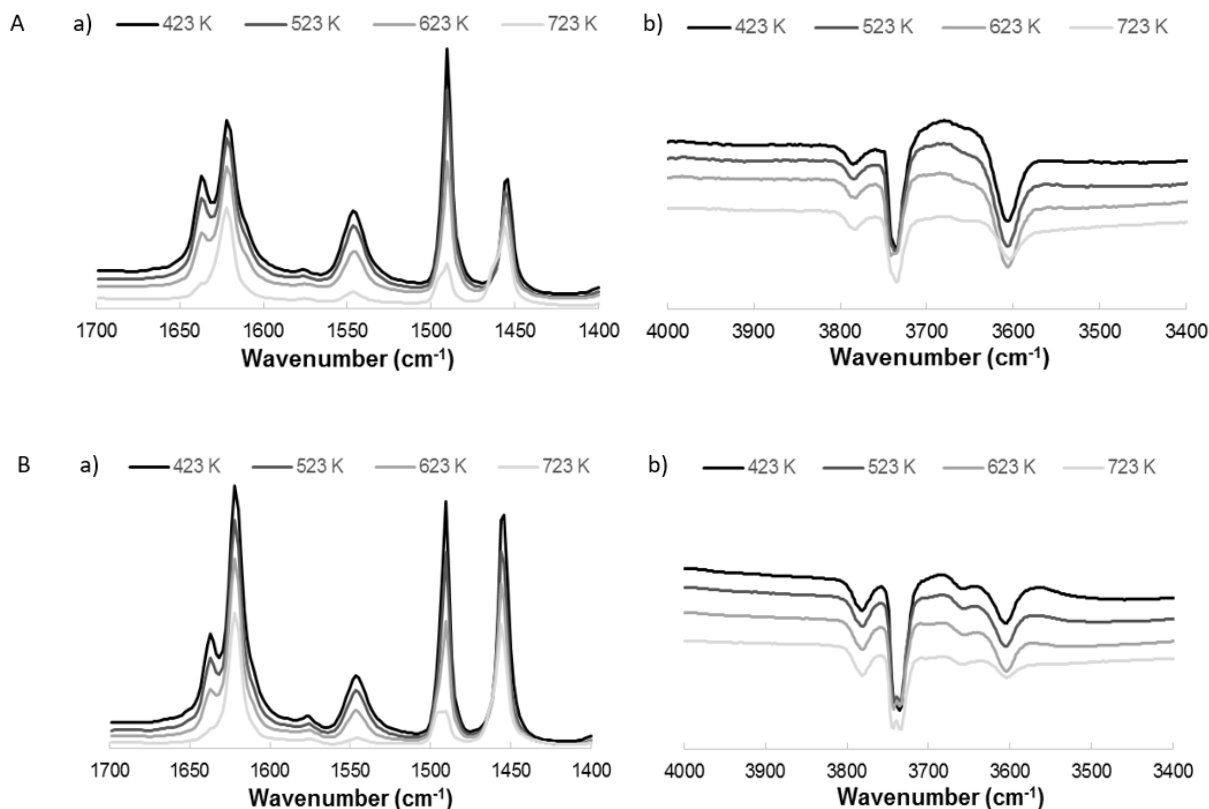


Figure 3.4 FTIR spectra of A) BEA35, and B) BEA38 at different temperatures in the a) pyridine region, and b) OH stretching region

The bands in the OH stretching region provide further information about the acidity of the zeolite samples. Both samples present a similar peak at 3736 cm^{-1} indicating silanol groups (SiOH) in the zeolite defects, which are very common in BEA zeolites²⁰. Both samples presented a peak at 3782 cm^{-1} confirming the presence of EFAl²⁴, which are known to be very strong Lewis acid sites²³. However, BEA38 presented a more significant peak which is consistent with the peaks at 3656 and 3743 cm^{-1} indicating aluminic species in extra-framework positions, and SiOH on external surface respectively^{28, 27}. Those above (EFAl sites) are probably due to the presence of water during calcination of the solid leading to dealumination

and, therefore, a higher concentration of Lewis acid sites; more EFAl sites in BEA38 can also be verified by the slightly larger contribution of peak h2 in Table A2. The appearance of the said peak depends on the whole procedure of synthesis^{22, 29}. As expected, BEA35 exhibited the largest peak at 3606 cm⁻¹ which corresponds to acid bridging Si-OH-Al groups (Brønsted acid sites)^{27, 30, 29}.

3.4.3 Mass-transfer resistance

The catalytic experiments were performed in the fixed bed set-up previously described (vide **Figure 3.1**). The geometrical characteristics of the bed and catalyst particles, as well as other relevant properties for both catalysts BEA35 and BEA38, are presented in **Table 3.2**.

Table 3.2 Column characterization of the catalysts

	BEA35	BEA38
Column diameter (D)	2.1 cm	2.1 cm
Column height (L)	31.1 cm	29.8 cm
Catalyst mass – dry (W_c)	70.6 g	69.8 g
Particle density (ρ_p)	1.05 g/mL	1.12 g/mL
Bed porosity (ε)	0.38	0.40
Particle volume-to-surface (cm) ratio (V_p/S_p)	0.050	0.033
Particle porosity (ε_p)	0.29	0.32

The existence of external and intraparticle mass-transfer limitations was carefully examined. Since the reaction rate is enhanced more than that of the mass transfer as the temperature increases and the highest conversions are observed at lower flow rates, the effect of the mass transfer was evaluated only at the highest temperature and the lowest flow rate. In Annex B,

Tables B1 and **B2** present the variables used to determine the influence of the external and internal mass-transfer resistances, respectively. The Carberry number, Ca , was calculated at the lowest flow rate and at 513 K, which was found to be far less than 0.05. Therefore, the external diffusion resistance can be neglected. The effectiveness factor η was used to compare the observed reaction rate to the reaction rate in the absence of internal diffusional resistance. The effectiveness factor can be computed through the following equation³¹:

$$\eta\phi^2 = \frac{R_{obs}\rho_p(V_p/S_p)^2}{D_e C_b} \quad (3.10)$$

where η is the effectiveness factor; ϕ is the Thiele modulus; R_{obs} is the observed reaction rate, mol/g_{cat} s; V_p is the particle volume, m³; S_p is the particle surface, m²; C_b is the bulk reactant concentration, mol/L; and D_e is the effective diffusion coefficient, m²/s. D_e can be calculated through eq 3.11:

$$D_e = D_m \varepsilon_p / \tau \quad (3.11)$$

where D_m is the molecular diffusivity, m²/s; ε_p is the particle porosity; and τ is the tortuosity factor. Since the experiments were conducted at low conversions, D_m can be considered as self-diffusion and calculated through³²:

$$\frac{D_{AA}\mu_A}{KT} = \frac{1}{2\pi} \left(\frac{\tilde{N}_A}{\tilde{V}_A} \right)^{1/3} \quad (3.12)$$

where D_{AA} is the self-diffusion coefficient, m²/s; μ_A is the viscosity of the pure compound, kg/(m s); K is the Boltzmann constant, m² kg/s² K; T is the Temperature, K; $\tilde{N}_A$ is the Avogadro number, mol⁻¹; and $\tilde{V}_A$ is the molar volume of the compound, m³/mol.

Since BEA35 zeolite is closer to sphere pellet, Thiele modulus ϕ can be calculated through:

$$\eta\phi^2 = \phi \left(\frac{1}{\tanh 3\phi} - \frac{1}{3\phi} \right) \quad (3.13)$$

while for BEA38 cylinder geometry should also be considered, therefore:

$$\eta\phi^2 = \phi \frac{I_1(2\phi)}{I_0(2\phi)} \quad (3.14)$$

With eqs 3.13 and 3.14 one can assess the internal mass-transfer existence on BEA38 at 513 K and BEA35 at 493 K; the computed values are presented in **Table B2**. For η near unity, the entire volume of the pellet can be considered to be active in the reaction at the same reaction rate as the surface conditions reaction rate because the reactant can diffuse quickly enough through the pellet not developing any internal concentration profiles.

3.4.4 Xylenes isomerization conversion on BEA38

The products distribution of xylene isomerization on BEA38 at 513, 493, and 473 K are presented in Annex B, **Tables B3 to B5**. The distribution of the products illustrates that the main products of the reaction are the other two isomers. Yet, traces of toluene and trimethylbenzene were observed, but with yields lower than 1%. For the mathematical study of xylene isomerization on BEA38, xylene disproportionation to toluene and trimethylbenzene was neglected.

The kinetic parameters of xylene isomerization on BEA38 at 513, 493, and 473 K were calculated based on the four models mentioned above, the results are presented in **Table B6**, and the results obtained for each temperature are presented in **Tables B7 to B9**. One can conclude from the experimental results that the linear scheme combined with the thermodynamic equilibrium equations proposed by Gonçalves and Rodrigues¹⁸ is a better representation of the reaction due to its simplicity and higher accuracy.

For all the studied temperatures, the kinetic constants from *o*-xylene to *m*-xylene reaction (k_1) are higher than the kinetic constants of the reverse reaction (k_2); additionally, the kinetic constants from *p*-xylene to *m*-xylene reaction (k_4) are also higher than its reverse reaction (k_3). A possible explanation is that *m*-xylene is more thermodynamic stable. In the study of Al-Khattaf et al.¹², they mentioned that the apparent rate constant for *p*- to *m*-xylene (k_4) reaction is on average 2.3 times that of the reverse reaction. In fact, Gonçalves and Rodrigues³³ found out that the value of $Keq_1=k_2/k_1$ and $Keq_2=k_4/k_3$ are functions of temperature. **Figure B1** shows the conversion of each isomer at 473, 493, and 513 K.

Furthermore, the kinetic constants for the isomerization of *m*-xylene to *p*-xylene (k_3) are slightly higher than that of *m*-xylene to *o*-xylene (k_2). This can be attributed to the smaller molecular size of *p*-xylene, which makes it easier to exit the particle. Taking that fact into consideration, one can postulate that if the crystal size of the catalyst is increased, the longer diffusion path promotes the selectivity towards the *p*-xylene. The kinetic constants for the isomerization of *p*-xylene to *m*-xylene (k_4) present the highest values. Besides the previously mentioned reasons, this may also be explained by the lower adsorption strength of *p*-xylene; weaker interaction with the solid can result in a faster diffusion of the *para*-isomer. The adsorption-diffusion of xylenes on acid catalysts is related to the dipole moment; *m*- and *o*-xylene have higher alkalinity and dipole moment than *p*-xylene and thus they are more strongly adsorbed by the acid sites than *p*-xylene.

The kinetic constants of isomerization of *o*- to *p*-xylene (k_5) and of *p*- to *o*-xylene (k_6) (triangular scheme) were one magnitude lower than other kinetic constants and with high uncertainty, especially at high temperature; this indicates that the interconversion between *o*- and *p*-xylene is difficult when compared to the others. This is by the existing literature,

which claims that the triangular reaction scheme is not adequate to represent the isomerization reaction scheme on large pore zeolites²³.

The activation energies and kinetic constants at centered temperature were also calculated based on the four models and using the Arrhenius law, and the results are presented in **Table B6**. The apparent activation energy for the isomerization of *p*- to *m*-xylene ($E_{a,4}$) is the lowest; this corroborates the conclusion that the conversion from *p*- to *m*-xylene is the easiest. The apparent activation energy of the isomerization reaction of *o*- to *m*-xylene ($E_{a,1}$) is lower than that of the reverse reaction ($E_{a,2}$), which indicates that it is much easier to react from *o*- to *m*-xylene than the reverse reaction. Gonçalves and Rodrigues¹⁰ studied the kinetic constants through *o*-xylene isomerization experiments at the temperature range of 473–513 K, and reported that the activation energy of isomerization from *o*- to *m*-xylene ($E_{a,1}$) on BEA35 is 144 kJ/mol, and from *m*- to *p*-xylene ($E_{a,3}$) is 140 kJ/mol. In this chapter, at the same experimental conditions, the activation energies of isomerization from *o*- to *m*-xylene ($E_{a,1}$) and from *m*- to *p*-xylene ($E_{a,3}$) are lower, 91 and 90 kJ/mol, respectively. This may attribute to the difference in the SAR; *i.e.*, differences in the amount of existing acid sites. However, for both results, the activation energies for isomerization of *o*- to *m*-xylene ($E_{a,1}$) and of *m*- to *p*-xylene ($E_{a,3}$) are very similar.

Cappellazzo and co-workers also reported data regarding xylene isomerization in the liquid phase⁸. Their experiments were conducted at 523–573 K over ZSM-5, and the activation energy of the *o*- to *m*-xylene reaction was 98.8 kJ/mol, which is lower than that of the reaction of *m*- to *p*-xylene (136 kJ/mol), this can be attributed to the diffusion constraints of *m*- and *o*-xylene on ZSM-5.

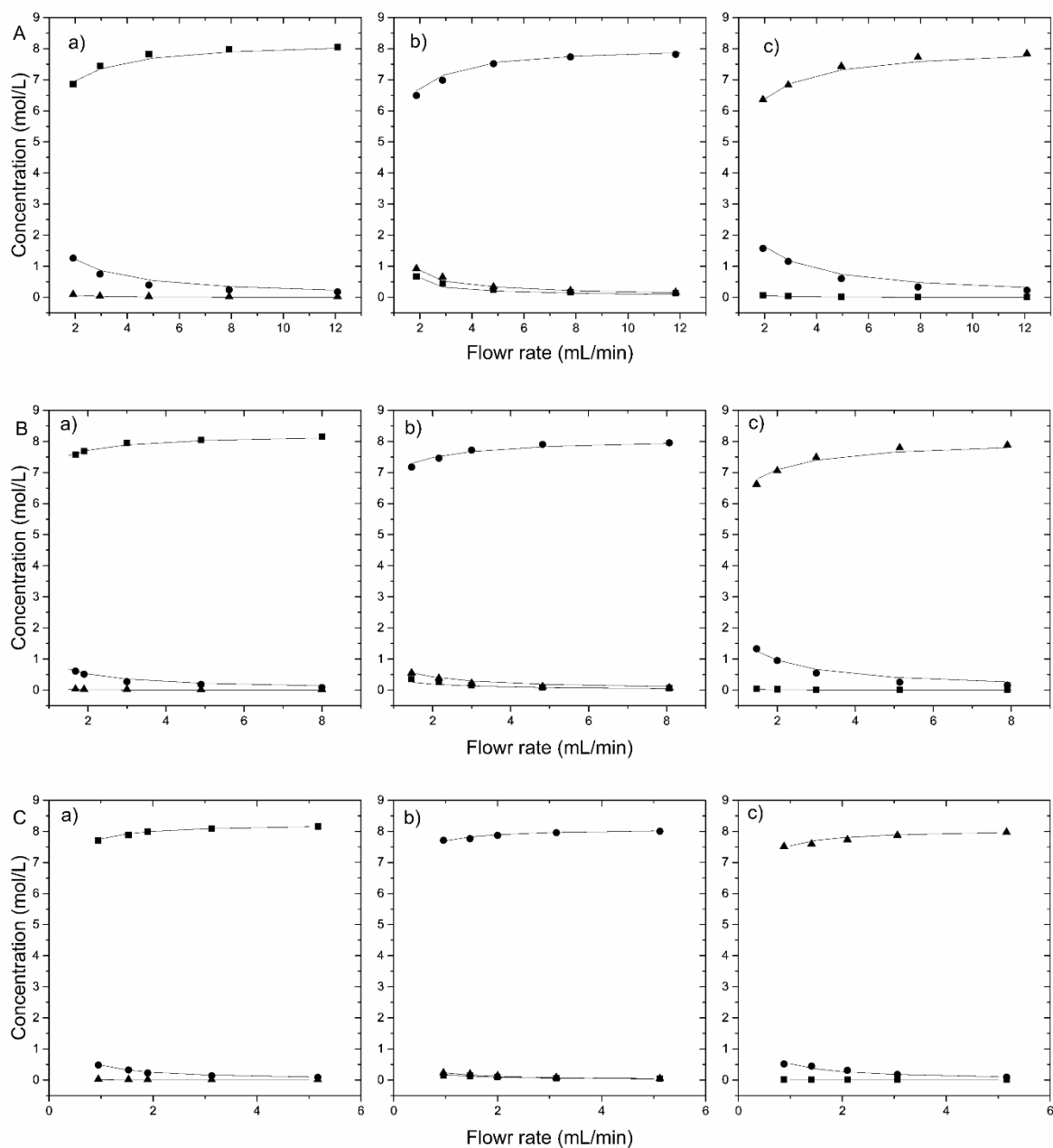


Figure 3.5 Comparison of a) OX, b) MX, and c) PX experimental data (■OX; ●MX; ▲PX) and corresponding simulated results in linear at A) 513 K, B) 493 K, and C) 473 K on BEA38

To check the validity of the estimated kinetic constants at the experimental conditions, the kinetic constants calculated by the linear model considering equilibrium from literature, which have the lowest uncertainty, were used in the plug-flow fixed bed model to simulate the

experimental results. The simulation results are compared to the experimental data, as shown in **Figures 3.5**. It is observed that the computed results compare very well with the experimental data. Since the linear model coupled with equilibrium constants from the literature achieved an accurate prediction of experimentally observed concentrations, it is verified that xylene isomerization happens through the 1,2-methyl shift mechanism.

3.4.5 Xylenes isomerization conversion on BEA35

The products distribution of xylene isomerization at 493, 473, and 453 K are presented in Annex B in **Tables B10 to B12**. The kinetic parameters of xylene isomerization on BEA35 at 493, 473, and 453 K were calculated based on the four models mentioned above, the results are presented in **Table B13**, and the results obtained for each temperature are presented on **Tables B14 to B16**.

As it has already been observed from the experiment results on BEA38, the linear scheme combined with the thermodynamic equilibrium from the literature showed better accuracy in representing the experimental results.

The reaction kinetic constants, on BEA35, also follow the same sequence k_4 (*p*-xylene to *m*-xylene) $> k_1$ (*o*-xylene to *m*-xylene) $> k_3$ (*m*-xylene to *p*-xylene) $> k_2$ (*m*-xylene to *o*-xylene). This is in agreement with the observed results on BEA38. Datka et al.³⁴ observed that weak Brønsted and Lewis acid sites show no activity for *o*-xylene isomerization. However, weak acid sites show activity for *p*-xylene isomerization³³, which contributed to an easier isomerization of *p*-xylene compared to the other two isomers. The kinetic constants on BEA35 are higher than that on BEA38; this can be attributed to the higher amount of acid sites on BEA35. In other words, as can be observed in the catalysts characterization (**Table 3.1**), BEA35 has approximately three times more Brønsted acid sites than BEA38, yet the kinetic

constants are more than five times higher for the isomerization reaction on BEA35 than on BEA38. This can be explained by the interaction between Brønsted and Lewis acid sites. Indeed, Derouane et al.²³ concluded that even though Lewis acid sites do not take part in the isomerization reaction, they still can strengthen the acidity of Brønsted acid sites. Moreover, the larger crystals of BEA38 (vide **Figure A2** and **A3**) may have affected the diffusion of the xylene isomers within the channels, leading to lower activity. **Figure B2** shows the conversion of each isomer at 453, 473, and 493 K.

For the results calculated through triangular reaction scheme, the kinetic constants of isomerization from *o*- to *p*-xylene (k_5) and from *p*- to *o*-xylene (k_6) are again turned out to be much lower than other kinetic constants and with higher uncertainty; this fact demonstrates further the difficulty of the direct conversion of *o*- to *p*-xylene.

Table 3.3 Kinetic parameters of xylene isomerization following the linear scheme considering the thermodynamic equilibrium for BEA38 and BEA35

	BEA 38	BEA 35
T_0 (K)	493	473
$E_{a,1}$ (kJ/mol)	91 ± 9	91 ± 7
$E_{a,3}$ (kJ/mol)	90 ± 8	84 ± 6
$k_{0,1} \times 10^8$ (m ³ /kg s)	3.5 ± 0.3	8.7 ± 0.5
$k_{0,3} \times 10^8$ (m ³ /kg s)	2.35 ± 0.12	4.4 ± 0.2

The activation energies and kinetic constants at centered temperature for the linear scheme incorporating the thermodynamic equilibrium from the literature for both catalysts are presented in **Table 3.3**. The activation energies on BEA35 and BEA38 are very similar. As an example, the activation energy of the isomerization of *o*- to *m*-xylene and of *m*- to *p*-xylene are respectively 91 and 90 kJ/mol on BEA38, 91 and 84 kJ/mol on BEA35. The apparent activation

energy for isomerization from *m*- to *p*-xylene ($E_{a,3}$), is slightly lower than that on BEA35, but their difference is still within the uncertainty interval. To conclude, since the apparent activation energies present no significantly different values for BEA38 and BEA35, one can say that the isomerization on both catalysts follow the same mechanism.

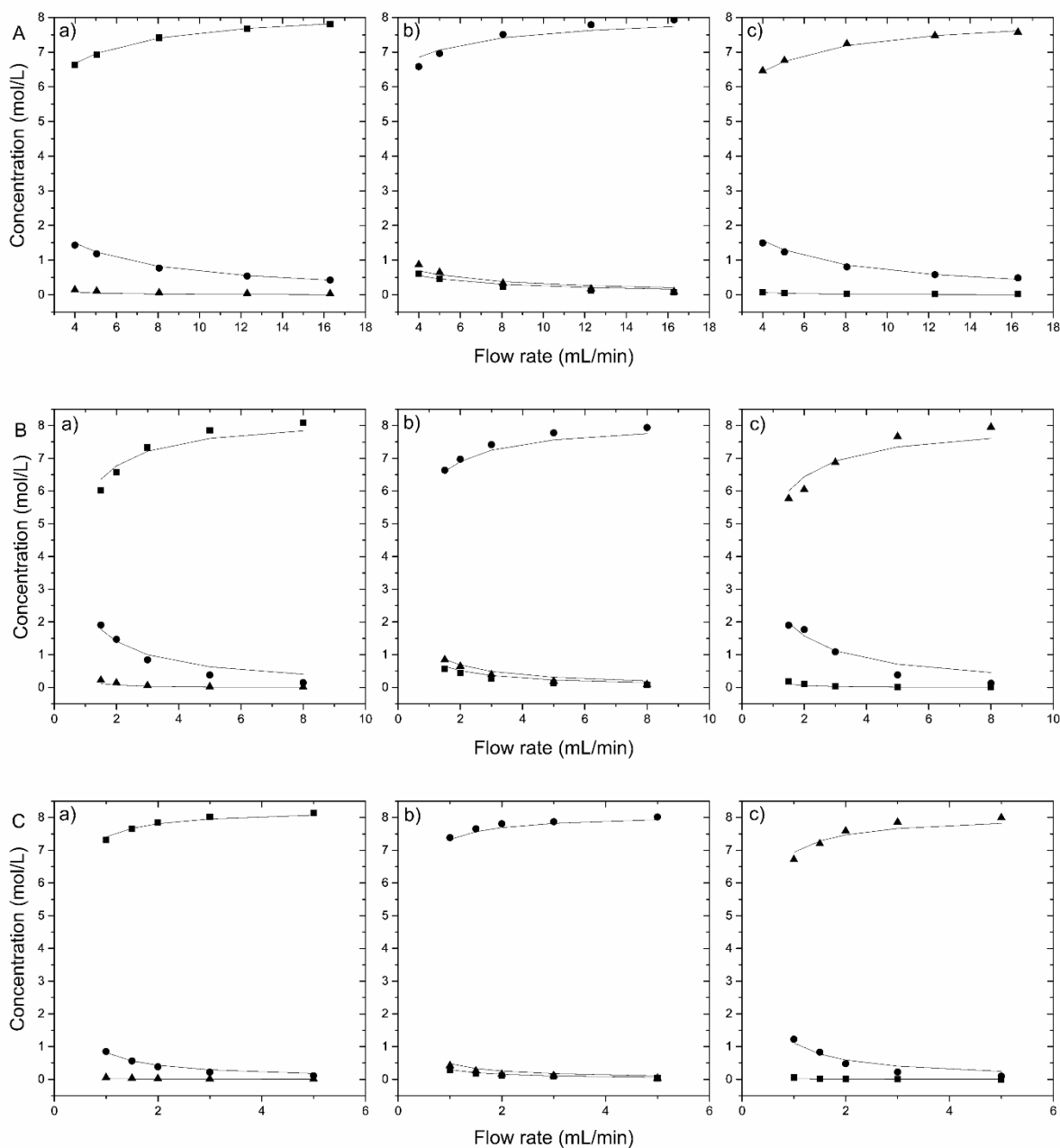


Figure 3.6 Comparison of a) OX, b) MX, and c) PX experimental data (■OX; ●MX; ▲PX) and corresponding simulated results in linear at A) 493 K, B) 473 K, and C) 453 K on BEA35

To check the validity of the estimated kinetic constants at the experimental conditions, on BEA35, the kinetic constants, determined by the linear model considering equilibrium from the literature, which have the lowest uncertainty, were used in the plug-flow fixed bed model to simulate the experimental results. The simulation results are compared to the experimental data, as shown in **Figures 3.6**. It is observed that the computed results compare very well with the experimental data.

3.5 Conclusions

An extensive study on the xylene isomers interconversion kinetics was carried out on BEA35 and BEA38 employing fixed bed experiments in the liquid phase. Four kinetic models, based on linear and triangular reaction schemes, and combined with the thermodynamic equilibrium data from the literature, were adopted to describe the reaction kinetics. According to the results, the linear reaction scheme combined with the equilibrium model from literature, besides being the simplest one, was the one presenting the lowest uncertainty. A good prediction of the experiment results by the proposed best model was obtained.

The kinetic constants of k_5 and k_6 , which indicate the direct conversion between *o*-xylene and *p*-xylene, are one order of magnitude lower than the other kinetic constants. Additionally, they presented high uncertainty, even not having physical meaning in some cases. The results provide conclusive evidence that conversion of *p*- to *o*-xylene, and its reverse reaction, in the liquid phase, on BEA catalysts go through the 1,2-methyl shift mechanism, having *m*-xylene as intermediate.

The reactivity of xylene isomers were found to decrease in the sequence *p*-xylene > *o*-xylene > *m*-xylene for BEA35 at all temperature studied. While for BEA38, the reactivity of *m*-xylene exceeds that of *o*-xylene only at the two highest temperatures, 513 and 493 K. It is most likely

due to the counterbalance of molecular size and dipole moment. The activity of *o*-xylene exceeds that of *m*-xylene when the contribution of molecular size to its reactivity overweighs that of its dipole moment.

The activation energies of isomerization from *o*- to *m*-xylene ($E_{a,1}$), and from *m*- to *p*-xylene ($E_{a,3}$) are respectively 91 and 90 kJ/mol on BEA38, and on BEA35 are 91 and 84 kJ/mol. Thus, the activation energies of reactions on BEA38 and BEA35 are similar. It demonstrates that the reactions on the two catalysts follow the same mechanism. The presence of a higher amount of acid sites on BEA35 than on BEA38 is reflected on the higher kinetic constant at centered temperature for BEA35 than for BEA38.

3.6 Nomenclature

C_i , molar concentration of component i (i =PX, MX, OX), mol/L

Ca, Carberry number

C_b , bulk reactant concentration, mol/L

D_{AA} , self-diffusion coefficient, m^2/s

D_m , molecular diffusivity, m^2/s

D_e , effective diffusion coefficient, m^2/s

$E_{a,j}$, activation energy of reaction j , kJ/mol

K , Boltzmann constant, $m^2 \text{ kg/s}^2 \text{ K}$

k_f , mass transfer coefficient, m/s

k_j , kinetic constant of reaction j (j =1,2,3,4,5,6), $m^3/\text{kg s}$

$k_{0,j}$, kinetic constant of reaction j (j =1,2,3,4,5,6) at centered temperature T_0 , $m^3/\text{kg s}$

$\tilde{N}_A$, Avogadro number, mol^{-1}

R , gas constant, J/mol K

R_{obs} , observed reaction rate, mol/g s

R_i , apparent reaction rate (i =PX, MX, OX), mol/kg s

S_p , particle surface, m^2

T , Temperature, K

T_o , Centered temperature, K

u , fluid interstitial velocity, m/s

$\tilde{V}_A$, molar volume of the compound, m³/mol

V_p , particle volume, m³

W_c , mass of catalyst, kg

z , axial coordinate

Greek letters

τ , tortuosity factor

ε , bed porosity

ε_p , particle porosity

ρ_p , particle density, kg/m³

η , effectiveness factor

ϕ , Thiele modulus

μ_A , viscosity of the pure compound, kg/m s

Superscripts and subscripts

i , number of components ($i = \text{PX, MX, OX}$)

Abbreviations

EFAI, Extra-framework aluminum

SMBR, Simulated Moving Bed Reactor

SAR, silica alumina ratio

3.7 References

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Chapter 4 Xylene Isomerization Side Reactions over Beta Zeolite

This chapter describes an experimental and parametric behavior study of disproportionation and transalkylation between C₈ aromatics and toluene. The experiments were carried out over mono-functional acid beta zeolite with a SiO₂/Al₂O₃ ratio of 35 (BEA35) and were performed in the liquid phase under the following conditions: 453, 473, and 493 K and 2.1 MPa. Ethylbenzene disproportionation and ethylbenzene-toluene transalkylation were identified as the main side reactions in the Simulated Moving Bed Reactor (SMBR). The reaction order and mechanism were verified. Additionally, the kinetics and activation energies of both reactions were estimated. Finally, an analytical solution was developed for the system.

This chapter is based on Shi, Q.; Gonçalves, J. C.; Ferreira, A. F. P.; Plaza, M. G.; Rodrigues, A. E. Xylene Isomerization Side Reactions over Beta Zeolite: Disproportionation and Transalkylation of C₈ Aromatics and Toluene. *Appl. Catal., A* 2018, 562, 198-205

4.1 Introduction

As mentioned in Chapter 2, the catalytic conversion of aromatic molecules and toluene via transalkylation or disproportionation is a fundamental process in the petrochemical industry. Ethylbenzene (EB) disproportionation is one of the methods for the production of *p*-diethylbenzene (PDEB) in the industry; compared with other processes, it needs lower installation costs, and has more extended catalyst life¹. PDEB is the most desirable diethylbenzene (DEB) isomer, with a wide range of applications in the chemical and petrochemical industry²; PDEB is also used as desorbent in adsorptive separation processes such as Parex from UOP and Eluxyl from IFP. However, for a Simulated Moving Bed Reactor (SMBR), integrating the isomerization and separation of xylenes in the same unit, toluene (TOL) has been proposed instead of PDEB to act as desorbent, because of the isomerization of PDEB^{3, 4, 5}. Therefore, besides xylene isomerization, side reactions like disproportionation and transalkylation between C₈ aromatics and toluene may also exist within the SMBR unit.

Most of the literature studies on disproportionation and transalkylation between C₈ aromatics and toluene focus on the influence of the acid sites, the different reaction mechanisms, and the type of catalysts used. Both disproportionation and transalkylation reactions are recognized to have a clear link with the Brønsted acid sites of the zeolite⁶, which promote the carbon-carbon bond scission⁷. In a study by Pan et al.⁸ on ZSM-5, they revealed that both internal and external surfaces contain strong and weak acid sites. They demonstrated that the strong acid sites are the active sites for cracking of PDEB and EB, but compared with strong acid sites, pore size has more effect on *para*-isomer selectivity in disproportionation and isomerization on ZSM-5. Das et al. proved that the acid sites on the outside surface of ZSM-5 play a dominant role in isomerization⁹.

According to Santilli¹⁰, two mechanisms are used to describe the transalkylation reaction. Firstly is the deethylation-ethylation mechanism, in which the alkyl group (R) is cleaved from the benzene ring to become R^+ by the acid sites, and subsequently adds to another benzene ring. Another mechanism is via diphenylethane intermediate; a bulky intermediate is formed with two aromatic rings bridged by an R group. Cleavage effect on the intermediate transfers the R group from one ring to the other. EB disproportionation reacts similarly; the second mechanism requires larger space inside the zeolite.

Disproportionation and transalkylation over ZSM-5 occur through the deethylation-ethylation mechanism¹¹. ZSM-5 is active for EB dealkylation, but hinders the disproportionation of toluene and ethylbenzene through the bulky intermediate, due to the steric constraint. For large pore zeolites, i.e., Y and mordenite, EB disproportionation generally involves diphenylethane intermediates; the reactions undergo through the bimolecular mechanism. The activation energy of bimolecular mechanism was proved to be lower than that of monomolecular on Y zeolite. Thus, a higher temperature is needed for EB disproportionation on medium pore zeolites than on large pore zeolites¹².

Min et al.⁶ provided experimental evidence for the transition state shape selectivity in zeolite catalysts. By analyzing the reaction intermediates, it was concluded that EB disproportionation over medium-pore zeolites could differ not only due to the size of 10-ring channels but also to the existence of cavities/channels larger than 10-rings⁶. In zeolites containing 10-ring channels and 14-ring cavities, besides monomolecular, the bimolecular mechanism could also occur.

The isomerization between the DEB isomers is expected to be 1,2-shift mechanism. According to Klemm et al.², the reaction scheme of the isomerization of dialkylbenzene is described as a linear reaction without direct conversion between *para*- and *ortho*-isomer. Olah et al.¹³ conducted experiments of EB disproportionation on an aluminum chloride catalyst.

They proposed a three compounds equilibration involving six rate constants. The kinetic study results indicated that the rate constant of *ortho-para*, as well as that of *para-ortho*, were equal to zero. In the study of Weiß et al.¹⁴, the thermodynamic equilibrium of DEB isomers at 453 K, calculated from the free enthalpies of formation in the gas phase, corresponds to 54% MDEB, 32% PDEB, and 14% ODEB. Typically, the reported distribution of DEB isomers is approximately 6:3:1 for MDEB: PDEB: ODEB. They also reported that the kinetically favored 1,4 isomer is primarily formed but with increasing residence time, the MDEB becomes the predominant isomer.

The performance of the catalysts is mostly based on the acid sites and zeolite structure. EB disproportionation and transalkylation were investigated over a variety of zeolites in the literature, such as mordenite¹¹, USY¹⁵, beta¹⁶, and ZSM-5¹⁷. ZSM-5, as an MFI-type medium pore zeolite, has interconnected channels of 10- membered rings (MR) 5.1×5.5 Å and 5.3×5.6 Å¹⁸. As mentioned previously, the transalkylation reaction mechanism changes according to the pore architecture of the zeolites. Even though mordenite, Y, and beta zeolites are all cataloged as large pore zeolites, they differ considerably from each other in the pore structure. Beta zeolite has two connected 12-MR channel system with dimensions 6.6×6.7 Å and 5.6×5.6 Å¹⁸. Mordenite zeolite contains two channel sizes, but only one channel in one direction is accessible to organic molecules, the size of the channel is 6.5×7.0 Å¹⁹. Zeolite Y has circular channel openings that are 7.4 Å in diameter that lead to larger cavities called supercages that are ~13 Å in diameter¹⁹. The presence of such cavities allows more space for the formation of bulky intermediates or products, but also can act as a trap for big molecules, leading to consecutive reactions¹⁸.

Wang et al.²⁰ revealed that zeolite activity in EB disproportionation decreases in the order beta > ZSM-5 >> Y ≈ mordenite, while the acidity decreases in the order ZSM-5 > beta >>

mordenite > Y. Higher activity of ZSM-5 was expected due to its higher siliceous content; however, zeolite beta had better activity in EB disproportionation. The authors concluded that acidity is not the only controlling factor for zeolite activity. Although having lower acidity, zeolite Y and mordenite had comparable activity to ZSM-5 in disproportionation of toluene (TOL). The reaction mechanism can be another critical factor that influences the activation energy and zeolite activity²⁰. Nemeth et al.²¹ pointed out that a catalyst containing 50 vol% beta and 50 vol% pentasil (MTW-type zeolite) was particularly effective in converting undesired ethylbenzene isomers while still achieving a good proportion of *p*-xylene (PX) in total xylene isomers.

As mentioned before, the desired SMBR unit integrates the isomerization and adsorptive separation process in the same unit for in-situ withdrawal of PX as it is formed to overcome the thermodynamic limitations in the isomerization of xylenes. The commercial aromatic streams usually contain considerable amounts of EB, 15-20% from reformat and 35-55% from pyrolysis gasoline²². Considering that the feed to the SMBR may include a relatively high amount of EB and that TOL may be used as desorbent instead of PDEB, it is necessary to study the disproportionation and transalkylation between C₈ aromatics and TOL under the operating conditions foreseen for the SMBR unit. The purpose of this chapter is focused on the side reactions that may occur in the SMBR over zeolite beta with a SiO₂/Al₂O₃ (SAR) ratio of 35 (BEA35) under the following experimental conditions: 453, 473, and 493 K, and 2.1 MPa in the liquid phase.

4.2 Experimental method

4.2.1 Materials

High purity (>99%) ethylbenzene (EB), toluene (TOL), *p*-xylene (PX), *m*-xylene (MX), *o*-xylene (OX), and heptane were purchased from ACROS ORGANICS and used without further purification. Same catalyst BEA35 as in the previous chapter was used in the study of the main side reactions in this chapter.

4.2.2 Experimental set-up and procedure

The fixed bed experimental set-up in this chapter was the same as depicted in the previous chapter. The experiment procedure is similar, except that after the column reached the desired temperature, the feedstock was switched from heptane to an aromatics mixture instead of pure xylene, to identify the main side reactions during xylene isomerization in the liquid phase. An EB-xylene mixture, as well as an EB-xylene-TOL mixture, were respectively used to conduct the experiments; the xylene content in the mixture was consistent with the thermodynamic equilibrium, the PX:MX:OX ratio was about 1:2:1. Then, pure species and binary mixtures were used as feedstock at three temperatures (493, 473, and 453 K) to determine the kinetic parameters of the identified main side reactions.

4.3 Kinetic models development

The EB disproportionation reaction is reported in the literature as a first order reaction, in the gas phase^{15, 17, 23}, and reported as second order reaction in some studies in the liquid phase²². Thus, the second order reaction was considered in this chapter; kinetic constants based on first

order were also investigated. Transalkylation of EB with other aromatics were also assumed as a second order reaction²².

DEB isomers were lumped and denoted as DEB, ethyl-xylene isomers were considered altogether and indicated as EX. Additionally, the internal and external mass-transfer resistance at the highest temperature for several flow rates were calculated to guarantee that the reactions were in the kinetic-controlled regime. The criteria used are described in Annex B; the values are presented in **Table B17** and **B18**.

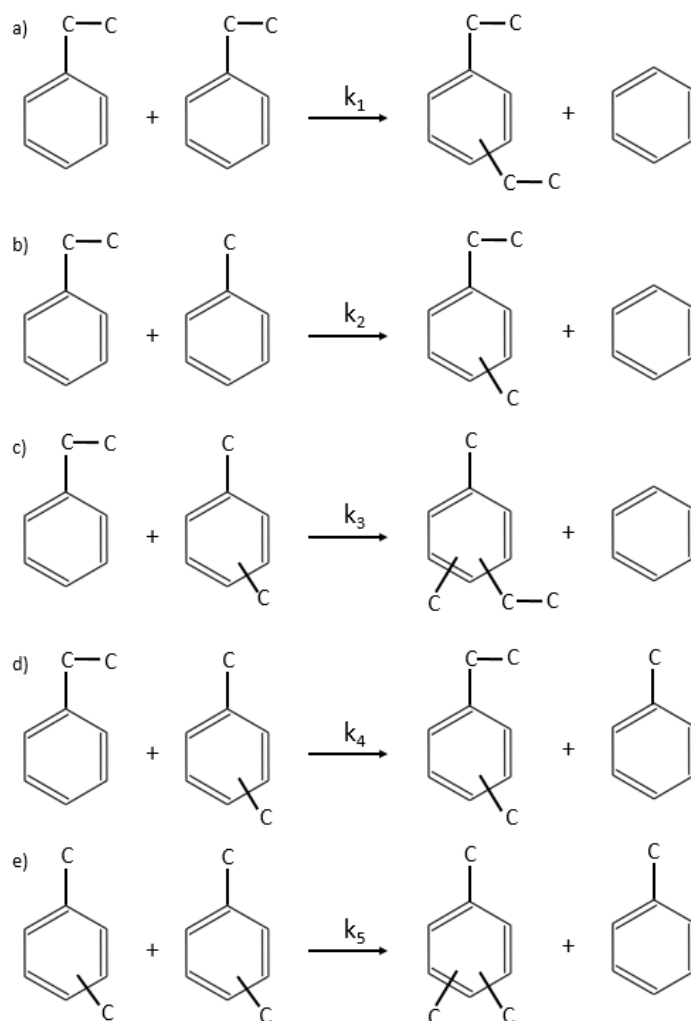


Figure 4.1 Side reactions during xylene isomerization in liquid phase. a) EB disproportionation; b) EB-TOL transalkylation; c) EB-Xylene transethylation; d) EB-Xylene transmethylation; e) Xylene disproportionation

Al-Khattaf et al.¹⁵ observed that the percentage of gaseous products is 1-3% at 723 K and 5-8% at 773 K. Indeed, with bi-functional catalysts (with metals such as Pt), the ethyl groups are hydrogenated promoting dealkylation over transalkylation²⁴. Since in this study, a mono-functional acid catalyst was used in the liquid phase, EB dealkylation to benzene (Bz) and ethane was not considered to occur. Therefore, under the conducted experimental conditions, no gaseous products were expected. The possible side reactions during xylene isomerization in the liquid phase are depicted in **Figure 4.1**.

Same equations as 3.1 and 3.2 were used to describe the mass balance for species *i* in a plug-flow reactor under isothermal conditions. The influence of the temperature on the kinetic constants was taken into account through the centered temperature form of the Arrhenius equation, as equation 3.9. The parameters were estimated through the commercial software gPROMS v4.2.0 from Process Systems Enterprise with the maximum likelihood method with constant variance and tolerance of 10^{-5} .

4.4 Results and discussion

4.4.1 Mixture experiments

Two experiments were carried out to identify the main side reactions during xylene isomerization in the liquid phase. The first was conducted with a mixture containing 40% EB, 15% PX, 30% MX, and 15% OX at 493 K and at a flow rate of 3 mL/min; the second mixture contained 25% TOL, 15% EB, 15% PX, 30% MX, and 15% OX at the same experimental conditions. The chromatographic analysis results of the two experiments are presented in **Figures 4.2 and 4.3**.

Ethylmethylbenzene (EMB), ethyl-xylene (EX), trimethylbenzene (TMBz), and DEB are the products of EB-TOL transalkylation, EB-Xylene transalkylation, xylene disproportionation, and EB disproportionation, respectively. According to **Figures 4.2** and **4.3**, DEB and EMB are the main products of the side reactions, TMBz and EX concentrations are significantly lower than DEB and EMB (i.e., lower than 10 wt%). Additionally, TMBz is significantly reduced in the presence of toluene. The SMBR with toluene as desorbent will present considerable amounts of toluene throughout the unit; thus, the disproportionation of xylenes can be neglected. However, the fact that TOL reacts with EB may lead to other problems within the unit, not only the converted TOL must be compensated but also the products of that reaction (i.e., EMB) may reduce the efficiency of the separation.

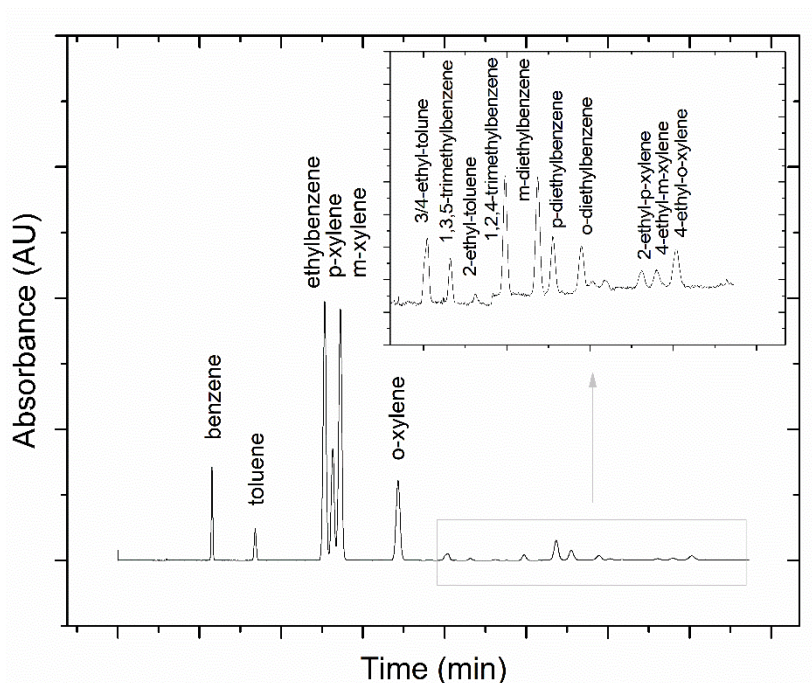


Figure 4.2 Chromatography of 40%EB+15%PX+30%MX+15%OX mixture at 493 K and at a flow rate of 3 mL/min

Moreover, EB reacted with any of the three xylene isomers. It was observed a higher peak of 4-ethyl-*o*-xylene than 4-ethyl-*m*-xylene and 2-ethyl-*p*-xylene. EB may preferentially “attack” *o*-xylene due to its structure. Indeed, alkyl groups attached at 1- and 3-positions of the benzene

ring create a more stable structure than the other isomers, reactivity follows the trend $1,2 > 1,4 > 1,3$ ⁷. Furthermore, with the addition of TOL, EB only appeared to react with OX. The amount of EX products is even lower than TMBz products. The EB-xylene transalkylation reactions (i.e., transmethylation and transethylation) can be considered negligible.

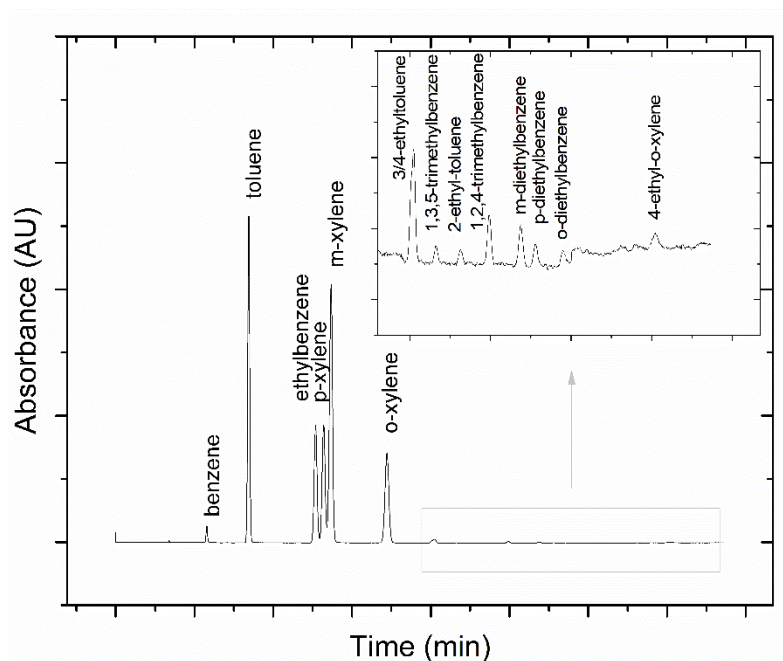


Figure 4.3 Chromatography of 25%TOL+15%EB+15%PX+30%MX+15%OX mixture at 493 K and at a flow rate of 3 mL/min

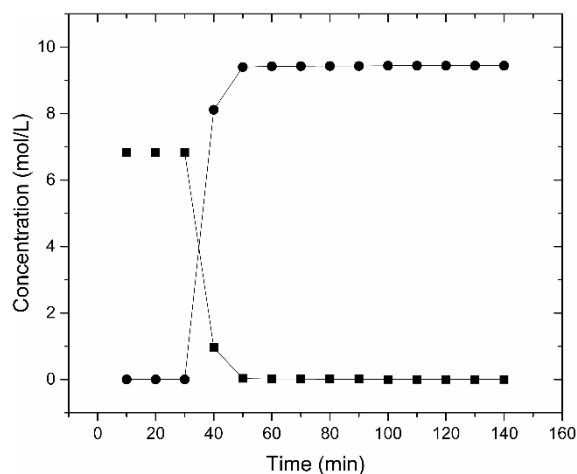


Figure 4.4 Toluene breakthrough curve on BEA35 at 493 K and at a flow rate of 3 mL/min (■Heptane, ●TOL)

A fixed bed experiment was also conducted with pure TOL at 493 K at a low flow rate (i.e., 3 mL/min). The breakthrough curve of TOL is presented in **Figure 4.4**. No trace of TOL disproportionation was observed; therefore, only EB disproportionation and EB-TOL transalkylation needed to be investigated as the main side reactions during xylene isomerization in the liquid phase. Moreover, in an SMBR with TOL as desorbent will not present side reactions if EB is not present in the feed.

4.4.2 EB disproportionation and EB-TOL transalkylation

Pure EB disproportionation experiments at 453, 473, and 493 K over BEA35 were conducted under various flow rates in the liquid phase. The products distribution is summarized in **Table B19**. Du et al.²⁵ studied the disproportionation of EB and DEB in the gas phase on FX-01 (modified beta zeolite), the results indicated that low temperatures (e.g., 493 K) are more favorable to the conversion of DEB, while high temperatures are more beneficial for EB disproportionation. Even though this work was conducted at low temperatures, no triethylbenzene was observed within the distribution of the products, for the EB disproportionation, which means no DEB disproportionation reaction occurred under the studied conditions.

The formation of DEB is assumed to take place inside the micropores, and only PDEB is produced; the isomerization of DEB is reported to occur mostly at the outer surface of the crystallites⁹. ODEB was produced in an extremely small amount in the EB disproportionation experiments conducted by Osman et al.²⁶ and Velasco et al.²⁷ at low temperatures. Velasco et al.²⁷ pointed out that ODEB yield was smaller than 2 wt% and it only existed in the early stage of the reaction. Two reasons may be ascribed, first, to that ODEB is the least favored in the thermodynamic equilibrium, second, the steric constraints of the two ethyl groups of ODEB.

These findings are consistent with the results of this chapter, at low temperature and high flow rate, a very small amount of ODEB was observed.

Transalkylation between EB and TOL was conducted with an equal mass proportion EB-TOL mixture at 453, 473, and 493 K in the liquid phase over BEA35 at various flow rates. The products distribution is presented in **Table B20**. The conversions and the proportion of EB involved in each reaction corresponding to each experiment are presented in **Table B21**.

Further experiments of EB-TOL mixtures with various EB-TOL ratios were also conducted in the liquid phase at 493 K to verify the influence of the concentrations of the reactants and to assess the competition for adsorption on the acid sites. The products distribution and the proportion of EB involved in each reaction are presented in **Table B22** and **Table B23**, respectively.

EB conversion and PDEB selectivity ($\text{PDEB selectivity} = \text{PDEB/DEB}$) at 493, 473 and 453 K in EB disproportionation and EB-TOL transalkylation experiments on BEA35 are shown in **Figures 4.5** and **4.6**. Illustrated on **Figures 4.5a** to **4.5c** are the conversion of EB at several temperatures and different concentrations, one can conclude that high temperatures and low flow rates favor the EB conversion. The PDEB selectivity in the reactions of pure EB and EB-TOL mixtures are presented in **Figures 4.6a** and **4.6b**, respectively. It can be seen that the PDEB selectivity, at low conversions, is reduced as temperature increases. In other words, at higher temperatures, the DEB isomerization rate is increased at a greater extent than the actual production of PDEB. It can be concluded that PDEB selectivity decreases with temperature. It can also be deduced that the lowest flow rate led to the highest conversion and lower selectivity towards PDEB; the existence of the external acid sites, together with long residence time, enhance the secondary isomerization of PDEB (to form the MDEB or ODEB)²⁸. On the other hand, at low conversions (high flow rates), the extent of PDEB isomerization is limited. At

high conversions, for all temperatures and concentrations studied, the PDEB selectivity was almost constant (i.e., ~ 0.3), which is close to the thermodynamic equilibrium value.

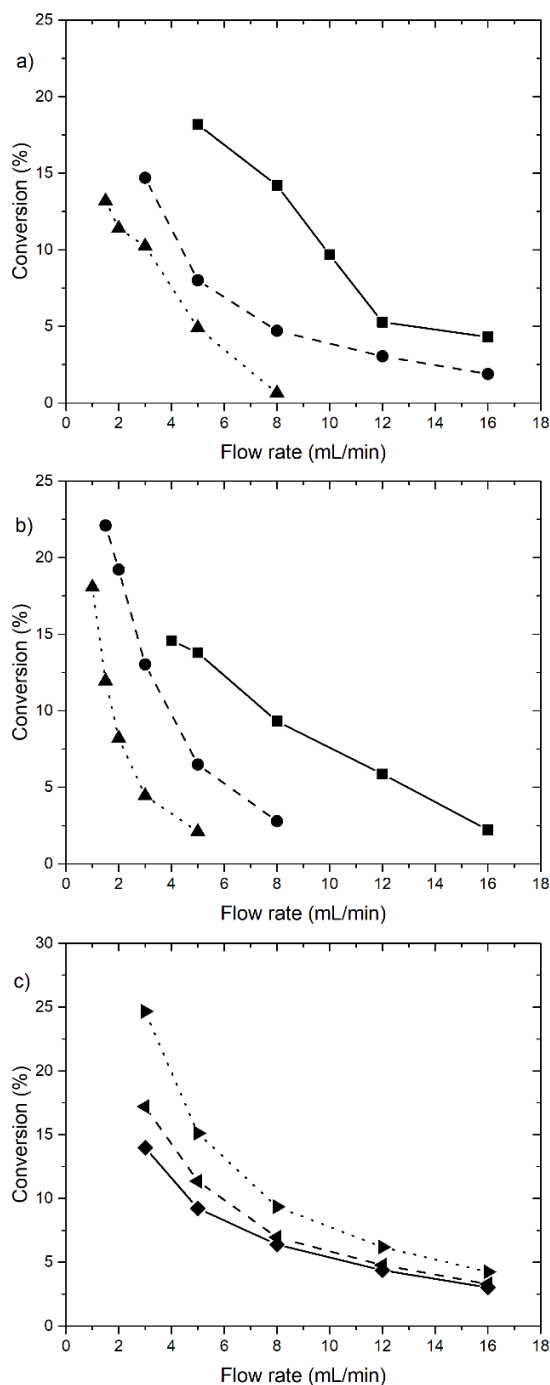


Figure 4.5 EB conversion as function of flow rate in a) pure EB (■493 K, ●473 K, ▲453 K), b) equal mass ratio EB-TOL (■493 K, ●473 K, ▲453 K), and c) various mass ratio EB-TOL mixture at 493 K (◆30%EB+70%TOL, ▶40%EB+60%TOL, ◀70%EB+30%TOL). Lines added to figure simply as a guide to the eye

Sharnappa et al.¹⁷ studied the disproportionation of EB in the presence of xylene isomers over ZSM-5 zeolite. PDEB selectivity was influenced by *p*-xylene inside the pores introducing hindrance to the PDEB. In this study, from the PDEB selectivity in various mass ratios of EB-TOL mixtures, it can be concluded that the selectivity was not affected by the parallel transalkylation reactions and the concentrations of other species.

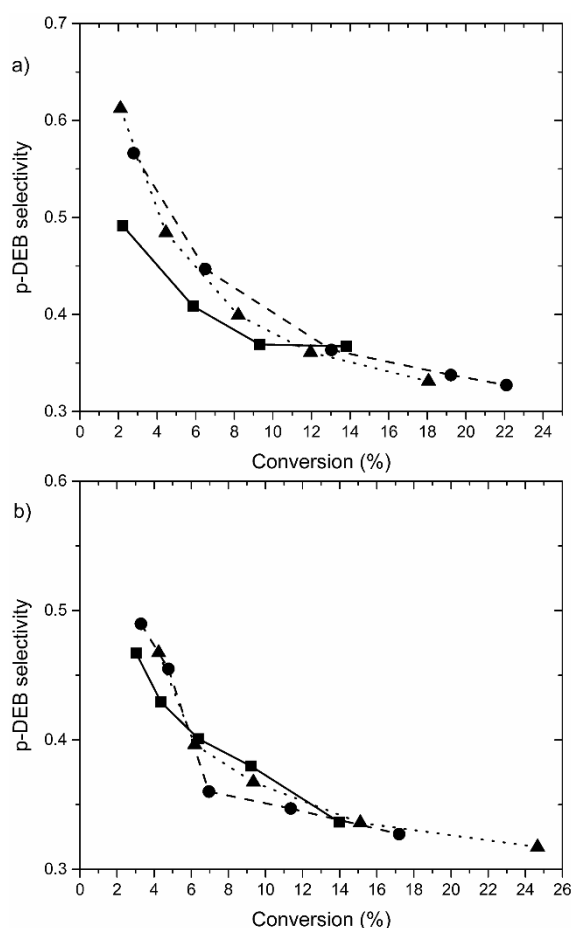


Figure 4.6 PDEB selectivity a) in equal mass ratio EB-TOL at various temperature (■493 K, ●473 K, ▲453 K) and b) in various mass ratio EB-TOL mixture at 493 K (■30%EB+70%TOL, ●40%EB+60%TOL, ▲70%EB+30%TOL). Lines added to figure simply as a guide to the eye

As mentioned in **Section 4.3**, products from cracking reactions were not expected. Bz/DEB ratios (molar ratio of Bz to DEB) close to 1, as it can be seen in **Table B19**, indicate that EB

conversion to lighter compounds did not happen. Values above 1 are due to the cracking reactions that produce excess benzene, Bz/DEB ratio has been reported to be at the range of 1.5-2.3 in the gas phase at the temperatures between 673 and 773 K¹⁵.

The side reaction rates decrease in the order EB disproportionation > EB-TOL transalkylation >> EB-xylene transalkylation > xylene disproportionation >> TOL disproportionation. The reason can be attributed to the fact that ethyl transfer is about six to ten times faster than methyl transfer^{22, 29}. Methyl groups are more difficult to cleave than ethyl groups due to their decreased carbonium ion stability^{10, 24}. Besides, ethyl carbonium preferentially adds to ethylbenzene and toluene rather than xylenes due to steric hindrance; the aforementioned does not occur with zeolite Y, which presents large cages¹⁰.

From another point of view, the investigation of Santilli¹⁰ on ZSM-5 showed that toluene disproportionation was very low compared to ethylbenzene, although the intermediate of toluene is smaller than that of ethylbenzene. Thus, it was concluded that the diphenylethane mechanism does not occur on ZSM-5. In the same context, even though beta zeolite possesses larger pores, the same conclusion can be drawn here since toluene did not react with itself. Moreover, according to Silva, et al.²⁴, xylene disproportionation occurs through diphenyl intermediates, the steric constraints exerted by the pore media of ZSM-5 zeolites on the formation of these bulky intermediates allows one to explain their low activity even with very favorable conditions (high xylene concentration). In this study, ethylbenzene disproportionation was significantly higher than xylene disproportionation; thus, we can conclude that the prevailing mechanism over beta zeolite, under these conditions, is the deethylation-ethylation mechanism.

The proportion of EB involved in each reaction was calculated with the following equations:

$$X_{EB \text{ into disproportionation products}} = \frac{2 \cdot C_{DEB}^0}{C_{EB}^i - C_{EB}^0} \quad (4.1)$$

$$X_{EB \text{ into transalkylation products}} = \frac{C_{EMB}^0}{C_{EB}^i - C_{EB}^0} \quad (4.2)$$

It can be seen in **Figures 4.7a** and **4.7b** that for equal mass ratio EB-TOL mixture experiments, the proportion of EB involved in disproportionation and transalkylation remained practically unchanged with different flow rates. EB involved into transalkylation was approximately 40%, while that involved in EB disproportionation was around 60%; additionally, it also stayed stable with the change of temperature. Both EB and TOL have similar molecule sizes, from which they are expected to diffuse at same rate within the channels of the zeolite. Additionally, both reactions occur through the deethylation-ethylation mechanism. Although DEB molecules are slightly larger than EMB molecules, PDEB selectivity was close to that according to the thermodynamic equilibrium; the selectivity only increased at very low conversions. From those mentioned above, it can be stated that no restrictions were observed for both reactions, that is, no reaction was favored at the expense of the other one under the studied conditions. Moreover, **Figures 4.2** and **4.3** show higher presence of 4-ethyl-*o*-xylene than 4-ethyl-*m*-xylene and 2-ethyl-*p*-xylene. Even though 5-ethyl-*m*-xylene is the most thermodynamic favored isomer³⁰, more 4-ethyl-*o*-xylene was produced, probably due to its smaller molecular size. Thus, the steric hindrance of beta zeolite under the studied conditions starts to appear for molecules with a size close to that of 5-ethyl-*m*-xylene.

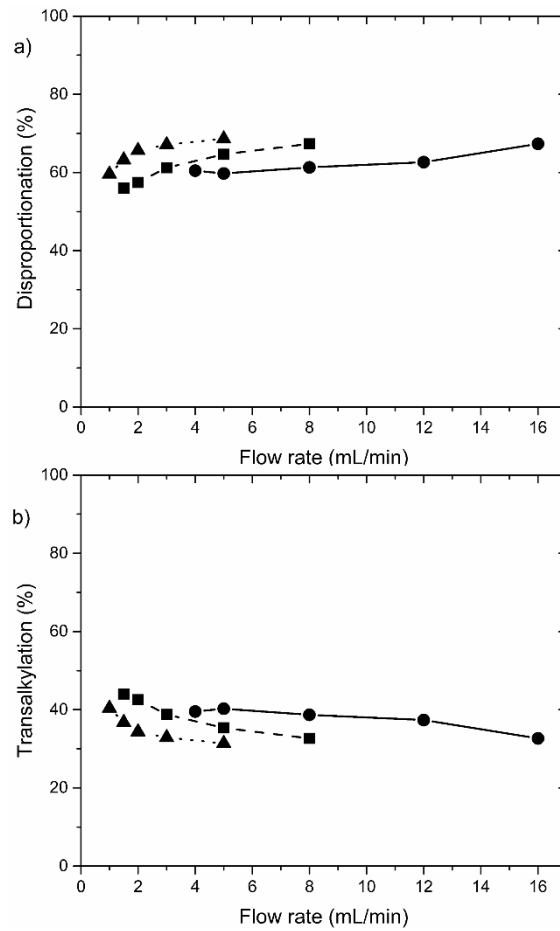


Figure 4.7 The proportion of ethylbenzene involved in a) disproportionation b) transalkylation as a function of flow rate in equal mass ratio EB-TOL mixtures over BEA35 (●493 K, ■473 K, ▲453 K). Lines added to figure simply as a guide to the eye

Considering only EB disproportionation and EB-TOL transalkylation as main side reactions, both as second order, the reaction rates of each species can be written as:

Rate of reaction for EB:

$$R_{EB} = -2k_1C_{EB}C_{EB} - k_2C_{EB}C_{TOL} \quad (4.3)$$

Rate of reaction for DEB:

$$R_{DEB} = k_1C_{EB}C_{EB} \quad (4.4)$$

Rate of reaction for Bz:

$$R_{Bz} = k_1C_{EB}C_{EB} + k_2C_{EB}C_{TOL} \quad (4.5)$$

Rate of reaction for TOL:

$$R_{TOL} = -k_2 C_{EB} C_{TOL} \quad (4.6)$$

Rate of reaction for EMB:

$$R_{EMB} = k_2 C_{EB} C_{TOL} \quad (4.7)$$

where k_1 and k_2 are the rate constants of each reaction defined in **Figure 4.1**, $\text{m}^6/\text{kg s mol}$; C_{Bz} , C_{TOL} , C_{EB} , C_{DEB} , C_{EMB} represent the concentration of benzene, toluene, ethylbenzene, diethylbenzene, and ethylmethylbenzene, respectively, mol/L ; R_{Bz} , R_{TOL} , R_{EB} , R_{DEB} , R_{EMB} are the apparent reaction rates of benzene, toluene, ethylbenzene, diethylbenzene, and ethylmethylbenzene, respectively, mol/kg s . The kinetic constants and activation energies based on the experimental results of pure EB and EB-TOL mixture over BEA35 at the centered temperature 473 K are presented in **Table 4.1**. The kinetic constants calculated considering only the experimental results from pure EB and EB-TOL mixture are compared in **Table B24**. Similar values were obtained, which indicates the absence of competition for adsorption sites between the two reactions.

Table 4.1 Kinetic constants and activation energies of ethylbenzene disproportionation and ethylbenzene-toluene transalkylation over BEA35 in liquid phase between 453 and 493 K

	EB disproportionation	EB-TOL transalkylation
$E_{a,j}$ (kJ/mol)	66 ± 3	57 ± 8
$k_{0,j} \times 10^{12}$ ($\text{m}^6/\text{kg s mol}$)	7.2 ± 0.2	7.3 ± 0.5

In the work of Osman. et al.²⁶, the activation energy of EB disproportionation was 19.5 kJ/mol, at the temperature range of 473-673 K and atmospheric pressure. While in the study of Sharnappa et al.¹⁷, the activation energy was 26.27 kJ/mol between 553-598 K and 36 kJ/mol between 603-643 K. Both studies were performed in the gas phase with ZSM-5 as catalyst. The activation energies reported here for EB disproportionation, and EB-TOL transalkylation are

66 kJ/mol and 57 kJ/mol over BEA35 in the liquid phase. Lower activation energy may be attributed to the slower intracrystalline diffusion within the smaller pores of zeolite ZSM-5 compared to beta^{31, 32, 33}. Considering only EB disproportionation and EB-TOL transalkylation, an analytical solution can be obtained (see Annex B). Eqs 4.8 and 4.9 present the solution for the reactants and the products respectively (provided $k_1 \neq k_2$):

$$\frac{C_{EB}}{C_{TOL}} = \frac{1}{1-k_1/k_2} + \frac{C_{TOL}^{k_1/k_2-1}}{C_{F,TOL}^{k_1/k_2}} \left(C_{F,EB} - \frac{C_{F,TOL}}{1-k_1/k_2} \right) \quad (4.8)$$

$$\frac{C_{DEB}}{C_{EMB}} = \frac{k_1/k_2}{1-k_1/k_2} - \frac{1}{C_{F,TOL}^{k_1/k_2-1}} \left(\frac{C_{F,EB}}{C_{F,TOL}} - \frac{1}{1-k_1/k_2} \right) \left[\frac{(C_{F,TOL}-C_{EMB})^{k_1/k_2} - C_{F,TOL}^{k_1/k_2}}{C_{EMB}} \right] \quad (4.9)$$

To validate the results, the analytical solution with the kinetic constants calculated from **Table 4.1** at 493 K was compared against the experimental values for several feed concentrations. The predicted and experimental data at 493 K for the reactants EB and TOL and the products DEB and EMB are presented in **Figures 4.8** and **4.9**; the simulated results predict the experimental data very well.

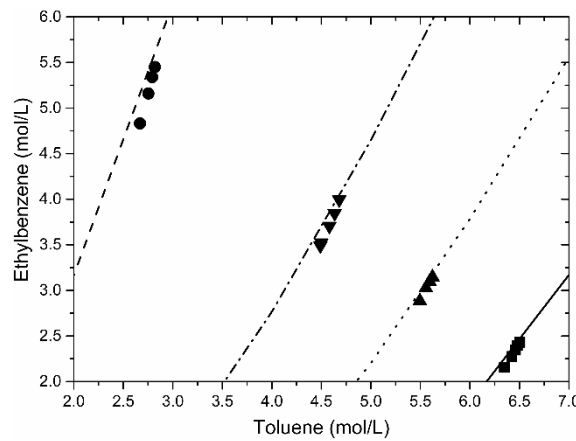


Figure 4.8 Reactants comparison of simulation (lines) and experimental (markers) values of EB and TOL at 493 K (■30%EB+70%TOL, ▲40%EB+60%TOL, ▼50%EB+50%TOL, ●70%EB+30%TOL)

In order to verify the order of the reaction, the reactants and products distribution were also simulated based on the assumption that EB disproportionation is a first order reaction. The results are presented in **Figures B3** and **B4**, the kinetic constants used are shown in **Table B25**. In the case of first order reaction, the simulation results deviate considerably from the experimental values, providing experimental evidence that EB disproportionation is a second order reaction under the experimental conditions.

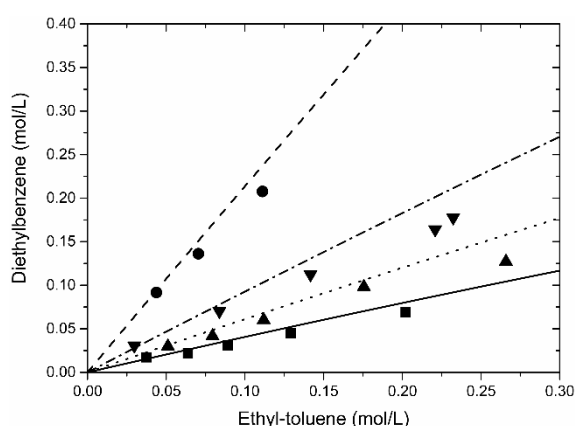


Figure 4.9 Products comparison of simulation (lines) and experimental (markers) values of DEB and EMB at 493 K (■30%EB+70%TOL, ▲40%EB+60%TOL, ▼50%EB+50%TOL, ●70%EB+30%TOL)

4.5 Conclusions

Disproportionation and transalkylation reactions between xylene, ethylbenzene, and toluene were investigated in the liquid phase over beta zeolite with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 35. The main reactions were disproportionation of ethylbenzene and transalkylation between ethylbenzene and toluene; deethylation-ethylation was the prevailing mechanism under the conditions studied. A kinetic study was then carried out between 453 and 493 K and 2.1 MPa; it was confirmed that both side reactions are second order reactions with no signs of competition for

adsorption sites. The activation energies for ethylbenzene disproportionation and ethylbenzene-toluene transalkylation were 66 and 57 kJ/mol respectively. Finally, an analytical solution was obtained for the system, including both reactions, the model with the kinetic parameters obtained agreed very well with the experimental data.

4.6 Nomenclature

C_i , mass concentration of component i (i = Bz, TOL, EB, DEB, ET), mol/L

$E_{a,j}$, activation energy of reaction j , kJ/mol

k_j , kinetic constant of reaction j , m⁶/kg s mol

$k_{0,j}$, kinetic constant of reaction j at centered temperature T_0 , m⁶/kg s mol

R_i , rate of reaction i (i = Bz, TOL, EB, DEB, ET), mol/kg s

Superscripts

i , inlet

o , outlet

Subscripts

F, feed

Abbreviations

Bz, benzene

DEB, diethylbenzene

EB, ethylbenzene

EMB, ethylmethylbenzene

EX, ethyl-xylene

MX, *m*-xylene

MR, membered rings

MDEB, *m*-diethylbenzene

OX, *o*-xylene

ODEB, *o*-diethylbenzene

PX, *p*-xylene

PDEB, *p*-diethylbenzene

SMBR, Simulated Moving Bed Reactor

SAR, silica alumina ratio

TOL, toluene

TMBz, trimethylbenzene

4.7 References

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Chapter 5 Adsorption of C₆-C₈ Aromatics over Ba-exchanged Zeolite X at High Temperature

In order to assess the adsorption equilibrium properties in conditions that can be suitable for a Simulated Moving Bed Reactor for the production of *p*-xylene, the adsorption of C₆-C₈ aromatics (*p*-xylene, *o*-xylene, *m*-xylene, ethylbenzene, toluene, and benzene) were investigated through batch experiments over a dry Ba-exchanged zeolite X at 450, 483, and 513 K, in the liquid phase, and the main results are presented in this chapter. Pseudo single-component adsorption equilibrium isotherms were obtained based on the adsorbed amount with various initial concentrations of the adsorbate in *i*-octane. Finally, the saturation capacity, the adsorption equilibrium constant, and the heat of adsorption were obtained for each compound.

This chapter is based on Shi, Q.; Gonçalves, J. C.; Ferreira, A. F. P.; Rodrigues, A. E., Adsorption of C₆-C₈ Aromatics over Ba-Exchanged Zeolite X at High Temperature. Chem. Eng. Technol. 0 (0).

5.1 Introduction

The interaction between the acid sites of the zeolite and the basic sites of the adsorbate is an important factor related to the adsorption performance. The selective adsorption depends on the physical properties of the zeolites, such as framework structure, the nature of the exchange cations, SiO₂/Al₂O₃ ratio, and zeolite water content, which mainly affects the acidity of the zeolite^{1,2}; those factors are highly correlated and cannot be analyzed separately³. Temperature also plays an important role in the separation performance.

Widely used in industry for *p*-xylene separation are Ba⁺ and/or K⁺ exchanged X and Y zeolites. They are both faujasite-type zeolites, which having a three-dimensional open framework of AlO₄⁻ or SiO₄ tetrahedral units connected to each other by the oxygen atoms⁴. The cations of the zeolite can be exchanged with others at varying degrees. There is a strong correlation between the total acidity of a zeolite and the ionic radius of the cation, as well as the valence charge of the exchanged cation⁴. Rasouli et al.¹ studied the separation of *p*-xylene from xylene mixtures on ion-exchanged zeolites with monovalent cations such as lithium, sodium, and potassium. The exchanged cations with lower ionic radii led to higher zeolite acidity in the order of K < Na < Li. In the case of zeolite X, it has been reported that BaX is selective for *p*-xylene⁵. Ba²⁺ and K⁺ have larger ionic diameter than Na⁺. The ion exchange can adjust the pore size and the acidity of the zeolite; additionally, Ba²⁺ and K⁺ together with the adsorbed water can change the distribution of the electrostatic field.

With the increase of the SiO₂/Al₂O₃ molar ratio, the zeolite acidity decreases due to the decrease of aluminum content. Therefore, the increase in SiO₂/Al₂O₃ molar ratio causes a decrease in PX selectivity¹. Acid-base interactions between zeolitic adsorbents and adsorbates do not always predict correctly the trend of the adsorbent selectivity⁶. This is illustrated by the

lower adsorptive separation of MX on KY adsorbent despite the lower amount of acid sites than the ones existing in NaY⁶.

It is generally known that zeolites have strong adsorption behavior for water and its molecules move freely through the aluminosilicate framework⁷. Water molecules enhance the acid properties of the Brønsted acid sites, which in turn affects the performance of the separation. Lahot et al.² studied the separation of C₈ aromatics on zeolite Y, the maximum adsorption capacity was found with a water content of 4-5.5 wt%, at 293 K. It was also mentioned that, if an excessive amount of water is added to the adsorbent, the adsorbent cannot be regenerated and this leads to its deactivation⁵.

All selective adsorption mechanisms proposed in the literature have their drawbacks. One theory sees C₈ aromatics as a series of Lewis bases, the selectivity changes with the interaction between the adsorbate and the acid sites of the zeolite. The relative basicity of C₈ aromatics follows the sequence MX > OX > PX > EB⁸. The relative basicity reported by Kilpatrick and Luborsky followed the same tendency; their study also presented benzene (Bz) as the aromatic with the lowest basicity followed by toluene (TOL)⁹. The order of the relative alkalinity is not consistent with the affinity towards the adsorbent in the industrial separation of *p*-xylene, which follows the order PX > EB > OX ≈ MX. Even though the selectivity order can be adjusted by changing the exchanged ion, the necessity of an optimum water content is not well explained by the mechanism. The distribution of the water molecules varies with the loading and the type of isomer^{10, 11}. Zhao et al.¹² revealed that Ba²⁺ cations are mainly located on the S_I' and the S_{II} sites in BaX zeolite. The Ba²⁺ at S_I' on beta cage made the framework of the zeolite X more stable, and each Ba²⁺ at S_{II} polarizes two coordinated water molecules, an adsorption force field with D₂ symmetry is then generated in the faujasite supercage. PX belongs to the D_{2h} symmetry group, which includes the D₂ subgroup; therefore, the BaX zeolite can selectively adsorb and

separate PX. This mechanism explains better the water content normally used in the industry (i.e., around 5%).

Parex (UOP) and Eluxyl (IFP) utilize X or Y zeolite adsorbent in combination with TOL or *p*-diethylbenzene (PDEB) as desorbent. Compared with TOL, PDEB has a higher boiling point, which favors the economics of its recovery by distillation¹. Nevertheless, TOL has been reported as desorbent in the recently developed light desorbent LD PAREX technology¹³, since it seems to be more advantageous, from the energy consumption point of view, when considering the overall process. Indeed, TOL and indan had been tested as desorbent for xylene separation on nano-zeolite KX¹ and microcrystalline zeolite NaY¹⁴, both presented good performance as desorbent but TOL was more efficient. Bz has also been used as desorbent in the industry¹⁵; the main advantage is the greater boiling point difference between benzene and xylenes than between xylene and PDEB; operating costs for the desorbent separation in extract and raffinate streams may be significantly reduced.

As it was already mentioned, the combination of reaction and separation in an SMBR requires a trade-off between the most favorable operating conditions of both when performed separately. The presence of water can be detrimental for zeolite-based catalyst activity through dealumination^{16, 17}, and the operating temperature must be high enough for the catalyst activity but low enough for the adsorbent/adsorbate interactions still be strong enough. Zeolite ZSM-5 had been studied for xylene isomerization in the liquid phase, its conversion at 493 K was low and the authors claimed that the reaction should be carried out above 523 K^{18, 19}. On the other hand, zeolite beta presented better performance than ZSM-5 at low temperatures but always above 473 K²⁰. Additionally, the selection of a suitable desorbent is crucial for the SMBR technology; since PDEB may isomerize due to the presence of the acid catalyst, TOL can be considered as the desorbent. However, TOL may still react with EB in the liquid phase, to a small extent though^{21,22}.

The objective of this chapter is the experimental study of the adsorption of the main components present in an SMBR unit (PX, MX, OX, and EB), including Bz and TOL as the possible desorbents, in a dry Ba-exchanged zeolite X. The experiments were conducted in the temperature range of 450-513 K in order to obtain adsorption parameters at suitable conditions for both reaction and separation of xylenes in the SMBR unit, since limited information is available at those conditions in the literature.

5.2 Experimental section

5.2.1 Materials

The adsorbates in the experiments, *o*-xylene (OX; purity $\geq$ 99.0 %), *p*-xylene (PX; purity $\geq$ 99.0 %), *m*-xylene (MX; purity $\geq$ 99.0 %), ethylbenzene (EB; purity 99.0 %), toluene (TOL; purity $\geq$ 99.8 %), benzene (Bz; purity $\geq$ 99.8 %), and *i*-octane (purity $\geq$ 99.5%) were purchased from ACROS ORGANICS and used without further purification. The adsorbent was provided in pellet form.

5.2.2 Characterization

X-ray diffraction (XRD) patterns were conducted with a Philips X'Pert diffractometer, operating in reflection geometry using $\text{CuK}_{\alpha 1,2}$ radiation, ($\lambda_1 = 1.540598\text{\AA}$ and $\lambda_2 = 1.544426\text{\AA}$) at the Laboratório Central de Análises of University of Aveiro, Portugal. The morphologic characterization was performed by Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray Spectroscopy (EDS), operated at 15 kV (FEI QUANTA 400 FEG ESEM) at Centro de Materiais da Universidade do Porto (CEMUP). At Laboratorio de Sólidos Porosos, Servicios Centrales de Apoyo a la Investigación (SCAI), Universidad de Málaga,

Spain, mercury porosimetry analyses were performed in a Micromeritics AutoPore IV 9500 to determine the density and (macro) pore size distribution. The specific surface area and the pore volume were determined with nitrogen adsorption isotherms at 77 K using Micromeritics ASAP 2420 and carbon dioxide adsorption at 273 K using a Micromeritics ASAP 2020 analyzer.

5.2.3 Adsorption equilibrium experiments

Experiments in batch mode were conducted to obtain the adsorbed amount of each species for several concentrations and temperatures; the experimental set-up is depicted in **Figure 5.1**. For each experiment, around 5 g (wet mass) of zeolite was packed in a column and dried overnight at 473 K under N₂ flow; a consecutive drying procedure was conducted to verify the dry condition of the adsorbent by measuring the mass change. After cooling down, the zeolite was weighted (dry mass) and placed in the adsorbent basket above the stirrer. Then, the autoclave was filled with the initial mixture at different concentrations of each aromatic compound (1 – 15 wt%) in *i*-octane (around 30 mL). *i*-Octane was employed since it is weakly adsorbed in the presence of xylenes and does not influence significantly the adsorption of xylene isomers in X and Y zeolites^{23, 24}. The density of the mixture was determined experimentally using the mass and volume of the mixture. After the autoclave was closed, an inert atmosphere of N₂ was introduced, by opening valve 1 successively to the vent and to the N₂ gas cylinder keeping valve 2 open, so the air inside the autoclave was totally purged. During that process, the adsorbent was in direct contact with air and may adsorb a small amount of water²⁵; in this study, water adsorbed by the solid was accounted to be well below 0.1 wt% and therefore neglected. Then, the autoclave was pressurized with N₂ by opening valves 1 and 2; afterwards, valve 2 was closed for the rest of the experiment. The temperature was increased by setting the temperature controller at 450, 483, or 513 K, depending on the target temperature for each experiment. A stirring velocity of 650 rpm

was used to eliminate the external mass-transfer resistance and guarantee homogenous concentration in the liquid mixture. An experiment with higher velocity (i.e., 1000 rpm) was conducted and compared to the one at 650 rpm to verify the absence of mass-transfer resistance. After the predefined temperature was achieved, the conditions were kept constant for five hours to guarantee that the equilibrium was reached. The pressure was around 4, 8, and 12 bar for temperatures 450, 483, and 513 K respectively. To avoid vaporization during the sampling, the line was placed in a thermostatic bath at 273 K. The line was cleaned by taking a 4 mL sample, corresponding to the total dead volume of the sampling line; afterwards, the actual sample was taken and analyzed with a gas chromatograph, model Shimadzu G 2010 Plus.

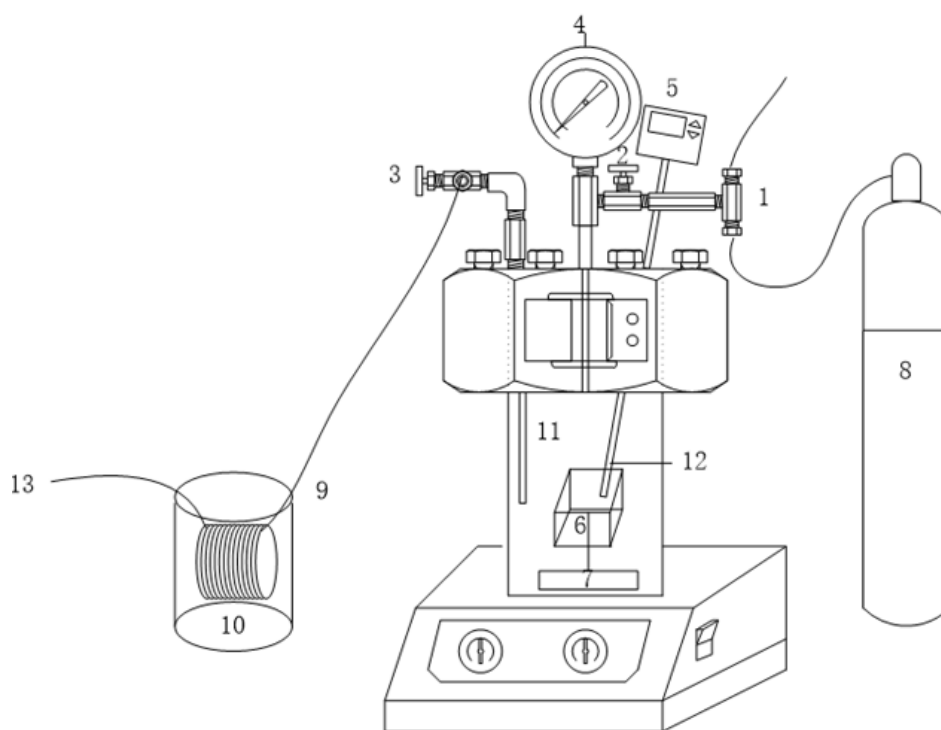


Figure 5.1 Experimental set-up. 1: 3-way valve; 2: Autoclave on-off valve; 3: Sampling valve; 4: Manometer; 5: Temperature controller; 6: Basket for adsorbent; 7: Magnetic stirrer; 8: Nitrogen gas cylinder; 9: Sampling line; 10: Water cooling bath; 11: Autoclave; 12: Temperature sensor; 13: Sample collection

5.3 Mathematical model

Based on the assumption that *i*-octane is not adsorbed, the adsorbed amount can be calculated by a mass balance considering the initial and final bulk phase concentrations:

$$q_i = \frac{m_{mix}(C_i^0 - \frac{C_{i-oct}^0}{C_i^f} C_i^f)}{m_{ads} \rho_{mix}} \quad (5.1)$$

where C_i^0 and C_{i-oct}^0 are the initial concentrations of component *i* and *i*-octane in the liquid, mol/L; C_i^f and C_{i-oct}^f are the final concentrations of component *i* and *i*-octane in the liquid, mol/L; q_i is the adsorbed amount of component *i*, mol/kg; m_{mix} is the mass of the mixture, g; ρ_{mix} is the density of the mixture, g/L; m_{ads} is the mass of the adsorbent on a dry basis, kg. The Langmuir isotherm was used to fit the experimental data:

$$q_i = \frac{q_{m,i} b_i C_i^f}{1 + b_i C_i^f} \quad (5.2)$$

where b_i represents the Langmuir constant, L/mol, and $q_{m,i}$ is the saturation capacity of component *i*, mol/kg. The heat of adsorption ($-\Delta H_{ads,i}$) was determined by the integration of the van't Hoff equation considering the saturation capacity constant with temperature:

$$b_i = b_{0,i} \exp \left[-\frac{\Delta H_{ads,i}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (5.3)$$

where R is the gas constant, J/mol K; T is the temperature, K; T_{ref} is the middle temperature of all the investigated temperatures, 481.5 K; $b_{0,i}$ is the Langmuir constant at the centered temperature T_{ref} , L/mol; and $\Delta H_{ads,i}$ is the adsorption enthalpy of component *i*, J/mol.

The parameters were estimated through the commercial software gPROMS v4.2.0 from Process Systems Enterprise with the maximum likelihood method with constant variance and tolerance of 10^{-5} .

5.4 Results

5.4.1 Characterization

In order to confirm the structure and crystallinity of the adsorbent, an XRD study was conducted. The XRD pattern of the adsorbent is shown in **Figure 5.2** and exhibits typical diffraction pattern of the FAU framework according to the International Zeolite Association (www.iza-structure.org).

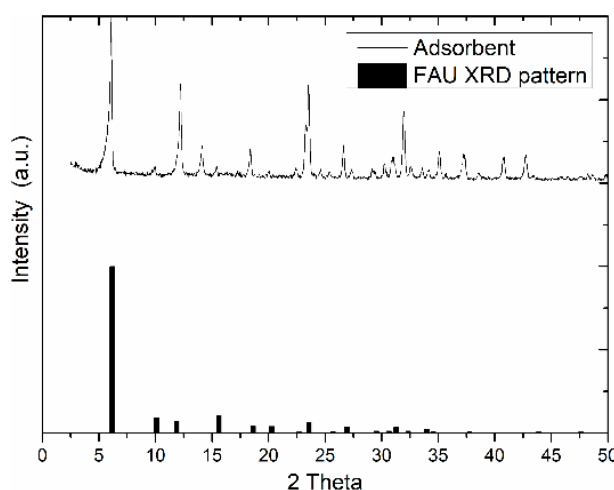


Figure 5.2 X-ray diffraction (XRD) of Ba-exchanged zeolite X compared to the reported powder pattern by International Zeolite Association (www.iza-structure.org)

The elemental compositions of the adsorbent was obtained through Energy-Dispersive X-Ray Spectroscopy (EDS), results are given in **Table 5.1**. Considering that the calculated $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is 2.42, it can be inferred that the adsorbent is Ba-exchanged zeolite X including a small amount of K.

Table 5.1 Elemental mass composition of the adsorbent

Element	O	Al	Si	K	Ba	Total
wt%	40.15	12.07	15.21	0.79	31.78	100.00

Nitrogen adsorption at 77 K and carbon dioxide adsorption at 273 K were used to study the textural properties of the adsorbent, such as surface area and pore volume. The nitrogen adsorption equilibrium isotherm on Ba-exchanged zeolite X is presented in **Figure 5.3** and the textural properties given by it are presented in **Table 5.2**. The micropores volume obtained by the nitrogen adsorption equilibrium isotherm at 77 K is compared to that obtained by CO₂ adsorption equilibrium isotherm at 273 K, as shown also in **Table 5.2**. The N₂ adsorbed amount reaches a maximum at low relative pressures, which is typical of microporous materials. Carbon dioxide at 273 K adsorption equilibrium isotherm is presented in **Figure A6** in Annex A.

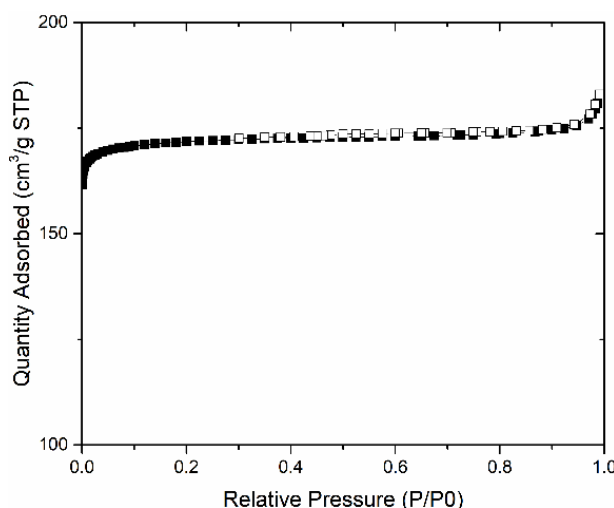


Figure 5.3 Nitrogen adsorption of Ba-exchanged zeolite X at 77 K ($P_0 = 1$ atm, ■ adsorption, □ desorption)

A summary of the main measured properties assessed by mercury intrusion and helium pycnometry is presented in **Table 5.3**, including the physical properties of the adsorbent, such as density and porosity.

Pore size distributions of the Ba-exchanged zeolite X was also investigated through mercury intrusion as presented in **Figure A7** in Annex A; the peak between 0.2 and 0.3 μm represents

the macropores of the secondary pore network, generated during the shaping of the sample. The Scanning Electron Microscopy (SEM) was used to estimate the crystal size and morphology of the zeolite. The adsorbent pellets have a diameter around 600 μm and an average crystal size around 1 μm , as shown in **Figure A8**.

Table 5.2 Textural properties of Ba-exchanged zeolite X by nitrogen adsorption at 77 K

Adsorbent	Ba-exchanged zeolite X
Surface area, m^2/g	751
Total volume in pores, cm^3/g	0.283
Volume in micropores, cm^3/g	0.265
Volume in micropores, $\text{cm}^3/\text{g}^{\text{a}}$	0.281

^a Determined by CO_2 adsorption at 273 K

Table 5.3 Physical properties of Ba-exchanged zeolite X

Adsorbent	Ba-exchanged zeolite X
Bulk density, g/cm^3	1.34
Skeletal density (helium pycnometry), g/cm^3	3.08
Skeletal density (mercury intrusion), g/cm^3	2.12
Particle porosity, %	36.8
Total porosity, %	56.5

5.4.2 Adsorption isotherms

In order to verify if the adsorption of *i*-octane can be neglected, the equation (equation B19) based on the surface excess introduced by Everett²⁶ was used. **Figures B5** and **B6** in Annex B present plots obtained from the results of the said equation. Since in all the experiments a straight line passing through near the origin was found, it can be concluded that the selectivity of the aromatic compound over *i*-octane is high enough, and the adsorption of *i*-octane can be neglected. Furthermore, the adsorption results of *p*-xylene, *m*-xylene, *o*-xylene, ethylbenzene,

toluene, and benzene for several concentrations and temperatures are presented in **Tables B26** to **B31** in Annex B. The fitted parameters of the adsorption isotherm model are presented in **Table 5.4** with the corresponding 95% confidence limit. To check the validity of the estimated parameters at the experimental conditions, the Langmuir constant, the saturation capacity, and the heat of adsorption were incorporated into the Langmuir model to simulate the results. The results are compared to the experimental data in **Figure 5.4**. It is observed that the computed results compare very well with the experimental data.

Most of the adsorption of all adsorbates took place at very low concentrations indicating the presence of micropores¹. All adsorption equilibrium isotherms present the typical behavior of type I (Langmuir) isotherms, according to IUPAC classification. The Langmuir constants of the components at three temperatures are presented in **Table B32** in Annex B.

Table 5.4 Pseudo single-component Langmuir adsorption isotherm parameters and heat of adsorption for *p*-xylene, *m*-xylene, *o*-xylene, ethylbenzene, toluene, and benzene; between 450 and 513 K and concentrations below 0.8 mol/L

Component	$b_{0,i}$, L/mol	$q_{m,i}$, mol/kg	$\Delta H_{ads,i}$, kJ/mol
<i>p</i> -Xylene	170 ± 7	1.479 ± 0.014	-20.9 ± 1.7
<i>m</i> -Xylene	98 ± 4	1.292 ± 0.025	-16.1 ± 2.3
<i>o</i> -Xylene	119 ± 7	1.388 ± 0.017	-16.5 ± 1.9
Ethylbenzene	97 ± 5	1.444 ± 0.020	-20.8 ± 1.8
Toluene	54.4 ± 2.4	1.763 ± 0.022	-18.7 ± 1.3
Benzene	16.0 ± 1.0	2.65 ± 0.06	-13.7 ± 1.5

The saturation capacity of the aromatics, in mole basis, follows the sequence Bz > TOL > PX > EB > OX > MX. Bz and TOL capacities are significantly higher, while only a slight difference between PX, EB, OX, and MX is observed; this may due to the different molecular

structures, molecules with fewer functional groups will pack more efficiently in the cages of the zeolite, hence the adsorbed amount is higher²⁷.

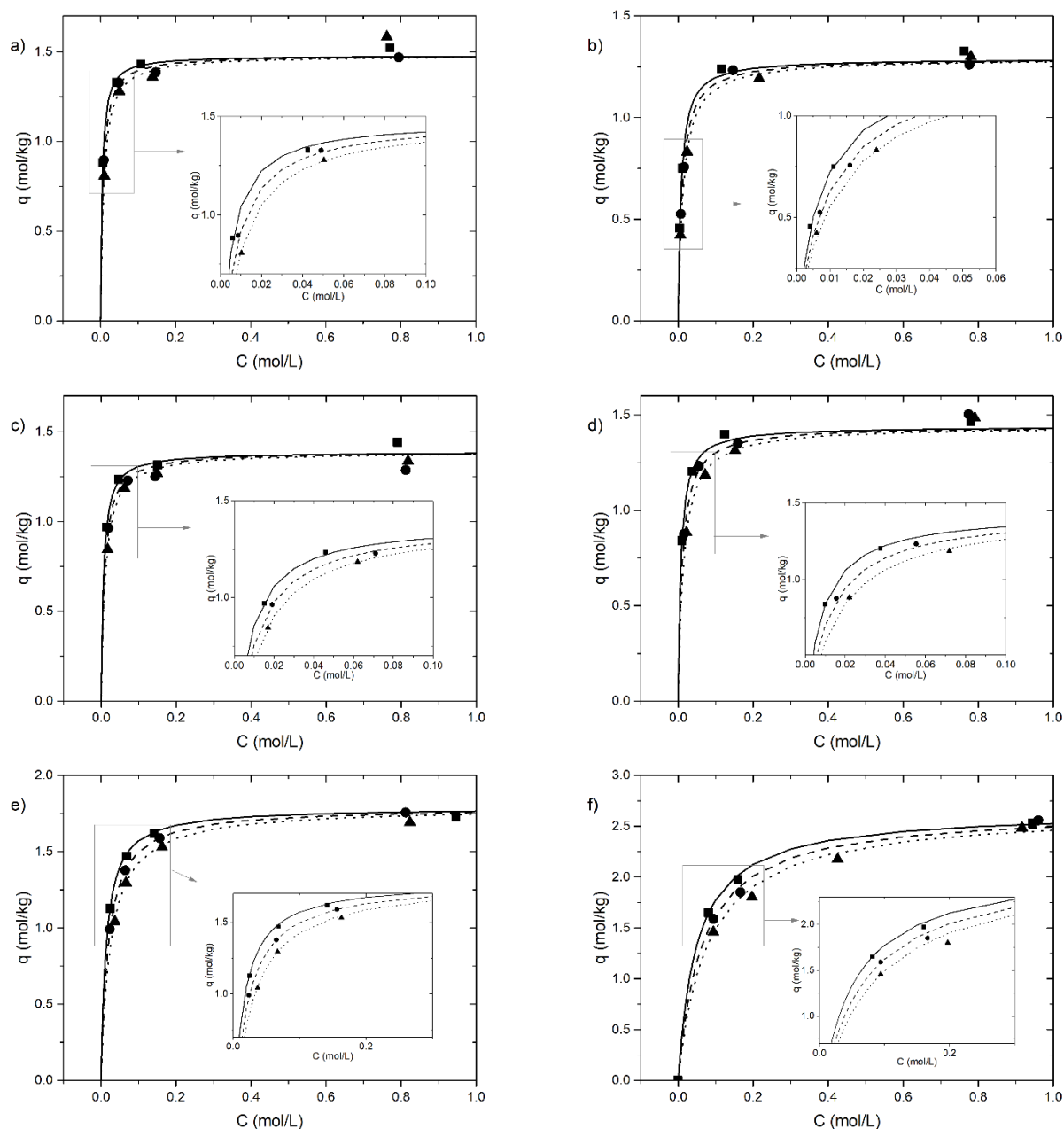


Figure 5.4 Adsorption isotherms of a) *p*-xylene; b) *m*-xylene; c) *o*-xylene; d) ethylbenzene; e) toluene; f) benzene determined at ■ 450 K, ● 483 K, ▲ 513 K: experimental data (symbols) and simulated Langmuir isotherm (lines)

The space restriction may also affect the phenomenon. Song et al.²⁸ reported that the presence of mesopores in zeolite beta provides more space for adsorption and increases the adsorption

capacity. Laboy et al.²⁹ studied the adsorption of benzene, toluene, and *p*-xylene in heulandite; with the increase of water content from 0% to 4%, the adsorption amount decreased significantly. Since a dry zeolite was used in this study, a larger space inside the adsorbent may be available for adsorption, which can lead to higher adsorption quantity. The adsorption parameters obtained were compared to that reported in the literature in **Table 5.5** under similar conditions using faujasite-type zeolites with different water content.

The pseudo single-component adsorption isotherms of *p*-xylene, *m*-xylene, *o*-xylene, ethylbenzene, toluene, and benzene at 450, 483, and 513 K are compared in **Figure 5.5a**, **5.5b**, and **5.5c**, respectively. The adsorption equilibrium constants reflect the interaction between the adsorbate and adsorbent. The adsorption equilibrium constants are similar to that reported by Minceva and Rodrigues³⁰ and Lee et al.³¹. The results reported by Lee et al.³¹ on zeolite X followed the order of $PX > OX > EB > MX > TOL$; in this study, the results follow the sequence $PX > OX > EB \approx MX > TOL > Bz$. Indeed, according to the literature, the adsorption equilibrium constants of MX, OX, and EB are very close³⁰. The presence of more methyl groups attached to the aromatic rings of the adsorbate causes an increase in the electron density of the aromatic ring and consequently provokes a decrease of the ionization potential of the adsorbate³⁴. The differences in the electronic environment as well as the steric effects of the methyl groups are responsible for the adsorption affinity differences. As the molecules have the electronic charge more localized, the interaction with the zeolite framework is stronger because of the electrostatic interactions, and as a result, the adsorption is stronger²⁷. Additionally, for more substituted alkylaromatics the basicity is higher⁹. In view of the acid-base interactions, the adsorbate with higher basicity introduces stronger adsorbate-adsorbent interactions, which results in higher adsorption equilibrium constants; thus, C₈ aromatics have higher adsorption equilibrium constants than TOL and Bz.

Table 5.5 Comparison between this work and literature data of adsorption over faujasite-type zeolites in the liquid phase at similar conditions

Temp.	Adsorbent (wt% H ₂ O)	Solvent	Sorbate	b_i , L/mol	$q_{m,i}$, mol/kg	$-\Delta H_{ads,i}$, kJ/mol	Reference
450- 513 K	BaX (dry)	<i>i</i> -octane	PX	245-124	1.479	20.9	This work
			MX	128-76	1.292	16.1	
			OX	158-92	1.388	16.5	
			EB	140-71	1.444	20.8	
			TOL	75-41	1.763	18.7	
			Bz	20-13	2.65	13.7	
453 K	Ba- exchanged faujasite (3-4 wt%)	<i>i</i> -octane	PX	206.9	0.96	27.2	30
			OX	94.7	0.86	18.6	
			EB	109.4	0.91	20.3	
450 K	X ^a	<i>n</i> -heptane	PX	278.27	1.31	31	
			MX	172.31	1.18		
			OX	237.18	1.16		
			EB	188.35	1.21		
450 K	Ba- exchanged faujasite (3.25 wt%)	<i>i</i> -octane	PX	295.31	1.256	25	
			MX	20.82	1.202		
			OX	25.45	1.224		
			EB	38.71	1.181		
			TOL	191.21	1.213		
450 K	Ba- exchanged faujasite (5 wt%)	nonane	PX	111.8	1.290	32	
			MX	33.4	1.253		
			OX	39.7	1.366		
			EB	69.2	1.243		
453 K	KY (4 wt%)	<i>n</i> -octane	PX	113.15	1.228	26.6 ^b	33
			MX	24.41	1.228	29.2 ^b	
			OX	20.00	1.228		
			EB	43.77	1.228		
			TOL	113.15	1.228		

^a The authors do not specified the cations and water content of the adsorbent^b Obtained experimentally between 313-353 K

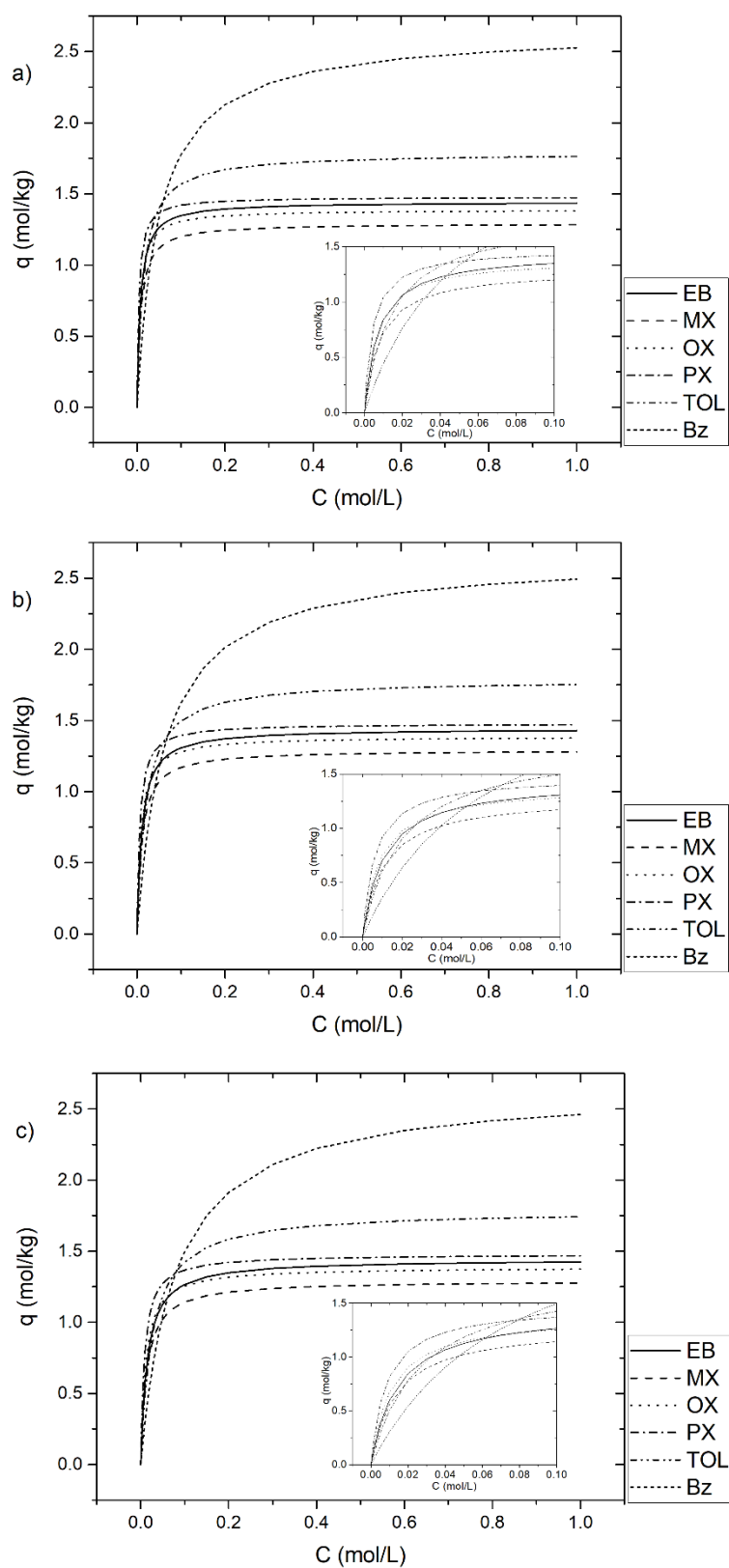


Figure 5.5 Adsorption isotherms of ethylbenzene (EB), *m*-xylene (MX), *o*-xylene (OX), *p*-xylene (PX), toluene (TOL), and benzene (Bz) at a) 450 K, b) 483 K, and c) 513 K

Indeed, the higher slope for *p*-xylene (see **Figure 5.5**) indicates that *p*-xylene has high affinity in comparison to the other three isomers. Also illustrated in **Figure 5.5**, is that C₈ aromatics have higher initial slope than TOL and Bz, which also indicates the higher equilibrium constants.

On the other hand, the components with higher saturation capacity have not achieved their full adsorption saturation at high temperatures. Indeed, TOL only achieves the saturation plateau at relative high concentrations and low temperatures, while Bz never achieves its saturation at the studied conditions. In conclusion, the results of this chapter compare well with those reported in the literature under similar conditions (see Table 5.5).

5.4.3 Heat of adsorption

In the case of the Langmuir isotherm, the heat of adsorption is considered to be constant³⁵. Moreover, following the surface excess analysis of Everett²⁶ and that *i*-octane was not adsorbed, the enthalpy change can be regarded as the heats of immersion of the solid in the pure adsorbate liquid (i.e., PX, MX, OX, EB, TOL, Bz). However, the influence of the weakly adsorbed compound becomes more significant as the mole fraction of the strongly adsorbed compound in equilibrium in the liquid phase tends to zero (see Annex B.18).

Even though there are several experimental studies in the gas phase^{36, 37, 38}, limited research has been conducted on the heat of adsorption of aromatics, on K- and/or Ba-exchanged zeolites, at high temperature in the liquid phase. Heats of adsorption of those studies in gas phase fall in the range between 60 and 100 kJ/mol at temperatures above 400 K on faujasite-type zeolites. The difference between the heat of adsorption from liquid phase and that from gas phase is mainly due to the heat of vaporization (see Annex B.19).

Compared with the results in **Table 5.5**, the heat of adsorption in this study is close to that found in the literature. Since the heat of adsorption, for all the studied components, is low (i.e., < 50 kJ/mol), their adsorption can be classified as physisorption, where the adsorption performance is not significantly influenced by the temperature and is reversible³⁹.

The heat of adsorption increases with the number of methyl groups⁴⁰. Indeed, a calorimetric study reported the different interactions of aromatic molecules adsorbed by various ion-exchanged Y zeolites. The interaction between methyl groups and aromatic rings influences the energy of adsorption⁴¹. Xylene and ethylbenzene have more methyl groups than benzene, this may explain the higher heat of adsorption of the xylene isomers than that of the benzene, as seen in **Table 5.4**. It was also reported that benzene is located in two distinct sites, one site is the S_{II} cation via π electron density, and the other site is at the circular windows between neighboring supercages, through van der Waals forces. Xylenes attach through the aromatics π electron interaction on the cation of S_{II} site, which is considerably stronger than the van der Waals forces⁴², the aforementioned may explain the lower average heat of adsorption of benzene.

5.5 Conclusions

A set of adsorption experiments, under batch conditions, of *p*-, *m*-, *o*-xylene, ethylbenzene, toluene, and benzene, were conducted at the temperature range of 450 to 513 K in the liquid phase. The experimental data was used to calculate the pseudo single-component adsorption parameters including the Langmuir adsorption constant, the saturation capacity, and the heat of adsorption for each compound. The Langmuir model described well the experimental data of the aromatic species. Over a dry Ba-exchanged zeolite X the saturation capacity in mole basis followed the sequence $Bz > TOL > PX > EB > OX > MX$; the values are higher than

those reported in the literature with zeolite water content around 3 wt%. The heat of adsorption of the components were very similar, around 20 kJ/mol, except that of Bz, which is lower due to the lack of methyl groups, affecting the adsorbent-adsorbate interaction.

5.6 Nomenclature

b_i , Langmuir constant of component i , L/mol

$b_{0,i}$, Langmuir constant at the centered temperature of component i , L/mol

C_i , bulk fluid phase concentration of component i , mol/L

C_{i-oct} , bulk fluid phase concentration of i -octane, mol/L

$\Delta H_{ads,i}$, adsorption enthalpy of component i , J/mol.

m_{ads} , mass of the adsorbent, kg

m_{mix} , mass of the liquid mixture, g

$q_{m,i}$, saturation capacity of component i , mol/kg

q_i , adsorbed amount of component i , mol/kg

R , gas constant, J/mol K

T , temperature, K

T_{ref} , middle temperature of all the investigated temperatures, K

Greek letters

ρ_{mix} , liquid density, kg/m³

Superscripts and subscripts

0 , initial

f , final

i , PX, MX, OX, EB, TOL, Bz

Abbreviations

Bz, benzene

EB, ethylbenzene

MX, *m*-xylene

OX, *o*-xylene

PDEB, *p*-diethylbenzene

PX, *p*-xylene

SMB, Simulated Moving Bed

SMBR, Simulated Moving Bed Reactor

TOL, toluene

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Chapter 6 Simulated Moving Bed Reactor for *p*-Xylene Production: Modeling, Simulation, and Optimization

In this chapter, the Simulated Moving Bed Reactor (SMBR) was investigated from simulation, and optimization point of view. Toluene and benzene were respectively considered as desorbent in the process. Experimental data of adsorption over a dry Ba-exchanged zeolite X and reaction over mono-functional acid beta zeolite with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 35 (BEA35) was adopted in the modeling of the SMBR. The arrangement of columns and optimum operating conditions that lead to maximum *p*-xylene productivity and minimum desorbent consumption were determined. Additionally, the operating temperature was optimized, and the heat integration in the process was discussed. Finally, an increase of about 25% in the recovery of PX, compared to the conventional SMB, was obtained.

This chapter is based on Shi, Q.; Gonçalves, J. C.; Ferreira, A. F. P.; Rodrigues, A. E., Simulated Moving Bed Reactor for *p*-Xylene Production: Modeling, Simulation, and Optimization. Chem. Eng. Sci. (Submitted).

6.1 Introduction

The most widely used technology for *p*-xylene (PX) separation is adsorptive separation in fixed-bed columns based on the simulated moving bed (SMB) technology. The SMB simulates the counter-current movement of the adsorbate and adsorbent by periodically and synchronously switching the inlet and outlet ports of the unit. In a typical aromatics complex, the product PX is recovered in the extract and the rest of the isomers is sent to the isomerization unit to reestablish the thermodynamic equilibrium; **Figure 6.1a** presents a simplified scheme where heavy desorbent (HD) is used within the SMB unit. Recently, to further improve *p*-xylene productivity, process intensification has attracted attention aiming to reduce the consumption of raw materials and emissions of greenhouse gases and pollutants. A modified aromatics complex was proposed by Gonçalves and Rodrigues¹; it involved a Simulated Moving Bed Reactor (SMBR) unit and a single stage crystallization unit to allow the further purification of the *p*-xylene rich stream (see **Figure 6.1b**). The SMBR integrates separation and isomerization in the same unit; the separation in situ of PX overcomes the thermodynamic equilibrium of the isomerization achieving higher production yields. Normally, eutectic constraints in the equilibrium mixture of xylenes limits the recovery of the traditional crystallization process. However, *p*-xylene rich streams, for example, from the SMBR, place the crystallization in a more valuable position due to the reduction of capital and utility costs¹.

². Based on the aforementioned, a milder requirement of purity (70 wt%) in the extract is permitted in the study of SMBR, which makes the homogeneous mixture of adsorbents and catalysts possible, since the reaction near the extract port reduces the PX purity. The combination of reaction and separation in one unit requires a tradeoff between the optimal operating conditions of both processes when performed separately. The parameters, under the

compromise conditions for SMBR, are extremely important for the establishment of the SMBR model and to foresee the performance of an industrial scale SMBR unit.

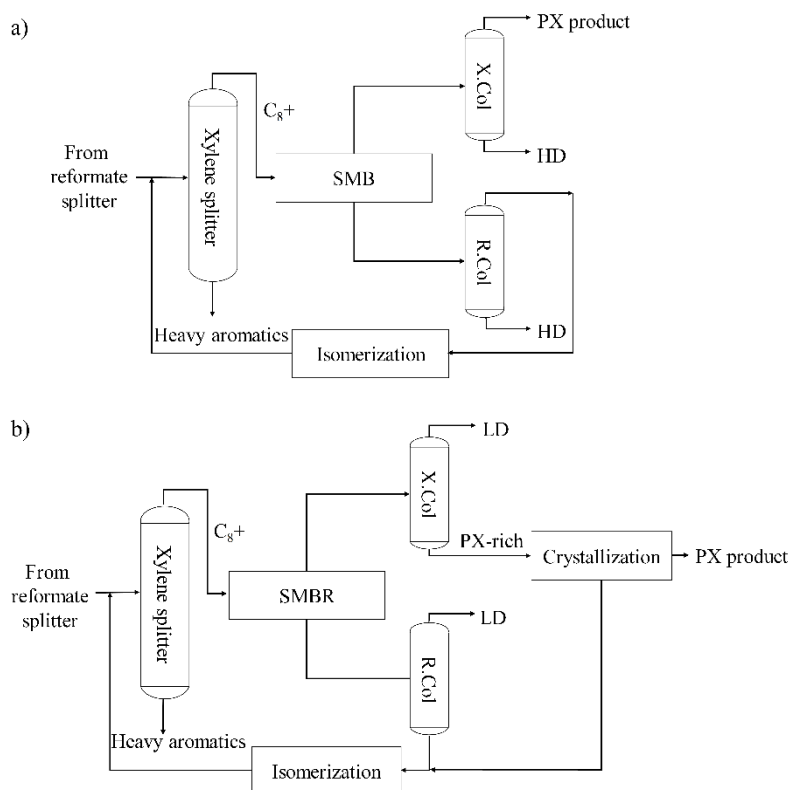


Figure 6.1 a) Current and b) Proposed aromatic complex (X.Col: Extract distillation column; R.Col: Raffinate distillation column; HD: Heavy desorbent; LD: Light desorbent.)

The minimization of investment and operating costs implies to maximize the recovery and productivity, and to minimize the desorbent consumption to cut downstream separation costs. Downstream separations represent a significant part of the operating costs in a petrochemical complex. Minimizing desorbent consumption is then a major requirement to minimize downstream distillation costs³. In fact, the minimum desorbent requirement has also received much attention in the separation of PX by SMB. The latest generation of heavy desorbent adsorbents from UOP, i.e., ADS-47, led to a reduction of 32% in the circulation of desorbent. LD ParexTM Aromatics Complex drives a step-change improvement in capital efficiency; only a slight modification is required to make the new adsorbent (ADS-50) compatible with a light

desorbent system⁴. The removal of heavy desorbent enables separation efficiencies that allow an optimized fractionation flow scheme. The new process proved 20% less in equipment and fractionation tray requirements, which reduces capital investment by 15-17%. It also eliminated the expensive external desorbent supply⁵.

The desorbent is present at relatively high concentration in all zones of the SMBR. Desorbent strength is, therefore, a key parameter for the flow stream tuning in the different zones and has a substantial impact on process performance. Storti et al.⁶ reported the influence of desorbent strength on desorbent consumption and productivity. The chosen desorbent should be adsorbed in zone I (i.e., between desorbent and extract port) to facilitate the desorption of *p*-xylene, and should be desorbed in zone IV (i.e., between raffinate and desorbent port) so the adsorbent can adsorb the lighter isomers. For a better performance in zone I, higher desorbent strength is recommended, since a strong desorbent can minimize the desorbent consumption; the opposite is needed in zone IV to be easy to desorb. Laroche et al.⁷ investigated a set of 11 desorbents with different strength through separation regions in an SMB. The authors pointed out that the optimal desorbent should be a compromise between high purity, good robustness in zone II (i.e., between extract and feed port) and III (i.e., between feed and raffinate port), and minimum desorbent consumption. Comparing to the desorbent with constant selectivity, the desorbent with decreasing strength allows a reduction of 14% of the desorbent requirement with equivalent feed flow rate.

Distillation is widely used in industrial separations. In spite of the well-known benefits and its widespread use, the major problem that must be considered is still the high energy requirement, which can significantly influence the overall plant profitability. About 3% of total energy consumption in the world is used in distillation units⁸. Therefore, extensive research studies have been devoted to the reduction of energy consumption through the overall system

integration including the distillation columns. Zaine et al.⁹ studied the energy efficiency of the distillation columns sequence of an aromatics separation process by using the driving force method. The authors observed that a maximum of 7% in the energy reduction could be achieved by changing the sequence of the columns. Masoumi and Kadkhodaie⁸ studied the indirect sequence, indirect sequence with forward energy integration, and indirect sequence with backward energy integration methods in a set of distillation columns to separate benzene, toluene, xylenes, and C_9^+ . The result shows that the energy consumption can be reduced by 33% and the total annual cost by 12%.

The purpose of this chapter is the modeling, simulation, and optimization of the SMBR unit. The SMBR was studied as part of a modified aromatics complex, including a single stage crystallization unit; therefore, milder *p*-xylene purity in the extract was allowed. It is based on the experimental data of adsorption and reaction in the liquid phase at above 450 K. Benzene and toluene were considered as desorbents of the unit. The optimization included the arrangement of columns, flow rates, and switching time for the SMBR as well as the operating temperature. Energy consumption and profit were used as objective functions considering shortcut methods for the associated distillation columns.

6.2 Simulated moving bed reactor modeling

6.2.1 Mathematical model

The TMBR approaches the SMBR after the cyclic steady-state (CSS) is reached; therefore, it is recognized as an efficient representation of the SMBR. In fact, the differences between the results obtained by the TMBR model and the SMBR model only become significant when it is considered 8 or less columns^{10,11}. Additionally, the TMBR strategy can significantly reduce the

computing time to obtain the CSS process performance parameters¹². Since the SMBR comprises a large number of columns, the unit was modeled through the continuous TMBR approach in this chapter. The model was numerically solved through the commercial software gPROMS v4.2.0, from Process Systems Enterprise (UK). The numerical method involved the discretization of the axial domain using second-order orthogonal collocation on 50 finite elements with 10^{-5} as tolerance.

The assumptions of the model included:

1. Isothermal conditions
2. Axial dispersed plug flow for the fluid phase
3. Plug flow for the solid phase
4. Variation of flow rate is considered in each zone
5. Mass transfer described by the linear driving force (LDF) approximation
6. Adsorbent and catalyst are mixed homogeneously, with same pellet size but possess different physical characteristics
7. Operating pressure was high enough to maintain the liquid phase, the pressure drop was calculated through the equation developed by Ergun¹³

Mass balance for species *i* in the bulk phase, adsorbent particle phase, and catalyst particle phase are given by Eqs. (6.1-6.3):

$$\frac{\partial C_i}{\partial t} = D_{ax} \frac{\partial^2 C_i}{\partial z^2} - \frac{\partial(uC_i)}{\partial z} - \frac{1-\varepsilon}{\varepsilon} \frac{3}{R_p} [K_{i,a}\varphi(C_i - C_{i,ads}) + K_{i,c}(1-\varphi)(C_i - C_{i,cat})] \quad (6.1)$$

$$\varepsilon_a \frac{\partial C_{i,ads}}{\partial t} + \rho_{ads} \frac{\partial q_i}{\partial t} = u_s \left[\varepsilon_a \frac{\partial C_{i,ads}}{\partial z} + \rho_{ads} \frac{\partial q_i}{\partial z} \right] + \frac{3}{R_p} K_{i,a}(C_i - C_{i,ads}) \quad (6.2)$$

$$\varepsilon_c \frac{\partial C_{i,cat}}{\partial t} = u_s \varepsilon_c \frac{\partial C_{i,cat}}{\partial z} + \frac{3}{R_p} K_{i,c}(C_i - C_{i,cat}) + \rho_{cat} R_i \quad (6.3)$$

Variation of the velocity is described in Eq. (6.4):

$$\frac{\partial u}{\partial z} = -\frac{1-\varepsilon}{\varepsilon} \frac{3}{R_p} \sum_i v_i [K_{i,a}\varphi(C_i - C_{i,ads}) + K_{i,c}(1-\varphi)(C_i - C_{i,cat})] \quad (6.4)$$

where the axial dispersion coefficient D_{ax} is estimated through the particle Peclet number ($Pe = 2u_{avg}R_p/D_{ax}$), which is about 0.45 for low Reynolds in liquids¹⁴, m²/s. ε is the bed porosity; ε_c is the particle porosity of catalyst; and ε_a is the particle porosity of adsorbent. u is the interstitial velocity, m/s; u_s is the solid velocity, m/s. v_i is the molar volume of component i , m³/mol; ρ_{ads} is the density of adsorbent, kg/m³; and ρ_{cat} is the density of catalyst, kg/m³. R_p is particle radius, m. $K_{i,a}$ and $K_{i,c}$ represent the mass transfer coefficient for the adsorbent and catalyst, respectively, m/s. C_i is the concentration of component i in the bulk phase, mol/m³. $C_{i,ads}$ and $C_{i,cat}$ represent the concentration of component i in the macropores of adsorbent and catalyst, respectively, mol/m³. q_i is the adsorbed concentration, mol/kg. R_i is the reaction rate of component i , mol/kg s. And φ represents the adsorbent/(adsorbent+catalyst) volume ratio. All time derivative terms are set to zero for the steady state using the TMBR method resulting in a simpler and faster model¹.

The boundary conditions for the bulk phase are:

$$D_{ax} \frac{\partial C_i}{\partial z} \Big|_{z=0} = u|_{z=0} (C_i|_{z=0} - C_{i,j}^{in}); \frac{\partial C_i}{\partial z} \Big|_{z=L} = 0 \quad (6.5)$$

$$u|_{z=0} = \frac{Q^{in}}{\pi \varepsilon R_D^2} \quad (6.6)$$

The boundary conditions for the solid phase are:

$$C_{i,ads} \Big|_{z=L}^{zone\ j} = C_{i,ads} \Big|_{z=0}^{zone\ j+1} \quad (6.7)$$

$$C_{i,cat} \Big|_{z=L}^{zone\ j} = C_{i,cat} \Big|_{z=0}^{zone\ j+1} \quad (6.8)$$

where L is the length of the zone, m; R_D is the radius of each column, m; and $C_{i,j}^{in}$ is the inlet concentration depending on the specific zone within the unit, mol/m³. The inlet concentration is determined by mass balances in each inlet and outlet port. The mass balances at the nodes

are given by Eqs. (6.9-6.12). In the equations, Q is the volumetric flow rate, where ‘in’ and ‘out’ refer to the inlet and outlet positions of a given zone, $C_{i,j}$ is the concentration of component i in zone j ($j=1,2,3,4$), mol/m³, $C_{i,k}$ is the concentration of component i in port k ($k=D,F,X,R$), mol/m³.

$$\text{Desorbent port: } Q_4^{out} + Q_D = Q_1^{in}; C_{i,4}^{out} Q_4^{out} + C_{i,D} Q_D = C_{i,1}^{in} Q_1^{in} \quad (6.9)$$

$$\text{Extract port: } Q_1^{out} - Q_2^{in} = Q_X; C_{i,1}^{out} = C_{i,2}^{in} = C_{i,X} \quad (6.10)$$

$$\text{Feed port: } Q_2^{out} + Q_F = Q_3^{in}; C_{i,2}^{out} Q_2^{out} + C_{i,F} Q_F = C_{i,3}^{in} Q_3^{in} \quad (6.11)$$

$$\text{Raffinate port: } Q_3^{out} - Q_4^{in} = Q_R; C_{i,3}^{out} = C_{i,4}^{in} = C_{i,R} \quad (6.12)$$

Molar volume of each component at different conditions was estimated using the Yamada and Gunn method¹⁵. The mixture viscosity μ_m (cP) was calculated with the method of Grunberg and Nissan for ideal mixtures¹⁵. With the molar volume and mixture viscosity, the molecular diffusivity D_m (m²/s) was calculated through the Wilke-Chang method modified to include the mixed solvent case by Perkins and Geankoplis¹⁵. Since nearly pure desorbent exists in zones I and IV, D_m can also be considered as self-diffusion¹⁶. With the molecular diffusivity D_m , the external mass transfer coefficient is estimated by the Wilson and Geankoplis correlation¹⁷; and the tortuosity was calculated with the correlation proposed by Wakao and Smith¹⁸. External and internal mass transfer resistances were coupled in a single global mass transfer coefficient¹⁹.

6.2.2 Reaction and adsorption parameters

As mentioned previously, the combination of reaction and separation in one unit requires a tradeoff between the optimal operating conditions of both processes. The presence of water can be detrimental for the zeolite-based catalyst activity through dealumination, and the operating temperature must be high enough for the catalyst activity but low enough for the

adsorbent/adsorbate interactions still be strong enough. Thus, reaction kinetics and adsorption equilibria under the aforesaid conditions are needed for the SMBR model development.

The main and side reactions in the SMBR are presented in **Figure 6.2**. Kinetic parameters of xylene isomerization and ethylbenzene (EB) disproportionation and transalkylation with toluene (TOL) on mono-functional acid beta zeolite with SiO₂/Al₂O₃ ratio of 35 (BEA35), at the temperature range of 453 to 513 K, obtained in Chapters 3 and 4 were adopted in the model. Adsorption isotherms parameters of C₆-C₈ aromatics (*p*-xylene, *o*-xylene, *m*-xylene, ethylbenzene, toluene, and benzene), over dry Ba exchanged zeolite X, at the temperature range of 450 to 513 K, obtained in Chapter 5, were also adopted in the model. A summary of the parameters is presented in **Table 6.1**.

When EB is present in the SMBR, EB disproportionation over BEA35, under the conditions stated, leads to the formation of diethylbenzene. In Chapter 4, it was observed that at low conversion, the main product was *p*-diethylbenzene (PDEB); thus, it is necessary to obtain the adsorption equilibrium parameters of PDEB for the model development. Neves²⁰ extended the adsorption parameters from 353 K to 453 K by assuming that the saturated capacity does not change with the temperature and the selectivity towards PX is constant ($q_{m-PDEB}K_{PDEB}/q_{m-PX}K_{PX}$). Minceva et al.²¹ adopted the same method in their study on SMB. Similar correlation between PDEB and PX was obtained from the literature^{22, 23, 24, 25}. In this chapter, the adsorption parameters of PDEB is calculated based on that of PX from Chapter 5, and is also presented in **Table 6.1**.

When EB is present in the SMBR and toluene used as desorbent, EB reacts with toluene and preferentially produces *p*-ethylmethylbenzene (PEMB) at low conversion, as was obtained in Chapter 4. Anderson²⁶ claimed that in the process for separating PX from a C₈ and C₉ aromatic mixture (with zeolite X or Y as adsorbent), PEMB is strongly adsorbed together with PX and

the desorbent. Zinnen²⁷ also mentioned that PEMB is more strongly adsorbed than the desired product PX (over zeolite X or Y exchanged with Group IA or IIA metal ions). Under the conditions studied in this chapter, the presence of TOL and EB leads to the formation of a small amount of PEMB. Since the concentration of PEMB was expected to be very low, the adsorption parameters of PEMB were assumed to be the same as PDEB.

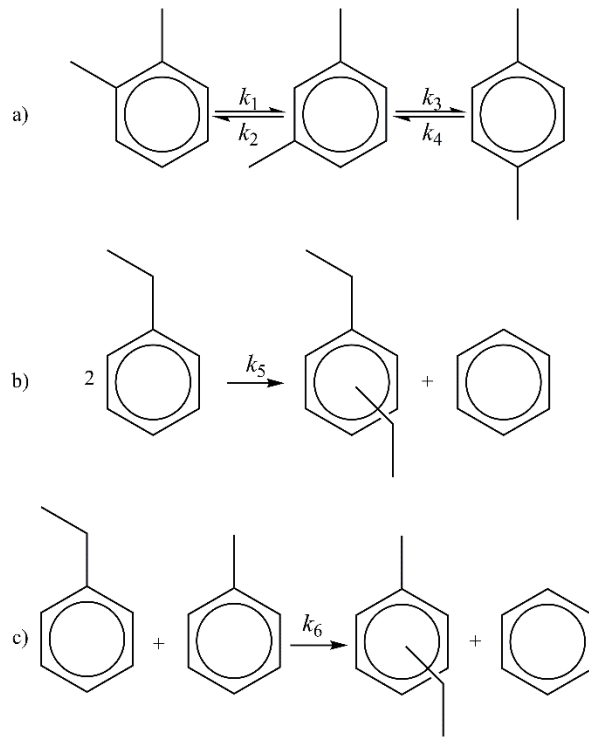


Figure 6.2 a) Main reaction: xylene isomerization b) Side reaction: ethylbenzene disproportionation c) Side reaction: ethylbenzene-toluene transalkylation

Considering all the reactions in **Figure 6.2**, the reaction rates of each compound was defined as below:

$$R_{OX} = k_2 C_{MX,cat} - k_1 C_{OX,cat} \quad (6.13)$$

$$R_{MX} = k_1 C_{OX,cat} + k_4 C_{PX,cat} - k_2 C_{MX,cat} - k_3 C_{MX,cat} \quad (6.14)$$

$$R_{PX} = k_3 C_{MX,cat} - k_4 C_{PX,cat} \quad (6.15)$$

$$R_{TOL} = -k_6 C_{EB,cat} C_{TOL,cat} \quad (6.16)$$

$$R_{PEMB} = k_6 C_{EB,cat} C_{TOL,cat} \quad (6.17)$$

$$R_{EB} = -2k_5 C_{EB,cat}^2 - k_6 C_{EB,cat} C_{TOL,cat} \quad (6.18)$$

$$R_{BZ} = k_5 C_{EB,cat}^2 + k_6 C_{EB,cat} C_{TOL,cat} \quad (6.19)$$

$$R_{PDEB} = k_5 C_{EB,cat}^2 \quad (6.20)$$

where k_j ($j=1,2,3,4$), $\text{m}^3/\text{kg s}$, k_j ($j=5,6$), $\text{m}^6/\text{kg s mol}$, are the kinetic constants of each reaction.

The center-type Arrhenius equation was used to take into account the variation of the kinetic constants with temperature:

$$k_j = k_{0,j} \exp \left[-\frac{E_{a,j}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (6.21)$$

where T is the temperature, K; R is the gas constant, J/mol K; $k_{0,j}$ is the kinetic constant of reaction j ($j=1,2,3,4$), $\text{m}^3/\text{kg s}$, and of reaction j ($j=5,6$), $\text{m}^6/(\text{kg s mol})$ at centered temperature T_0 (473 K); $E_{a,j}$ is the activation energy of reaction , J/mol.

The adsorption amount was calculated with the generalized Extended Langmuir isotherm.

$$q_i = \frac{q_{m,i} b_i C_{i,ads}}{1 + \sum_i b_i C_{i,ads}} \quad (6.22)$$

where $q_{m,i}$ is the saturation capacity of component i , mol/kg; b_i is the adsorption equilibrium constant of component i , m^3/mol .

The adsorption equilibrium constant at the operating temperature was determined by the integration of the van't Hoff equation:

$$b_i = b_{0,i} \exp \left[-\frac{\Delta H_{ads,i}}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \quad (6.23)$$

where $b_{0,i}$ is the adsorption equilibrium constant of component i at centered temperature T_{ref} (481.5 K), L/mol; and $\Delta H_{ads,i}$ is the enthalpy of adsorption of component i , J/mol.

Table 6.1 Summary of the simulation parameters for the cases study of an SMBR

Unit dimensions and solid properties		Reaction kinetics ^a		Adsorption equilibrium		$b_{0,i}$ m ³ /mol		$q_{m,i}$ mol/kg	ΔH_i kJ/mol
Length of each column, m	1.14	$E_{a,1}$ (kJ/mol)	91	<i>p</i> -Xylene	0.1703	1.479	-20.9		
Diameter of each column, m	4.12	$E_{a,3}$ (kJ/mol)	84	<i>m</i> -Xylene	0.0976	1.292	-16.1		
Bed porosity	0.39	$k_{0,1} \times 10^8$ (m ³ /kg s)	8.7	<i>o</i> -Xylene	0.1187	1.388	-16.5		
Particle porosity of adsorbent	0.22	$k_{0,3} \times 10^8$ (m ³ /kg s)	4.4	Ethylbenzene	0.0972	1.444	-20.8		
Particle porosity of catalyst	0.29	$E_{a,5}$ (kJ/mol)	66	Toluene	0.0544	1.763	-18.7		
Radius of particle, mm	0.31	$k_{0,5} \times 10^{12}$ (m ⁶ /kg s mol)	7.2	Benzene	0.0160	2.651	-13.7		
Catalyst density, kg/m ³	1050	$E_{a,6}$ (kJ/mol)	57	<i>p</i> -Diethylbenzene	0.2604	0.969	-20.9		
Adsorbent density, kg/m ³	1340	$k_{0,6} \times 10^{12}$ (m ⁶ /kg s mol)	7.3	<i>p</i> -Ethylmethylbenzene	0.2604	0.969	-20.9		
Feed (wt%)					Desorbent				
EB	PX	MX	OX	TOL	Bz				
Case A	-	0.274	0.578	0.148	-	1			
Case B ^b	0.140	0.236	0.497	0.127	-	1			
Case C	-	0.274	0.578	0.148	1	-			
Case D ^b	0.140	0.236	0.497	0.127	1	-			

^a Parameters of reverse reactions ($E_{a,2}$, $E_{a,4}$, $k_{0,2}$, $k_{0,4}$) were calculated with the thermodynamic equilibrium equations proposed by Gonçalves and Rodrigues. ^b Ethylbenzene can be separated by extractive distillation.

6.2.3 Distillation columns model

The desorbent consumption is an important unit performance parameter; the actual desorbent recovery units, distillation columns, were considered together with the SMBR to evaluate the energy and economic performance of the system. Since the optimum operating conditions of the SMBR is a tradeoff between separation and reaction, the operating temperature of the SMBR was expected to be higher than that of the SMB in industry. Thus, the cost for increasing the temperature in the SMBR was also included through heat exchangers in the inlet and outlet streams. A simplified scheme is depicted in **Figure 6.3**. PX-rich stream is recovered in the extract distillation column (X.Col), while PX-lean stream is collected through the raffinate distillation column (R.Col). Since the main components in the X.Col are *p*-xylene and desorbent, *p*-xylene was set as the heavy key compound and PX-rich stream was collected at the bottom of the X.Col, while the desorbent as the light key was collected at the top of the distillation column and sent back to the SMBR unit. The R.Col separates C_8^+ aromatics depleted of *p*-xylene from the desorbent. EB or MX (according to the volatility sequence EB>PX>MX>OX) were respectively set as the heavy key in the R.Col to achieve the separation. The desorbent, as the light key went back to the SMBR unit from the top of the distillation column.

The distillation column model is based on shortcut methods assuming constant molar flow rate within each column section and constant relative volatilities throughout the columns. In the distillation columns, knowing the pressure, the temperature of the top and bottom part of the distillation columns were calculated with Antoine coefficients from Yaws²⁸. The fugacity of the vapor and liquid were calculated through Peng-Robinson equation of the state to determine the equilibrium constants²⁹. Peng-Robinson equation is commonly used for the

calculation for aromatics^{8,30}. The minimum reflux was calculated according to the Underwood equation, setting the mole fraction of the light and heavy key compound in 0.001, with no distribution of the rest of the compounds. Indeed, 1.3 times of the minimum reflux was used as actual reflux³¹. The flow rates in the condenser and reboiler were estimated with the actual reflux considering the feed as a saturated liquid. Enthalpy of vaporization and heat capacity from Yaws were used to calculate the duty associated with the distillation columns and heat exchangers²⁸.

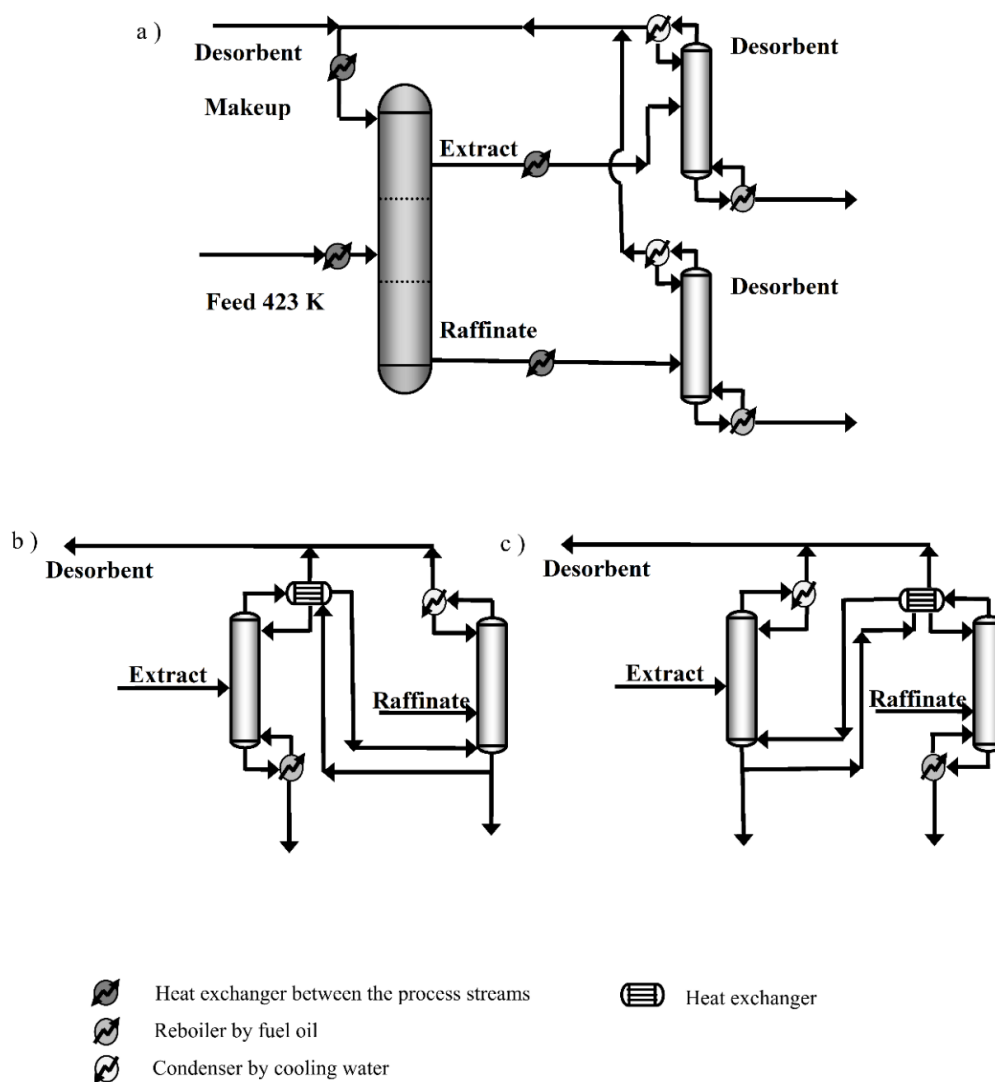


Figure 6.3 Simplified scheme for the SMBR combined with the distillation columns. a) both extract and raffinate distillation columns operate at near atmospheric pressure; b) extract distillation column operates at high pressure; c) raffinate distillation column operates at high pressure

The feed of the SMBR was fixed at the corresponding flow rate of 80 m³/h at 453 K³², and the temperature of the feed was around the temperature of the condenser of the xylene splitter operated at near atmospheric pressure (i.e., 423 K). While for the desorbent, the temperature was determined based on the condenser of the distillation columns. As a first approach, the distillation columns were operated at near atmospheric pressure; the pressure at the top of both columns was set at 20 psia, with a total pressure drop of 10 psia³³. To further study and analyze the energy saving improvements, heat integration was considered. The idea behind the integration is to use the heat from the condenser for the reboiler. Part of the energy from one distillation column can be transferred to the other column by setting one of the distillation columns at higher pressure. A minimum temperature difference of 25 K was maintained in all heat exchangers³⁴.

6.3 Methodology

Due to the huge expenses for new devices, the SMBR is based on an existing SMB comprising 24 adsorption beds with length and diameter respectively of 1.14 m and 4.12 m. Physical properties of adsorbent and catalyst are given in **Table 6.1**. The feed used was 23.6 wt% *p*-xylene; 49.7 wt% *m*-xylene; 12.7 wt% *o*-xylene; 14 wt% ethylbenzene, which was also adopted by Minceva et al.²¹. For the cases without EB involved in the feed, the relative proportion of each xylene was kept (i.e., 27.4 wt% *p*-xylene, 57.8 wt% *m*-xylene, 14.8 wt% *o*-xylene). Ethylbenzene can be separated from C₈ aromatics by extractive distillation^{35, 36}.

Considering toluene and benzene as desorbent, four cases were proposed in this chapter. Case A adopted Bz as desorbent, and EB was not involved in the feed. Case B also considered Bz as desorbent, however, EB was present in the feed. In Case B, by-products such as PDEB and Bz from side reaction EB disproportionation were taken into account. Case C used TOL as

desorbent, EB was not involved in the feed. Finally, in Case D TOL was also the desorbent with EB present in the feed. Similarly, in Case D side reactions EB-TOL transalkylation and EB disproportionation were taken into account.

The optimization solver CVP_SS of the commercial software gPROMS was used for the optimization of the SMBR under several constraints. The purity (desorbent free) of extract and raffinate must be equal or higher than 70% and 95%, respectively. The maximum pressure drop per bed was 5.1 psia²⁴. The recovery of PX should be higher than 97%. Purity, recovery, desorbent consumption, and productivity were calculated in each optimization, considering PX in the extract as the desired target product according to the same method as in the previous work¹.

To conduct a comprehensive analysis, it is necessary to identify some operational variables as well as performance indicators, thereby helping to define design targets as well as to generate better optimization plan. In this chapter, criteria such as minimum desorbent consumption, maximum productivity, minimum energy consumption per kilogram of PX produced, and maximum profit, were used as the objective functions, to identify the influence of the operational variables, as presented in **Table B33 to B36**. It is worth noting that the product from SMBR is the high content *p*-xylene stream. The price of the high content PX stream was estimated based on the value from Gentry et al.³⁷ and extrapolated using the cost of TOL from Turton et al.³⁸. Whenever external cooling was required (e.g., column condenser), cooling water was used. Similarly, a furnace using fuel oil was employed for external heating (e.g., column reboiler). The values for cooling water and fuel oil, also from Turton et al.³⁸, are presented in **Table 6.2**. The costs for the feed, crystallization, and the eventual separation of ethylbenzene were not taken into account.

Table 6.2 Cost of cooling water, fuel oil, and high content PX stream

Cooling water	0.354 USD/GJ
Fuel oil	14.20 USD/GJ
High content PX	1.196 USD/kg

6.4 Results and discussion

6.4.1 Minimum desorbent consumption

The minimum desorbent consumption was investigated for various configurations at 453 K and 513 K for the four cases; detailed results are presented in **Table B37** to **B40** in Annex B. In every optimization, the adsorbent/(adsorbent+catalyst) volume ratio (φ) went to 1 in order to minimize the desorbent consumption (DC). In other words, less DC is needed to achieve the purity requirements when there is no reaction. The switching time, t_s , in each case at the same temperature was almost constant. For each case, at lower temperatures, the switching time was longer than that at a higher temperature. At lower temperatures the mass-transfer decreases which is compensated by longer contact times through the switching time³⁹. On the other hand, at lower temperature lower DC was observed, this is probably due to the reduction of selectivity of PX with respect to the other isomers as temperature increases.

Seen from **Figure 6.4**, for both temperatures, with the increase of columns in zone I, reduction on DC was observed, as well as the pressure drop per bed in zone I (see **Table B37** to **B40** in Annex B). It can be deduced that the columns number in zone I is an important factor for the separation process in the SMBR. Wu et al. pointed out that shorter section length in zone I and zone IV, together aim at the regeneration of adsorbent and desorbent, can lead to higher desorbent flow rate⁴⁰. The productivity at minimum DC does not change significantly

with the variation of the configuration and temperature. Cases A and C (without EB in the feed) led to higher productivity and lower desorbent consumption than cases B and D (with EB in the feed), this is mainly due to the higher amount of PX in the feed. Since TOL is more adsorbed than Bz, a larger amount of Bz is needed for the desorption of PX in zone I. Higher number of columns in zone I can reduce the consumption of desorbent, however, the consumption in Cases A and B (Bz as desorbent) still indicated higher value than cases C and D (TOL as desorbent).

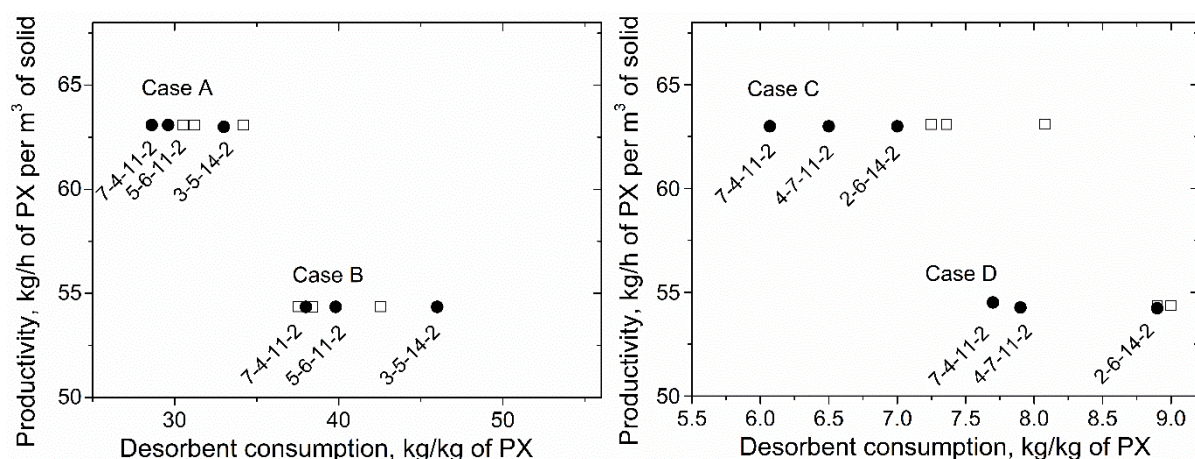


Figure 6.4 Minimized desorbent consumption for various configurations at different temperatures (● 453 K; □ 513 K)

6.4.2 Productivity VS. desorbent consumption

Configurations 7-4-11-2, 8-3-11-2, 10-3-9-2 have higher number of columns in zone I, and consumed less desorbent than other configurations as concluded in **Section 6.4.1**; therefore, they were expected to show better performance in productivity. Those three configurations were optimized for maximum productivity under different desorbent consumption constraints for cases A and B. Traditional column arrangement 5-9-7-3 used in industrial SMB did not

show good performance for those cases, thus it is not compared here. Configuration 7-3-10-4 has higher number of columns in zone I, 4-3-15-2 has higher number of columns in zone III, those two configurations were investigated for case C and D as comparison. Traditional configuration 5-9-7-3 was also studied. The behavior of productivity vs. desorbent consumption at various temperatures for different configurations are presented in **Figure 6.5**.

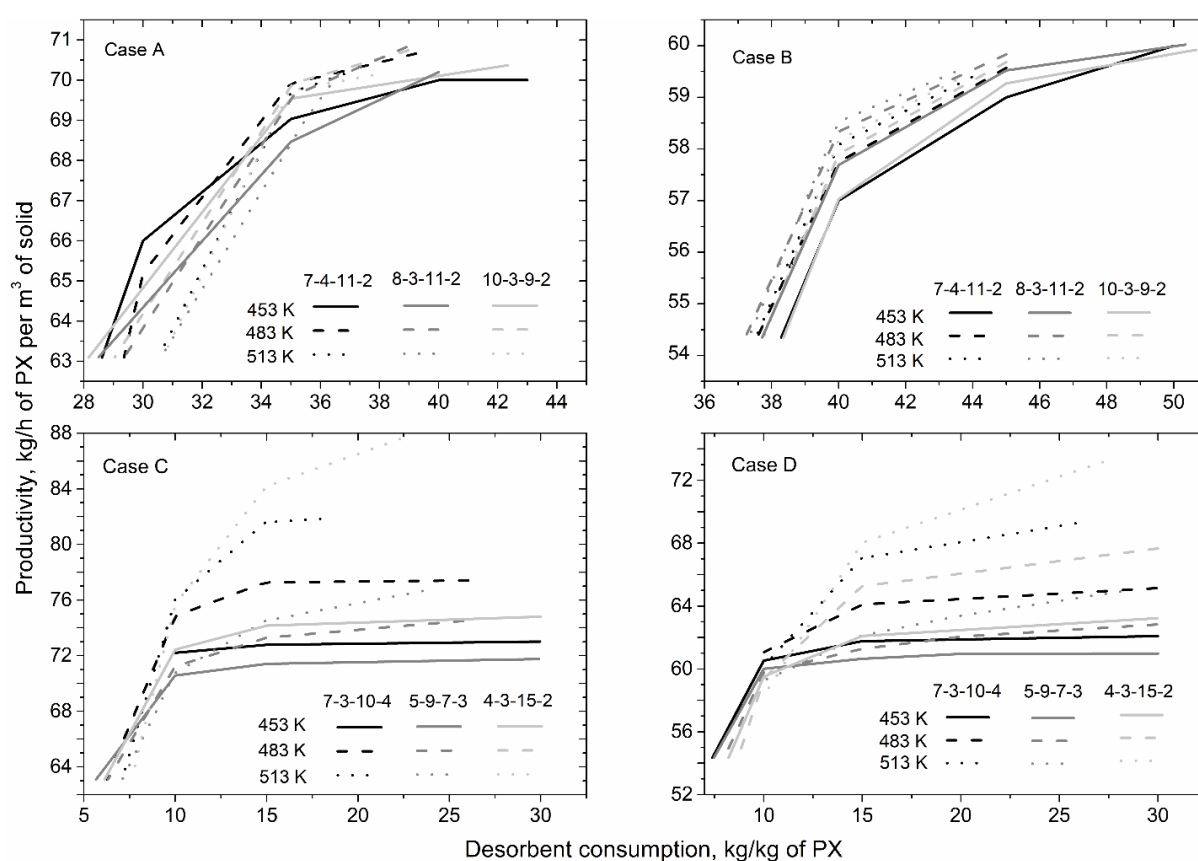


Figure 6.5 Maximized productivity under different desorbent consumption constraints for various configurations and temperatures.

For all the cases, at lower DC, the maximum productivity was dominated by DC and increased rapidly. For higher DC values, the maximum pressure drop per bed became the controlling factor. At low DC constraints, to satisfy the constraint,

adsorbent/(adsorbent+catalyst) volume ratio (φ) tended to 1, the main process occurring in the SMBR is separation. The difference among various configurations is not significant, as well as the influence of the temperature. At the minimum DC, the same results were obtained as in **Section 6.4.1**. However, as the restriction on DC is relaxed, more isomerization occurs in the SMBR and the difference among configurations become more significant. In cases C and D, 7-3-10-4 showed better performance at low DC constraints, but led to lower productivity than 4-3-15-2 at high DC constraints. It is deduced that, when the reaction occurs in the SMBR, the columns in zone III have a great influence on the performance. The concentration is higher on MX/PX (compared with the equilibrium value), and it shifts the isomerization reaction towards PX, which is more adsorbed and taken to zone II by the adsorbent and obtained in the extract. Considering that the reaction starts to appear in SMBR under high DC constraints, 4-3-15-2 showed superior performance than others. Similarly, the reaction also increases with the temperature, it enhances the difference among configurations and ultimately the figure results in a spray-like pattern.

For cases A and B, φ was close to 1, the main process in the SMBR is separation, thus no spray pattern was observed. The configuration 10-3-9-2 showed better performance than the other two configurations (7-4-11-2; 8-3-11-2). As previously mentioned, Bz is less adsorbed than TOL, higher flow rates of Bz are needed in cases A and B for the regeneration of adsorbent in zone I, which strengthen the point that columns in zone I is an important factor in this type of process. For cases C and D, 4-3-15-2 showed better performance and the traditional configuration 5-9-7-3 showed the worst behavior. With more appropriate desorbent (toluene), higher proportion of reaction process is allowed within the SMBR system, and better performance of the SMBR can be achieved. Considering the reaction process in the SMBR,

more columns are needed in zone III, due to the higher xylene concentration and higher requirement of the purity in raffinate than in extract.

For cases A and C (without EB in the feed), higher productivity was obtained than cases B and D (with EB in the feed) under the same conditions. For cases A and B (Bz as desorbent), lower productivity was obtained than cases C and D (TOL as desorbent) under the same conditions. Generally, feed without EB and TOL as desorbent leads to better performance of the SMBR system.

Compared to cases A and B, more catalyst was possible to be included in case C. The adsorbent/(adsorbent+catalyst) volume ratio (φ) was always above 0.5 in order to achieve the desired purity due to the nature of the reverse reaction. Additionally, with restriction on DC tighten, the ratio φ increases, production of PX decreases, and the switching time increases. When the switching time increases to a certain point, with even lower DC, the mass transfer resistant become significant and prevent the unit to achieve the desired purity^{1, 39}.

6.4.3 Influence of the temperature on energy performance

In this section, both distillation columns were set at near atmospheric pressure. Minimum energy consumption per kilogram of PX produced in the extract was used to identify the influence of temperature. Energy performance of the four cases was investigated at several temperatures; along with the flow rate in each zone, the configuration was also included as decision variable in the optimization, the results are presented in **Figure 6.6**.

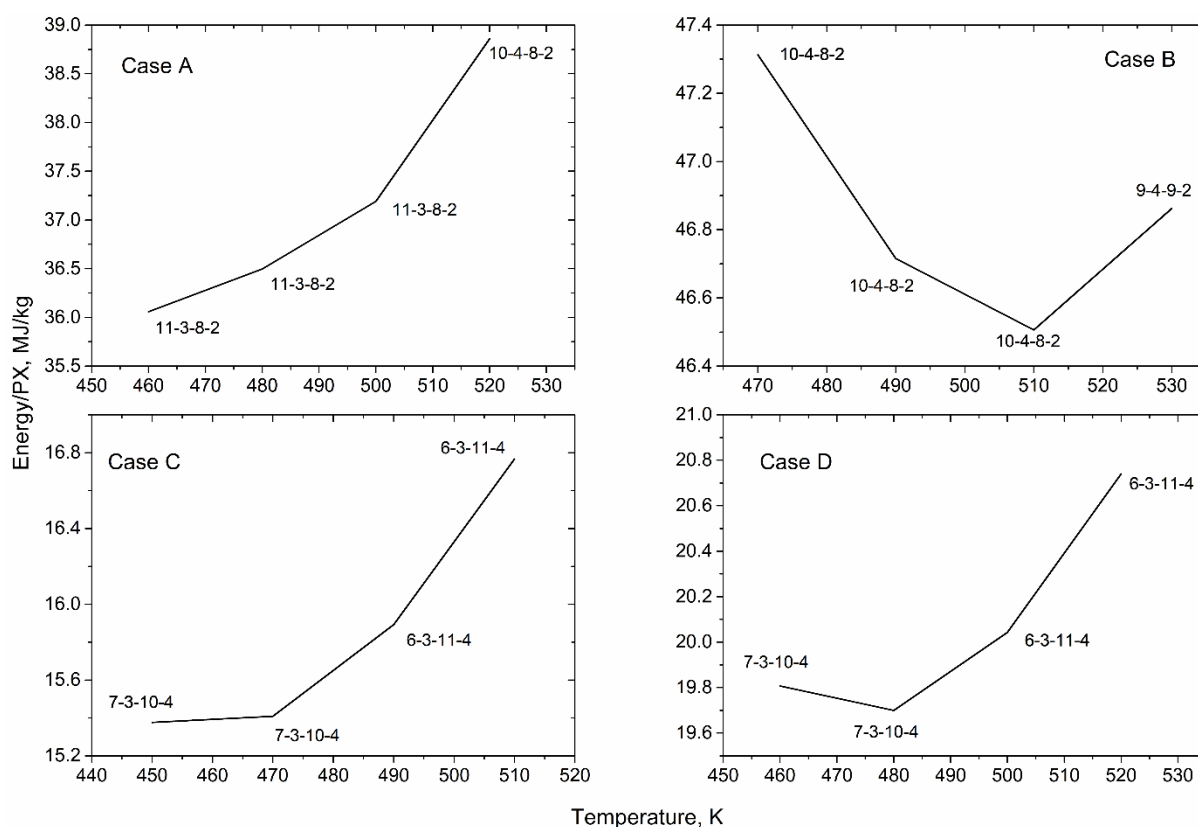


Figure 6.6 Minimized energy consumption at different set temperatures for the four cases.

For cases A and B, adsorbent/(adsorbent+catalyst) volume ratio (φ) after optimization went to 1, the main process occurring within the SMBR was the separation. This explains the high number of columns in zone I for the optimal configuration. While in cases C and D, reaction also took place, thus, more columns in zone III were obtained. In all cases, with the increase of the temperature, the ratio φ increased, the SMBR turned into a classical SMB; the energy consumption caused by increasing the temperature outweighed the increase in productivity.

For cases B and D, higher energy was consumed than cases A and C respectively. Since the heat in the heat exchangers only took around 1% of all the energy consumed, the energy consumed was mainly from the distillation columns. The detail energy consumption description for different cases at different temperatures are presented in **Table B41** in Annex B. Comparing B to A, energy consumed in both distillation columns increased, but energy

consumed in R.Col increased at higher extent. However, the energy consumed in X.Col was always significantly higher than that of the R.Col. Due to the EB present in the feed, higher desorbent flow rates were observed in the raffinate and extract streams, thus more energy was consumed in the distillation columns. Additionally, less PX was produced in case B due to the feed limitation (only 23.6 wt% PX in feed for case B). Thus, higher energy per PX was observed for cases with EB in the feed.

For cases A and B, higher energy was consumed than cases C and D. From case C to A, with the desorbent changing from toluene to benzene, the energy consumed in both distillation columns increased, with the increase in the X.Col being more significant. The separation of PX from desorbent was conducted through X.Col, the higher energy consumption is explained by the higher proportion of desorbent in case A (Bz) than in case C (Tol).

Observed in **Figure 6.6**, cases show different patterns. For the four cases, the energy consumed in the R.Col shows an increasing trend with temperature (**Table B41**). Checking the composition of the raffinate stream at different temperatures (see **Table B42** in Annex B), it can be concluded that the feed to the column always increased with temperature leading to greater energy consumption. On the other hand, the energy consumed within the X.Col presents a minimum in cases B and D. The selectivity of PX with respect to the rest of the species decreases with temperature except for EB, which stays almost constant due to the similar enthalpy of adsorption. Among the desorbents, the selectivity with respect to Bz decreases more rapidly than that of TOL, which may shift the minimum to a higher temperature when comparing cases B and D. Moreover, the energy in the X.Col for cases A and C always increased with temperature.

As concluded from **Section 6.4.1**, temperature may have opposite effect on the productivity under different DC constraints, this is due to the opposite effect of temperature on reaction and

separation processes. When reaction takes place to a greater extent, it is observed higher desorbent consumption, leading to higher energy consumption. In general, case C showed the best performance under the criterion of energy consumption. Objective function of minimum energy consumption per kilogram of PX produced could satisfy the study requirement for separation process. However, the amount of energy consumed outweighs the amount of PX produced when reaction process is also present in the SMBR. Thus, a different objective function such as maximum profit may provide additional information.

The distillation model was validated against rigorous method from Aspen Plus. As presented in **Table B43** to **B46** in Annex B, the results obtained with the model matches with those from Aspen Plus.

6.4.4 Maximization of profit

To study its economic performance, the SMBR was optimized using profit as the objective function. The heat integration, discussed in **Section 6.3**, was included for comparison. The results are presented in **Table 6.3**.

To guarantee that the temperature difference between the condenser of the X.Col (or R.Col) and the reboiler of the R.Col (or X.Col) was higher than 25 K, a minimum pressure of 200 psia was required in cases A and B and 100 psia was required in cases C and D for the corresponding high pressure distillation column.

Table 6.3 Energy performance changes with configuration and pressure for the four cases

	Case A: Bz as desorbent, feed without EB			Case B: Bz as desorbent, feed with EB		
Pressure	Both low	X.high_200	R.high_200	Both low	X.high_200	R.high_200
Configuration	8-3-11-2	8-3-11-2	8-3-11-2	10-3-9-2	10-3-9-2	10-3-9-2
Energy/PX extract, MJ/kg	41.4	38.6	38.0	47.6	42.3	42.2
SMBR Temperature, K	501	504	502	519	523	522
Desorbent consumption, kg/kg	36	36	36	41	43	41
Ads./((Ads.+Cat.) Ratio	0.91	0.92	0.91	1.00	1.00	1.00
PX extract / PX feed, %	100	100	100	98	97	97
Total profit $\times 10^{-3}$, USD/h	21.1	21.4	21.4	17.0	17.4	17.5
	Case C: Tol as desorbent, feed without EB			Case D: Tol as desorbent, feed with EB		
Pressure	Both low	X.high_100	R.high_100	Both low	X.high_100	R.high_100
Configuration	4-3-15-2	4-3-15-2	4-3-15-2	4-3-15-2	4-3-15-2	4-3-15-2
Energy/PX extract, MJ/kg	34.7	31.2	28.1	39.6	35.2	31.8
SMBR Temperature, K	540	540	539	556	555	555
Desorbent consumption, kg/kg	19	19	19	21	22	22
Ads./((Ads.+Cat.) Ratio	0.87	0.87	0.86	0.91	0.91	0.91
PX extract / PX feed, %	126	126	127	123	123	124
Total profit $\times 10^{-3}$, USD/h	28.2	28.7	29.4	23.3	23.8	24.3

Note: Both low – both extract and raffinate distillation column set at normal pressure; X.high_200 – Extract column set at 200 psia; R.high_200 – Raffinate column set at 200 psia; X.high_100 – Extract column set at 100 psia; R.high_100 – Raffinate column set at 100 psia

It can be seen that the temperature of the SMBR, the adsorbent/(adsorbent+catalyst) volume ratio (φ), and the configuration was not influenced by the consideration of the heat integration. All the optimizations in **Table 6.3** came to the same configuration for the same case. For cases A and B, the optimized configuration was 8-3-11-2 and 10-3-9-2, respectively. For cases C and D, the optimal configuration was the same for both, 4-3-15-2. In case B, since φ went to 1, only separation process occurred in the SMBR, thus more columns were obtained in zone I. For cases A, C, and D, φ was below 1, reaction process became more significant in the SMBR, therefore more columns in zone III was obtained.

The study and analysis of the energy saving improvement for the SMBR by setting high pressure for X.Col or R.Col was successfully performed. A total of 34.7 MJ/kg energy was used to obtain 126% product yield (PX extract/PX feed, %) in case C with both distillation columns set at low pressure. When the pressure of the X.Col or R.Col was raised, a total of 31.2 or 28.1 MJ/kg energy respectively was consumed to achieve 126% and 127% yield of product. The results show that a maximum of 19% energy reduction is possible to achieve by setting one of the distillation columns to higher pressure. In terms of profit, for case C, an increase of 1200 USD/h was achieved by setting the R.Col at higher pressure. That increase results in almost 10 million USD per year assuming 330 days of operation. Similar trend was observed for the other cases.

Illustrated in **Table 6.3**, the case with R.Col set at high pressure performs better than when X.Col was set at high pressure, both in energy and profit wise. As seen in **Table B47** in Annex B, the energy consumed in X.Col is at higher order of magnitude than that of R.Col. Since the higher pressure leads to higher energy consumption, it is more economical to increase the pressure of the column consuming less energy.

The bulk phase concentration profiles of the four cases optimized in the SMBR with the R.Col set at high pressure are presented in **Figure 6.7**.

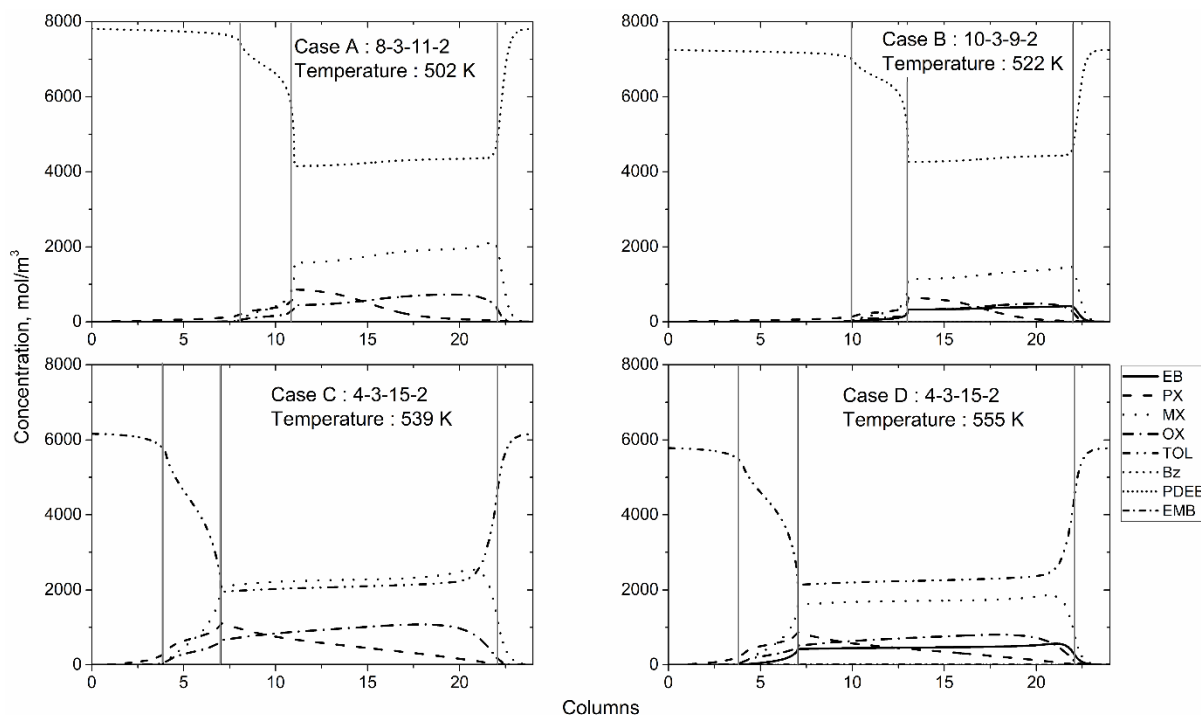


Figure 6.7 Bulk phase concentration profiles for SMBR with raffinate distillation column set at high pressure for the four cases

For case B, since EB was involved in the feed, the EB disproportionation reaction may be observed in the SMBR unit. PDEB was observed at extremely low concentration in the profile. Thus, it can be assumed that EB disproportionation does not influence the unit performance. In case D, besides EB disproportionation, EB-TOL transalkylation is also involved. Both PDEB and PEMB were produced as byproducts. The highest PDEB concentration was 1.12 mol/m^3 and that of PEMB was 12.48 mol/m^3 . Since EB-TOL transalkylation has similar activation energy and reaction rate to EB disproportionation, the concentration of PEMB was higher due to the concentration of toluene.

Comparing cases A and B, the concentration profiles are very similar, the main difference is observed for the EB concentration. Additionally, with EB, the concentration of MX and OX in zone III is much lower, which causes less production of PX, since EB cannot be converted to PX in the liquid phase. Only a slight difference in the configuration was found between case A and B, and that may be explained by the isomerization involved in case A. With existence of reaction process, longer length of zone III is observed. The lower desorbent concentration in zone I and IV in cases B and D (comparing with cases A and C), is explained by the density of the desorbent, which is influenced by the temperature.

In case D, the existence of PEMB does not necessary influence the result. It is not always necessary to remove PEMB from *p*-xylene, terephthalic acid is the final product of the oxidation of both *p*-xylene and PEMB²⁷. Besides, PMEB has much lower melting point than PX, which makes the separation through crystallization possible. On the other hand, Bresler and Frey⁴¹ mentioned that the PDEB as desorbent presents difficulty in separating from C₉ aromatics due to the proximity of boiling points. The consideration of toluene as desorbent avoids the problem and improves the flexibility of the feed.

6.5 Conclusions

The feed without EB is more appropriate for the SMBR unit, since lower temperature, lower adsorbent/(adsorbent+catalyst) ratio, lower desorbent consumption, lower energy consumption, and higher yield are observed than those when EB is present in the feed. Toluene has better performance than benzene as desorbent in the study of SMBR, since toluene is more adsorbed than Bz. With toluene as desorbent, the reaction extent is more significant in the SMBR, and leads to higher yield of PX. The study and analysis of the energy saving improvement for the SMBR by setting high pressure for extract column or raffinate column

proved feasibility. Energy is reduced in 19% and profit increased in 4% by setting the raffinate column at higher pressure. Additionally, the configuration, temperature, and the adsorbent/(adsorbent+catalyst) volume ratio are not influenced by the heat integration; from which the optimization of the SMBR can be conducted separately from the whole aromatics complex. For the best case studied, 127% of the PX in the feed was obtained in the extract, which compared to the industrial SMB and assuming a recovery of 95% in the crystallization, results in an increase of about 25% in the recovery of PX.

6.6 Nomenclature

b_i , adsorption equilibrium constant of component i , L/mol

$b_{0,i}$, adsorption equilibrium constant of component i at centered temperature T_{ref} , L/mol

C_i , concentration of component i in the bulk phase, mol/m³

$C_{i,j}$, concentration of component i in zone j ($j=1,2,3,4$), mol/m³

$C_{i,k}$, concentration of component i in port k ($k=D,F,X,R$), mol/m³

$C_{i,ads}$, average particle concentration of component i in the macropores of adsorbent, mol/m³

$C_{i,cat}$, average particle concentration of component i in the macropores of catalyst, mol/m³

D_{ax} , axial dispersion coefficient, m²/s

DC, desorbent consumption, kg/kg

D_m , molecular diffusivity, m²/s

$E_{a,j}$, activation energy of reaction j , J/mol

$\Delta H_{ads,i}$, adsorption enthalpy of component i , J/mol

k_j , kinetic constant of reaction j ($j=1,2,3,4$), m³/kg s

k_j , kinetic constant of reaction j ($j=5,6$), m⁶/kg s mol

$k_{0,j}$, kinetic constant of reaction j ($j=1,2,3,4$) at centered temperature T_0 , m³/kg s

$k_{0,j}$, kinetic constant of reaction j ($j=5,6$) at centered temperature T_0 , m⁶/(kg s mol)

$K_{i,a}$, mass-transfer coefficient between the adsorbent and the bulk phase, m/s

$K_{i,c}$, mass-transfer coefficient between the catalyst and the bulk phase, m/s

ΔP , Pressure drop, Pa

PR, productivity, kg/h of PX per m³ of solid

$q_{m,i}$, saturation capacity of component i , mol/kg.

q_i , adsorbed amount of component i , mol/kg

Q_j , volumetric flow rate in zone j ($j=1,2,3,4$), m³/h

Q_k , volumetric flow rate in port k ($k=D,F,X,R$), m³/s

R_i , reaction rate of component i , mol/kg s

R_p , particle radius, m

R_D , column radius, m

R , gas constant, J/mol K

T , temperature, K

T_0 , centered temperature for the kinetic constant, 473 K

T_{ref} , centered temperature for the adsorption equilibrium constant, 481.5 K

t_s , switching time, s

u , interstitial velocity, m/s

u_s , solid velocity, m/s

Greek letters

ε , bed porosity

ε_c , particle porosity of catalyst

ε_a , particle porosity of adsorbent

ρ_i , density of component i , kg/m³

ρ_{ads} , density of adsorbent, kg/m³

ρ_{cat} , density of catalyst, kg/m³

φ , adsorbent/(adsorbent+catalyst) volume ratio

Superscripts and subscripts

avg average

in, inlet

out, outlet

D, desorbent

F, feed

R, raffinate

X, extract

Abbreviations

Bz, benzene

CSS, cyclic steady-state

EB, ethylbenzene

PEMB, *p*-ethylmethylbenzene

HD, heavy desorbent

LD, light desorbent

LDF, linear driving force

MX, *m*-xylene

OX, *o*-xylene

PDEB, *p*-diethylbenzen

PEMB, *p*-ethylmethylbenzene

PX, *p*-xylene

R.Col, raffinate distillation column

SMB, simulated moving bed

SMBR, simulated moving bed reactor

TMB, true moving bed

TMBR, true moving bed reactor

TOL, toluene

X.Col, extract distillation column

6.7 Reference

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Chapter 7 Conclusions and Suggestions for Future Work

This chapter summarizes the main conclusions of the thesis, and the accomplishment of several specific objectives. Additionally, the suggestions for future research are briefly described. Those are the selection of desorbents, and parametric behaviour study of the appropriate catalyst, binary and ternary adsorption experiments to get further insight into the adsorbent performance, and the proposing of different aromatics complex schemes.

7.1 Conclusions

A Simulated Moving Bed Reactor (SMBR) model, based on the conventional Simulated Moving Bed (SMB), but comprising a homogeneous mixture of adsorbent and catalyst was studied from the simulation and optimization point of view; that includes:

- (i) Experimental and parametric behavior study of xylene isomerization.
- (ii) Identification of the main side reactions that may occur in the SMBR, and determination of the reaction rates and activation energies of the reactions.
- (iii) Investigation of the saturation capacity, the adsorption equilibrium constant, and the heat of adsorption of C₆-C₈ aromatics.
- (iv) SMBR unit design based on the experimentally obtained parameters.
- (v) Determination of the best operating conditions of the SMBR, together with the role of energy consumption and energy savings in the process.

In chapters 3 and 4, xylene isomerization, and disproportionation and transalkylation between C₈ aromatics and toluene that may occur in the SMBR were investigated, as part of the development of a SMBR unit for the production of *p*-xylene in the liquid phase. Toluene was included in the experiments since it has been used as promising desorbent in the separation of xylenes. For the reaction part, mono-functional acid beta zeolites with SiO₂/Al₂O₃ ratio (SAR) of 35 (BEA35) and 38 (BEA38) were used as catalysts. The fixed bed experiments were carried out under the following conditions: 513, 493, 473, and 453 K at 2.1 MPa in the liquid phase.

Firstly, xylene isomerization is the main reaction in the SMBR, kinetic constants were estimated with four different models. For the triangular reaction scheme, xylenes convert through mutual interconversion, allowing the 1,3-methyl shift mechanism, whereas, for the

linear reaction scheme, *o*-xylene can only convert to *p*-xylene via *m*-xylene as intermediate through the 1,2-methyl shift mechanism. Two of the models included the xylene isomerization thermodynamic equilibrium from the literature. The linear reaction scheme, including the thermodynamic equilibrium from the literature, presented a better fit to the experimental values. Higher conversion of *p*-xylene was observed when compared with the conversion of the other two isomers. This may be attributed to its smaller molecular size. BEA35 presented better performance due to its higher amount of Brønsted acid sites. Activation energies of xylene isomerization, as well as the interconversion kinetics over the catalysts, were estimated. The center-type Arrhenius equation was used where the centered temperature was 493 K for BEA38 and 473 K for BEA35. The activation energies of isomerization from *o*- to *m*-xylene and from *m*- to *p*-xylene were respectively 91 and 90 kJ/mol on BEA38, 91 and 84 kJ/mol on BEA35. The activation energies presented similar values over the two catalysts; it can be concluded that the isomerization on both catalysts follows the same mechanism.

Secondly, two experiments were carried out to identify the main side reactions during xylene isomerization in the liquid phase, those are C₈ aromatics mixture experiments with and without toluene. Those experiments were conducted only on BEA35 since it was the catalyst offering better performance on xylene isomerization. By analyzing the distribution of the products, of the two experiments, ethylbenzene disproportionation and ethylbenzene-toluene transalkylation were identified as the main side reactions that may occur in a SMBR in the liquid phase. Both reactions were verified to be second order. Similar kinetic constants obtained respectively from pure ethylbenzene, and ethylbenzene-toluene experiments indicated the absence of competition for the adsorption sites between the two reactions under the studied conditions. Additionally, ethylbenzene disproportionation and ethylbenzene-toluene transalkylation undergo through the deethylation-ethylation mechanism; it was verified that the

bulky diphenylethane-based mechanism was suppressed by the narrow channels of the zeolite. The activation energies of the side reactions were 66 and 57 kJ/mol, respectively. Moreover, by conducting ethylbenzene-toluene experiments with different mass ratios, it was concluded that the existence of a parallel reaction, as well as the feed concentration, showed no effect on the *p*-diethylbenzene selectivity. The *p*-diethylbenzene selectivity was reduced as temperature increases at low conversions; in other words, at higher temperatures, diethylbenzene isomerization rate was increased at a greater extent than the actual production of *p*-diethylbenzene. It can also be deduced that the lower flow rate led to the higher conversion and lower selectivity towards *p*-diethylbenzene.

In chapter 5, the adsorption of C₆-C₈ aromatics (*p*-xylene, *o*-xylene, *m*-xylene, ethylbenzene, toluene, and benzene) was investigated on a dry Ba-exchanged zeolite X at 450, 483, and 513 K in the liquid phase. The experimental data were used to calculate the adsorption parameters including Langmuir adsorption constant, saturation capacity, and the heat of adsorption for each compound. Reliable adsorption equilibrium parameters for further investigation of the SMBR unit for the production of *p*-xylene in the liquid phase were obtained. The saturation capacity in mole basis followed the sequence of Bz > TOL > PX > EB > OX > MX; higher values were obtained than those reported in the literature with zeolite water content around 3%. Additionally, the heat of adsorption of the components were around 20 kJ/mol, except that of Bz, which is slightly lower.

Lastly, four cases were respectively investigated for the SMBR through simulations and optimizations under different constraints with several objective functions. Those cases consisted in EB present or not in the feed, and toluene or benzene as desorbent. The feed without EB was more appropriate for the SMBR unit, since lower temperature, lower adsorbent/(adsorbent+catalyst) mass ratio, lower desorbent consumption, lower energy consumption, and higher yield were obtained than those with EB involved in the feed. Toluene

had better performance than benzene as desorbent in the study of the SMBR, both in terms of energy and economics. With toluene as desorbent, the SMBR system led to higher yield. The study and analysis of the energy saving improvement for the SMBR by setting high pressure for extract distillation column or raffinate distillation column proved feasibility. The energy was reduced by 19% and profit increased 4% by considering heat integration. Finally, the configurations, temperature, and the adsorbent/(adsorbent+catalyst) mass ratio were not influenced by the heat integration. For the best case studied, an optimization based on costs resulted in yield of 127%, and productivity of 89 kg/h of PX per m³ of solid at the operating temperature of 539 K with the configuration of 4-3-15-2.

7.2 Suggestions for future work

Based on the work developed in this thesis, many interesting subjects could be investigated in the future.

Since the adsorbent in the SMBR is completely dry, the experimental study of adsorption equilibrium could be extended to binary or ternary components system over dry adsorbent. It not only provides information about the influence of the mixture composition on selectivity, but also states the importance of desorbent on the selectivity between C₈ aromatics and PX. Additionally, the impact of the water content on C₈ aromatics selectivity could be investigated, to get a more in-depth insight into the role that water plays in adsorption at higher temperatures.

More attention should also be paid to the selection of desorbent. The selection of desorbent can be conducted through binary adsorption (with desorbent+PX mixture) experiments, from where the desorbent strength could be evaluated. The desorbent strength plays an important role for searching appropriate desorbent for the SMBR. The desorbent with affinity to the

adsorbent between *p*-xylene and other C₈ isomers could be a promising choice for SMBR for the separation of *p*-xylene.

Since the SMBR allows a milder purity of the stream from the extract port (70%), it could be feasible to reduce the total number of beds required for the SMBR. The reduction in the number of beds implies the reduction of the grids, and a smaller number of beds allows the possibility of turning two columns into single column operation, which makes the adsorption chamber control simpler. Additionally, it has potential to enlarge the operating capacity.

Annex A: Characterization of the Catalysts and Adsorbent

A.1 X-ray diffraction (XRD) of BEA35 and BEA38

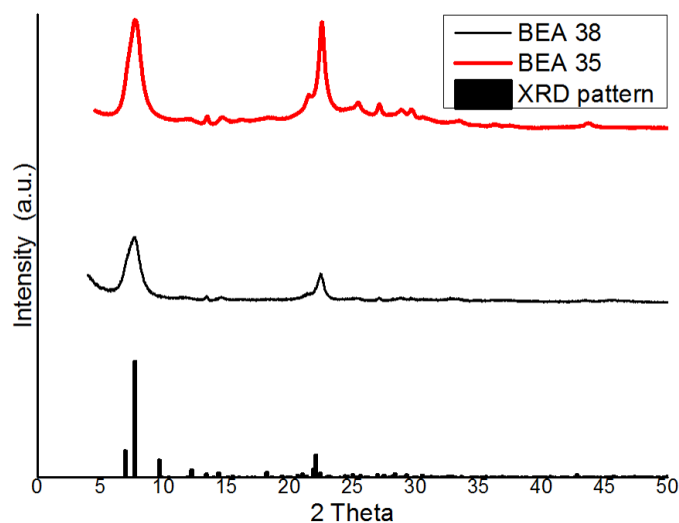


Figure A1 X-ray diffraction (XRD) of BEA35 and BEA38 compared to reported powder pattern by International Zeolite Association (www.iza-structure.org)

A.2 Single particle crushing strength of BEA35 and BEA38

Table A1 Crushing strength data in Newton (N) obtained by application of the tablet tester

			BEA35	BEA38
Number of particles (n)	n		50	50
Average	N		54.8	8.3
Standard deviation (s)	N		28.8	3.0
Relative standard deviation (RSD)	%		52.6	36.5
95 % Confidence interval	N		8.0	0.8
Range	Minimum (x)	N	5	3
	Maximum (x)	N	114	17

A.3 Scanning electron microscopy (SEM) of BEA35 and BEA38

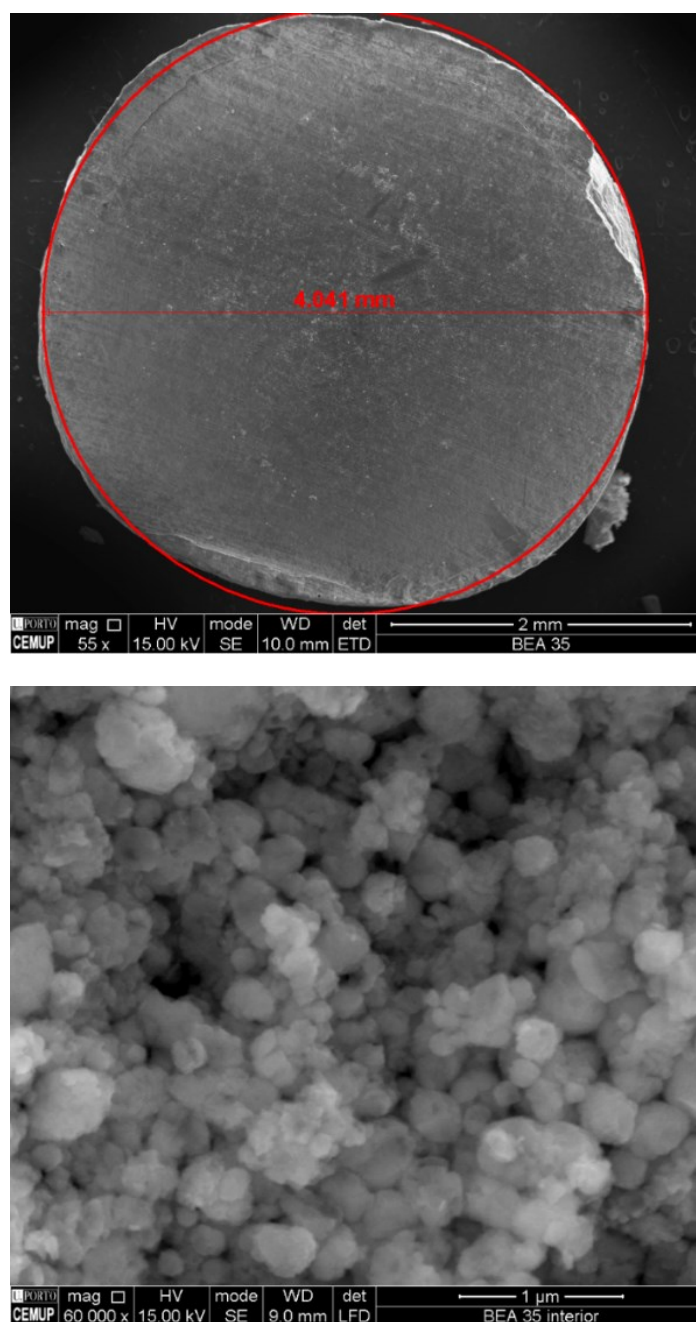


Figure A2 Scanning electron microscopy (SEM) images of BEA35

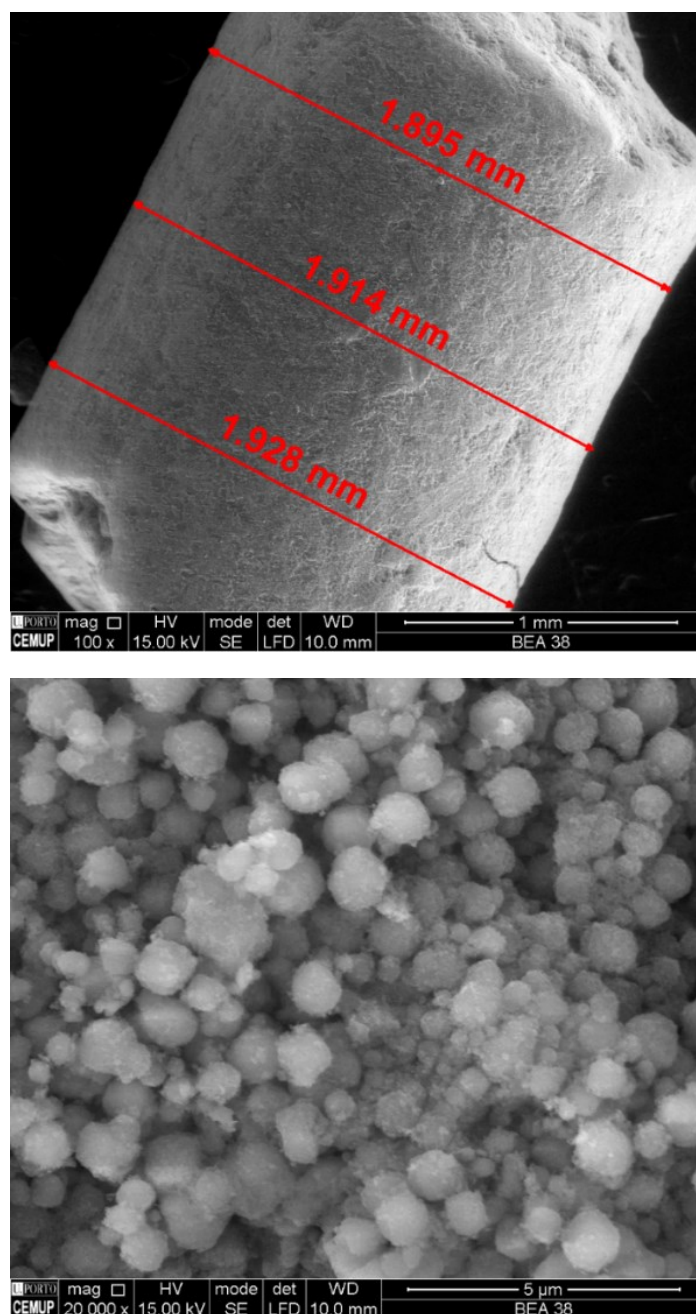


Figure A3 Scanning electron microscopy (SEM) images of BEA38

A.4 Nitrogen adsorption of BEA35 and BEA38

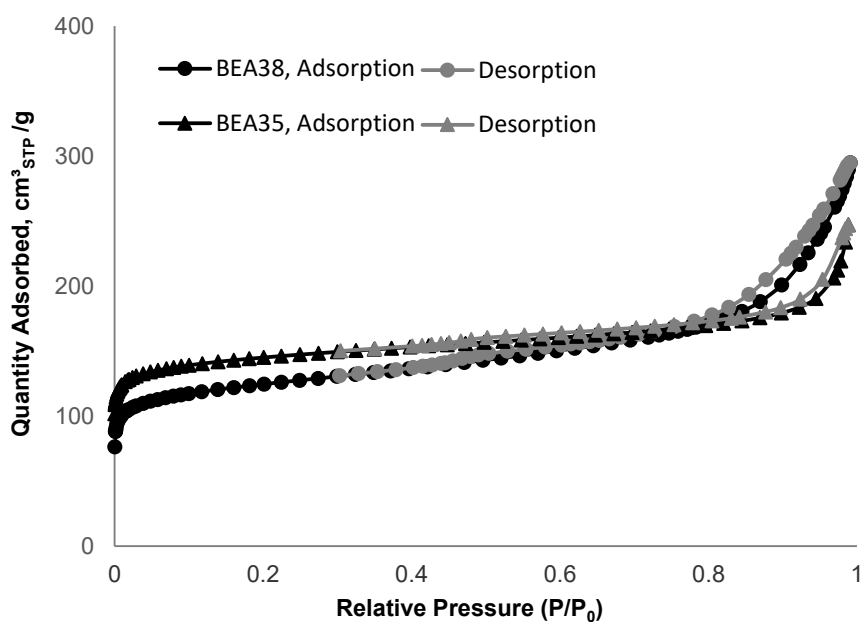


Figure A4 Nitrogen adsorption equilibrium isotherms on BEA35 and BEA38 pellets at 77 K

A.5 NH₃ temperature programmed desorption (TPD) of BEA35 and BEA38

Table A2 Estimated concentration of acid sites of BEA35 and BEA38

	BEA35	BEA38
Total amount of NH ₃ desorbed (mmol/g)	0.91	0.65
Ammonia desorbed from weak adsorption sites (peak 1) (mmol/g)	0.32	0.18
Ammonia desorbed from acid sites (peak h1) (mmol/g)	0.53	0.40
Ammonia desorbed from acid sites (peak h2) (mmol/g)	0.06	0.07

A.6 Deconvolution of NH₃-TPD of BEA35 and BEA38

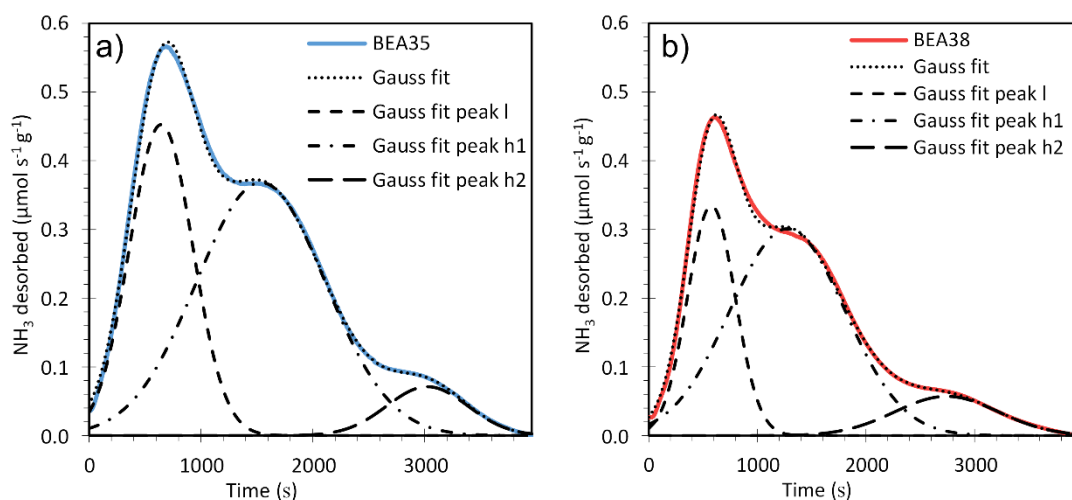


Figure A5 Deconvolution of Ammonia TPD spectra of a) BEA35 and b) BEA38 into three Gaussian peaks

A.7 Carbon dioxide and nitrogen adsorption of the adsorbent

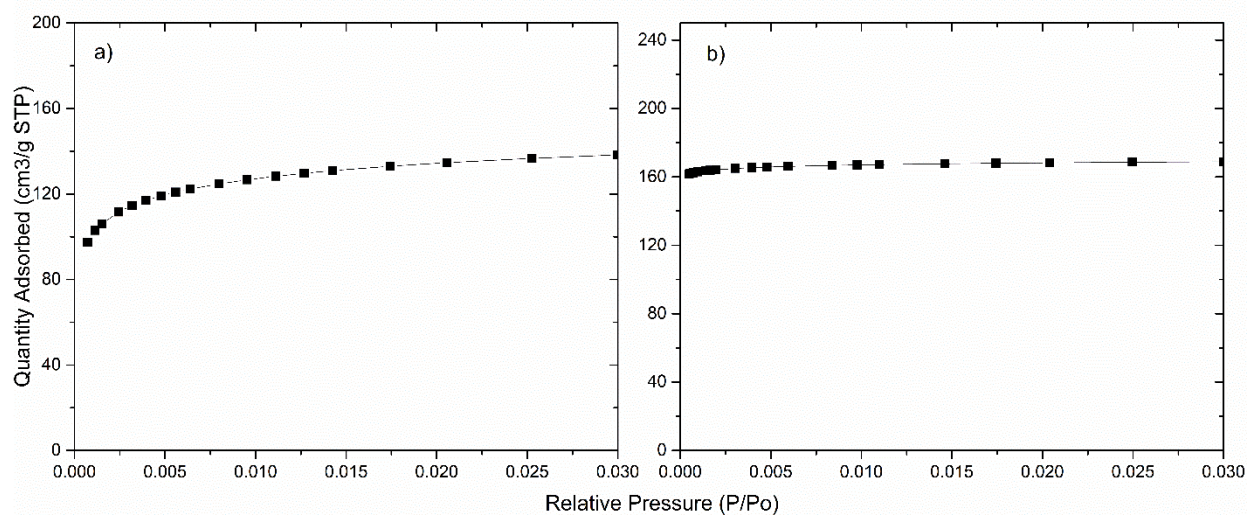


Figure A6 a) CO₂ adsorption at 273 K, b) N₂ adsorption at 77 K of Ba-exchanged zeolite X

A.8 Mercury intrusion of the adsorbent

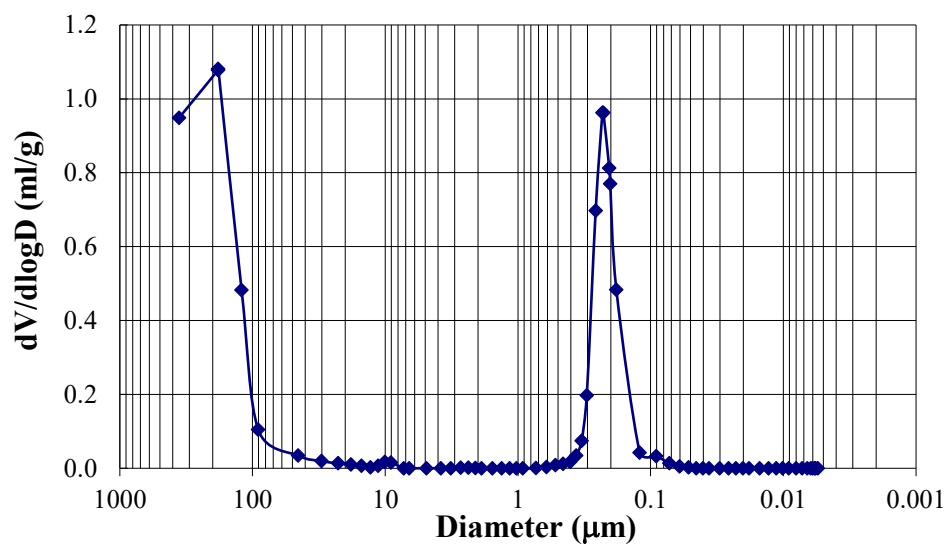
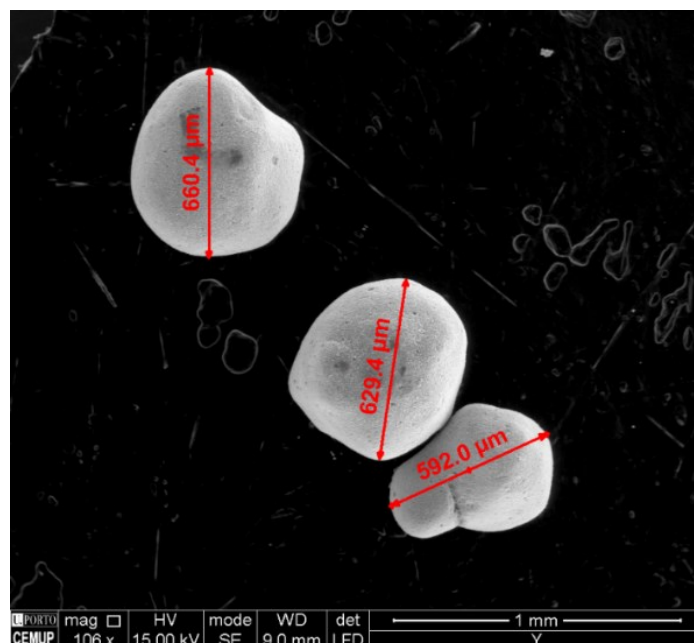


Figure A7 Pore size distributions by mercury intrusion of Ba-exchanged zeolite X

A.9 Scanning Electron Microscopy (SEM) of the adsorbent



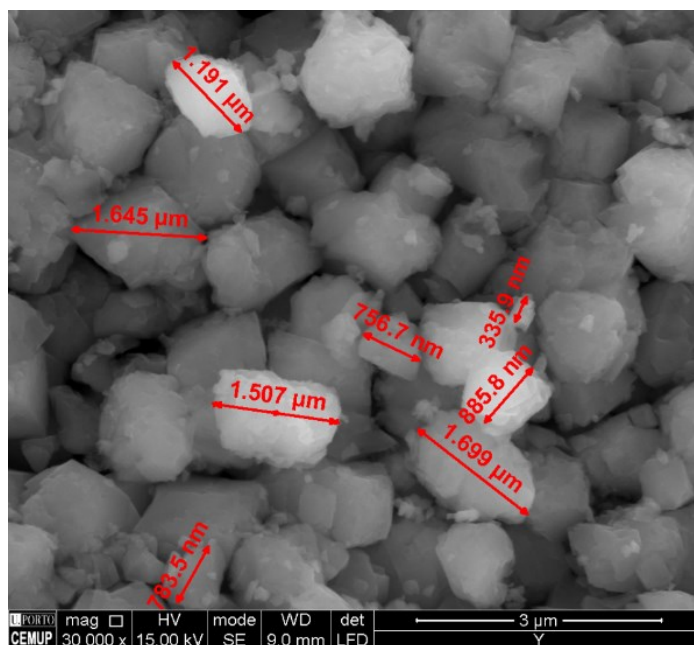


Figure A8 Scanning Electron Microscopy (SEM) images of Ba-exchanged zeolite X

Annex B: Experimental Results and Analysis

B.1 External and internal mass-transfer resistances of xylenes isomerization

Carberry number is the ratio of the rate of reaction to the external diffusion rate. If this criterion is less than 0.15, the external diffusion resistance is low and can be neglected¹:

The Carberry number was calculated through:

$$Ca = \frac{R_{obs}\rho_p(V_p/S_p)}{k_f C_b} \quad (B1)$$

Since the conversion of xylene isomerization is low, R_{obs} can be calculated through:

$$R_{obs} = (C_{in} - C_{out}) Q / (W_c \cdot 60 \cdot 1000) \quad (B2)$$

where ρ_p is the particle density of the catalyst, g/L; C_b is the bulk reactant concentration, mol/L; C_{in} is the concentration of component i in feed, mol/L; C_{out} is the concentration of component i in effluent, mol/L; k_f is the external mass-transfer coefficient estimated by the Wilson and Geankoplis correlation², m/s; V_p is the particle volume, m³; S_p is the particle surface, m². Q is the flow rate, mL/min; W_c is the catalyst mass, g.

The effectiveness factor η is used to compare the actual production rate to the rate in the absence of internal diffusional resistance. The effectiveness factor can be computed through the following equation:

$$\eta\phi^2 = \frac{R_{obs}\rho_p(V_p/S_p)^2}{D_e C_b} \quad (B3)$$

where D_e is the effective diffusion coefficient, m²/s. D_e can be calculated through:

$$D_e = D_m \varepsilon_p / \tau \quad (B4)$$

where D_m is the molecular diffusivity, m²/s; τ is the tortuosity factor. Since the experiments were conducted at low conversions, D_m can be considered as self-diffusion and calculated through:

$$\frac{D_{AA}\mu_A}{KT} = \frac{1}{2\pi} \left(\frac{\tilde{N}_A}{\tilde{V}_A} \right)^{1/3} \quad (\text{B5})$$

where D_{AA} is the self-diffusion coefficient, m^2/s ; μ_A is the viscosity of the pure compound, $\text{kg}/\text{m s}$; K is the Boltzmann constant, $\text{m}^2 \text{kg}/\text{s}^2 \text{K}$; T is the temperature, K ; $\tilde{N}_A$ is the Avogadro number, mol^{-1} ; $\tilde{V}_A$ is the molar volume of the compound, m^3/mol . Since the shape of the catalyst is somewhere between a sphere and a cylinder, the Thiele modulus was determined for both geometries according to eqs (B6) and (B7), respectively.

$$\eta\phi^2 = \phi \left(\frac{1}{\tanh 3\phi} - \frac{1}{3\phi} \right) \quad (\text{B6})$$

$$\eta\phi^2 = \phi \frac{I_1(2\phi)}{I_0(2\phi)} \quad (\text{B7})$$

Table B1 External mass-transfer of xylenes isomerization experiments on BEA38 at 513 K and BEA35 at 493 K

Catalyst	Feed	Flow (mL/min)	R_{obs} (mol/(g s))	Re	D_m (m^2/s)	k_f (m/s)	Ca
BEA38	OX	1.92	5.68×10^{-7}	1	4.59×10^{-9}	2.45×10^{-5}	0.0012
	MX	1.87	7.67×10^{-7}	1	6.10×10^{-9}	2.94×10^{-5}	0.0014
	PX	1.94	8.63×10^{-7}	2	6.46×10^{-9}	3.07×10^{-5}	0.0015
BEA35	OX	4.00	1.53×10^{-6}	3	1.29×10^{-8}	1.29×10^{-6}	0.0028
	MX	4.00	1.57×10^{-6}	4	1.28×10^{-8}	1.28×10^{-6}	0.0025
	PX	4.00	1.59×10^{-6}	6	1.27×10^{-8}	1.27×10^{-6}	0.0021

Table B2 Internal mass-transfer of xylenes isomerization experiments on BEA38 at 513 K and BEA35 at 493 K

Catalyst	Feed	Flow (mL/min)	D_e (m^2/s)	$\eta\phi^2$	Sphere/cylinder	
					ϕ	η
BEA38	OX	1.92	1.34×10^{-9}	7.10×10^{-3}	0.08	1.00
	MX	1.87	1.47×10^{-9}	9.31×10^{-3}	0.10	0.99
	PX	1.94	1.49×10^{-9}	1.06×10^{-2}	0.10	1.00
BEA35	OX	4.00	1.06×10^{-9}	5.71×10^{-2}	0.24	0.97
	MX	4.00	1.06×10^{-9}	5.63×10^{-2}	0.24	0.97
	PX	4.00	1.05×10^{-9}	5.35×10^{-2}	0.23	0.97

B.2 Products distribution of xylenes isomerization on BEA38

Table B3 Products distribution of pure xylene feedstock on BEA38 at 513 K

Run	Feed	Flow (mL/min)	Conversion	Effluent concentration (mol/L)		
				OX	MX	PX
1	OX	1.92	16.9%	6.856	1.258	0.092
2	OX	2.95	8.9%	7.444	0.745	0.039
3	OX	4.83	5.2%	7.821	0.395	0.026
4	OX	7.92	3.2%	7.982	0.240	0.023
5	OX	12.09	2.4%	8.048	0.175	0.023
6	MX	1.87	19.9%	0.664	6.493	0.923
7	MX	2.87	13.8%	0.454	6.982	0.649
8	MX	4.83	7.2%	0.245	7.515	0.334
9	MX	7.79	4.6%	0.159	7.731	0.214
10	MX	11.84	3.5%	0.128	7.817	0.158
11	PX	1.94	21.2%	0.065	1.572	6.360
12	PX	2.91	15.4%	0.040	1.154	6.829
13	PX	4.95	7.9%	0.013	0.604	7.432
14	PX	7.90	4.3%	0.009	0.331	7.721
15	PX	12.09	2.9%	0.008	0.226	7.836

Table B4 Products distribution of pure xylene feedstock on BEA38 at 493 K

Run	Feed	Flow (mL/min)	Conversion	Effluent concentration (mol/L)		
				OX	MX	PX
1	OX	1.68	8.1%	7.579	0.609	0.033
2	OX	1.90	6.9%	7.681	0.511	0.025
3	OX	3.00	3.6%	7.950	0.270	0.024
4	OX	4.90	2.5%	8.041	0.180	0.016
5	OX	8.00	1.2%	8.150	0.083	0.016
6	MX	1.46	11.5%	0.358	7.174	0.553
7	MX	2.16	7.9%	0.256	7.458	0.383
8	MX	3.00	4.7%	0.158	7.718	0.224
9	MX	4.82	2.4%	0.084	7.904	0.112
10	MX	8.07	1.8%	0.062	7.954	0.078
11	PX	1.47	17.9%	0.043	1.329	6.622
12	PX	2.00	12.6%	0.027	0.948	7.056
13	PX	3.00	7.2%	0.011	0.544	7.485
14	PX	5.14	3.4%	0.005	0.253	7.795
15	PX	7.90	2.4%	0.008	0.158	7.880

Table B5 Products distribution of pure xylene feedstock on BEA38 at 473 K

Run	Feed	Flow (mL/min)	Conversion	Effluent concentration (mol/L)		
				OX	MX	PX
1	OX	0.95	6.5%	7.712	0.480	0.024
2	OX	1.53	4.5%	7.882	0.324	0.015
3	OX	1.90	3.2%	7.990	0.226	0.013
4	OX	3.13	1.9%	8.091	0.139	0.010
5	OX	5.17	1.2%	8.154	0.085	0.009
6	MX	0.96	4.8%	0.151	7.710	0.233
7	MX	1.47	4.2%	0.134	7.764	0.194
8	MX	2.00	2.9%	0.093	7.869	0.137
9	MX	3.13	1.8%	0.059	7.955	0.081
10	MX	5.12	1.2%	0.040	8.003	0.049
11	PX	0.88	6.9%	0.014	0.516	7.515
12	PX	1.41	5.9%	0.010	0.445	7.595
13	PX	2.10	4.2%	0.007	0.312	7.732
14	PX	3.06	2.4%	0.008	0.178	7.875
15	PX	5.16	1.2%	0.006	0.092	7.972

B.3 Kinetic parameters of xylenes isomerization on BEA38

Table B6 The kinetic parameters of xylene isomerization on BEA38 with the corresponding 95% confidence limit

	Linear – Equilibrium from Literature	Linear	Triangular - Equilibrium from Literature	Triangular
$E_{a,1}$ (kJ/mol)	91 ± 9	89 ± 9	88 ± 10	89 ± 10
$E_{a,2}$ (kJ/mol)	-	116 ± 24	-	100 ± 20
$E_{a,3}$ (kJ/mol)	90 ± 8	87 ± 14	89 ± 6	106 ± 14
$E_{a,4}$ (kJ/mol)	-	85 ± 6	-	87 ± 6
$E_{a,5}$ (kJ/mol)	-	-	-	60 ± 200
$E_{a,6}$ (kJ/mol)	-	-	65 ± 1200	60 ± 400
$k_{01} \times 10^8$ (m ³ /kg s)	3.5 ± 0.3	3.3 ± 0.2	3.5 ± 0.3	3.3 ± 0.3
$k_{02} \times 10^8$ (m ³ /kg s)	-	1.5 ± 0.3	-	1.7 ± 0.3
$k_{03} \times 10^8$ (m ³ /kg s)	2.35 ± 0.12	2.6 ± 0.3	2.36 ± 0.12	2.3 ± 0.3
$k_{04} \times 10^8$ (m ³ /kg s)	-	5.3 ± 0.2	-	5.1 ± 0.3
$k_{05} \times 10^8$ (m ³ /kg s)	-	-	-	0.1 ± 0.2
$k_{06} \times 10^8$ (m ³ /kg s)	-	-	0.02 ± 0.19	0.07 ± 0.2

Table B7 The kinetic parameters of xylene isomerization on BEA38 at 513 K with the corresponding 95% confidence limit

Parameter	Linear - Equilibrium from Literature	Linear	Triangular - Equilibrium from Literature	Triangular
$k_1 \times 10^8$ (m ³ /kg s)	8.4 ± 0.7	7.9 ± 0.6	8.3 ± 0.8	7.7 ± 0.6
$k_2 \times 10^8$ (m ³ /kg s)	-	4.4 ± 0.6	-	4.3 ± 0.6
$k_3 \times 10^8$ (m ³ /kg s)	5.3 ± 0.4	6.1 ± 0.7	5.2 ± 0.4	6.1 ± 0.6
$k_4 \times 10^8$ (m ³ /kg s)	-	10 ± 2	-	10.00 ± 1.4
$k_5 \times 10^8$ (m ³ /kg s)	-	-	-	0.2 ± 0.6
$k_6 \times 10^8$ (m ³ /kg s)	-	-	0.1 ± 0.6	0.7 ± 0.9
Keq1	0.383 ^a	0.557	0.383 ^a	0.558
Keq2	2.243 ^a	1.639	2.243 ^a	1.639
Keq3	-	-	1.162 ^a	3.500

^a $k_2=k_1 \cdot \text{Keq1}$; $k_4=k_3 \cdot \text{Keq2}$; $k_5=k_6 \cdot \text{Keq3}$. Linear with equilibrium and triangular with equilibrium mean the models combined with the thermodynamic equilibrium equations proposed by Gonçalves and Rodrigues.

Table B8 The kinetic parameters of xylene isomerization on BEA38 at 493 K with the corresponding 95% confidence limit

Parameter	Linear - Equilibrium from Literature	Linear	Triangular - Equilibrium from Literature	Triangular
$k_1 \times 10^8$ (m ³ /kg s)	3.2 ± 0.3	3.1 ± 0.3	3.2 ± 0.3	3 ± 0.4
$k_2 \times 10^8$ (m ³ /kg s)	-	1.7 ± 0.3	-	1.7 ± 0.3
$k_3 \times 10^8$ (m ³ /kg s)	2.79 ± 0.15	2.6 ± 0.4	2.79 ± 0.14	2.6 ± 0.3
$k_4 \times 10^8$ (m ³ /kg s)	-	6.4 ± 0.3	-	6.3 ± 0.4
$k_5 \times 10^8$ (m ³ /kg s)	-	-	-	0.18 ± 0.3
$k_6 \times 10^8$ (m ³ /kg s)	-	-	0.10 ± 0.22	0.18 ± 0.3
Keq1	0.377 ^a	0.548	0.377 ^a	0.567
Keq2	2.268 ^a	2.461	2.268 ^a	2.423
Keq3	-	-	1.169 ^a	1.000

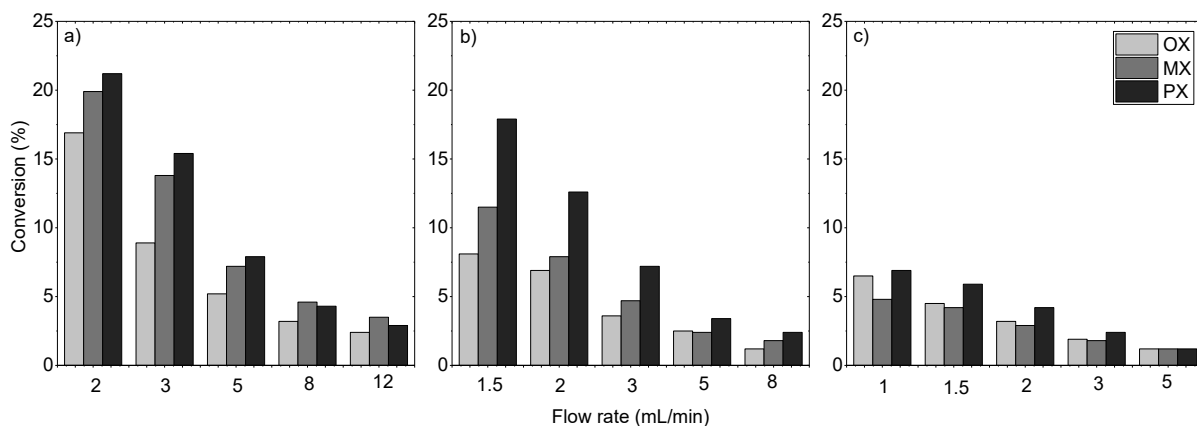
^a $k_2=k_1 \cdot \text{Keq1}$; $k_4=k_3 \cdot \text{Keq2}$; $k_5=k_6 \cdot \text{Keq3}$. Linear with equilibrium and triangular with equilibrium mean the models combined the thermodynamic equilibrium equations proposed by Gonçalves and Rodrigues.

Table B9 The kinetic parameters of xylene isomerization on BEA38 at 473 K with the corresponding 95% confidence limit

Parameter	Linear - Equilibrium from Literature	Linear	Triangular - Equilibrium from Literature	Triangular
$k_1 \times 10^8$ (m ³ /kg s)	1.80 ± 0.40	1.57 ± 0.38	1.4 ± 0.3	1.40 ± 0.13
$k_2 \times 10^8$ (m ³ /kg s)	-	0.5 ± 0.4	-	0.48 ± 0.14
$k_3 \times 10^8$ (m ³ /kg s)	0.72 ± 0.15	0.8 ± 0.4	0.7 ± 0.1	0.81 ± 0.14
$k_4 \times 10^8$ (m ³ /kg s)	-	1.61 ± 0.37	-	1.68 ± 0.13
$k_5 \times 10^8$ (m ³ /kg s)	-	-	-	0.05 ± 0.14
$k_6 \times 10^8$ (m ³ /kg s)	-	-	0.10 ± 0.2	0.6 ± 0.13
Keq1	0.370 ^a	0.318	0.370 ^a	0.343
Keq2	2.296 ^a	2.012	2.296 ^a	2.074
Keq3	-	-	1.177 ^a	12.00

^a $k_2=k_1 \cdot \text{Keq1}$; $k_4=k_3 \cdot \text{Keq2}$; $k_5=k_6 \cdot \text{Keq3}$. Linear with equilibrium and triangular with equilibrium mean the models combined the thermodynamic equilibrium equations proposed by Gonçalves and Rodrigues.

B.4 Conversion of xylene isomers on BEA38

**Figure B1** Comparison of the conversions of pure xylenes over BEA38 at different flow rates at a) 513 K, b) 493 K, and c) 473 K

B.5 Products distribution of xylenes isomerization on BEA35

Table B10 Products distribution of pure xylene feedstock on BEA35 at 493 K

Run	Feed	Flow (mL/min)	Conversion	Concentration (mol/L)		
				OX	MX	PX
1	OX	4.00	19.66%	6.628	1.432	0.142
2	OX	5.05	15.99%	6.931	1.181	0.106
3	OX	8.06	10.11%	7.416	0.767	0.058
4	OX	12.30	6.94%	7.678	0.539	0.038
5	OX	16.30	5.43%	7.802	0.423	0.032
6	MX	4.00	18.76%	0.607	6.582	0.868
7	MX	5.05	14.08%	0.456	6.961	0.649
8	MX	8.06	7.31%	0.235	7.509	0.331
9	MX	12.30	3.84%	0.125	7.791	0.167
10	MX	16.30	2.13%	0.069	7.929	0.086
11	PX	4.00	19.89%	0.068	1.494	6.465
12	PX	5.05	16.23%	0.049	1.234	6.760
13	PX	8.06	10.28%	0.028	0.803	7.241
14	PX	12.30	7.35%	0.021	0.581	7.477
15	PX	16.30	6.11%	0.021	0.486	7.577

Table B11 Products distribution of pure xylene feedstock on BEA35 at 473 K

Run	Feed	Flow (mL/min)	Conversion	Concentration (mol/L)		
				OX	MX	PX
1	OX	1.50	27.01%	6.022	1.903	0.220
2	OX	2.00	20.34%	6.572	1.468	0.139
3	OX	3.00	11.17%	7.328	0.841	0.055
4	OX	5.00	4.79%	7.855	0.379	0.020
5	OX	8.00	1.89%	8.094	0.144	0.010
6	MX	1.50	18.10%	0.569	6.635	0.844
7	MX	2.00	13.95%	0.444	6.972	0.644
8	MX	3.00	8.48%	0.270	7.415	0.389
9	MX	5.00	4.00%	0.134	7.778	0.183
10	MX	8.00	2.03%	0.070	7.938	0.089
11	PX	1.50	28.51%	0.184	1.898	5.769
12	PX	2.00	25.07%	0.105	1.765	6.047
13	PX	3.00	14.84%	0.035	1.085	6.872
14	PX	5.00	5.04%	0.009	0.380	7.663
15	PX	8.00	1.47%	0.006	0.127	7.951

Table B12 Products distribution of pure xylene feedstock on BEA35 at 453 K

Run	Feed	Flow (mL/min)	Conversion	Concentration (mol/L)		
				OX	MX	PX
1	OX	1.00	11.40%	7.310	0.850	0.052
2	OX	1.50	7.28%	7.650	0.562	0.030
3	OX	2.00	4.93%	7.843	0.384	0.021
4	OX	3.00	2.74%	8.024	0.219	0.014
5	OX	5.00	1.34%	8.139	0.110	0.011
6	MX	1.00	8.86%	0.285	7.384	0.418
7	MX	1.50	5.53%	0.177	7.654	0.257
8	MX	2.00	3.62%	0.117	7.809	0.159
9	MX	3.00	2.85%	0.094	7.871	0.118
10	MX	5.00	1.05%	0.031	8.017	0.033
11	PX	1.00	16.82%	0.054	1.225	6.713
12	PX	1.50	10.82%	0.018	0.831	7.197
13	PX	2.00	5.95%	0.008	0.475	7.590
14	PX	3.00	2.66%	0.003	0.222	7.855
15	PX	5.00	0.96%	0.000	0.095	7.992

B.6 Kinetic parameters of xylenes isomerization on BEA35

Table B13 The kinetic parameters of xylenes isomerization on BEA35 with the corresponding 95% confidence limit

	Linear – Equilibrium from Literature	Linear	Triangular - Equilibrium from Literature	Triangular
$E_{a,1}$ (kJ/mol)	91 ± 7	90 ± 7	93 ± 8	91 ± 9
$E_{a,2}$ (kJ/mol)	-	100 ± 25	-	96 ± 26
$E_{a,3}$ (kJ/mol)	84 ± 6	99 ± 18	83 ± 7	100 ± 18
$E_{a,4}$ (kJ/mol)	-	80 ± 6	-	80 ± 8
$E_{a,5}$ (kJ/mol)	-	-	-	95 ± 124
$E_{a,6}$ (kJ/mol)	-	-	68 ± 90	72 ± 145
$k_{01} \times 10^8$ (m ³ /kg s)	8.7 ± 0.5	8.8 ± 0.5	8.3 ± 0.6	8.4 ± 0.6
$k_{02} \times 10^8$ (m ³ /kg s)	-	2.9 ± 0.6	-	2.8 ± 0.6
$k_{03} \times 10^8$ (m ³ /kg s)	4.4 ± 0.2	4.1 ± 0.6	4.4 ± 0.2	4.2 ± 0.6
$k_{04} \times 10^8$ (m ³ /kg s)	-	10.4 ± 0.5	-	10.1 ± 0.6
$k_{05} \times 10^8$ (m ³ /kg s)	-	-	-	0.6 ± 0.6
$k_{06} \times 10^8$ (m ³ /kg s)	-	-	0.5 ± 0.4	0.5 ± 0.6

Table B14 The kinetic parameters of xylene isomerization on BEA35 at 493 K with the corresponding 95% confidence limit

Parameter	Linear - Equilibrium from Literature	Linear	Triangular - Equilibrium from Literature	Triangular
$k_1 \times 10^8$ (m ³ /kg s)	20.8 ± 1.3	20.7 ± 1.3	20.6 ± 1.4	20.1 ± 1.5
$k_2 \times 10^8$ (m ³ /kg s)	-	7.8 ± 1.4	-	7.8 ± 1.5
$k_3 \times 10^8$ (m ³ /kg s)	9.9 ± 0.6	11.1 ± 1.5	9.7 ± 0.6	11.0 ± 1.5
$k_4 \times 10^8$ (m ³ /kg s)	-	21.9 ± 1.4	-	21.7 ± 1.6
$k_5 \times 10^8$ (m ³ /kg s)	-	-	-	1.1 ± 1.5
$k_6 \times 10^8$ (m ³ /kg s)	-	-	0.5 ± 0.9	0.3 ± 1.5
Keq1	0.377 ^a	0.377	0.377 ^a	0.388
Keq2	2.268 ^a	1.973	2.268 ^a	1.973
Keq3	-	-	1.169 ^a	0.273

^a $k_2=k_1 \cdot \text{Keq1}$; $k_4=k_3 \cdot \text{Keq2}$; $k_5=k_6 \cdot \text{Keq3}$. Linear with equilibrium and triangular with equilibrium mean the models combined with the thermodynamic equilibrium equations proposed by Gonçalves and Rodrigues.

Table B15 The kinetic parameters of xylene isomerization on BEA35 at 473 K with the corresponding 95% confidence limit

Parameter	Linear - Equilibrium from Literature	Linear	Triangular - Equilibrium from Literature	Triangular
$k_1 \times 10^8$ (m ³ /kg s)	9.7 ± 0.9	10.0 ± 0.8	9.1 ± 1.0	9.5 ± 1.0
$k_2 \times 10^8$ (m ³ /kg s)	-	3.0 ± 0.9	-	3.0 ± 1.0
$k_3 \times 10^8$ (m ³ /kg s)	4.9 ± 0.4	4.5 ± 0.9	4.7 ± 0.4	4.4 ± 1.0
$k_4 \times 10^8$ (m ³ /kg s)	-	11.5 ± 0.9	-	11.2 ± 1.1
$k_5 \times 10^8$ (m ³ /kg s)	-	-	-	0.7 ± 1.0
$k_6 \times 10^8$ (m ³ /kg s)	-	-	0.8 ± 0.7	0.8 ± 1.0
Keq1	0.370 ^a	0.300	0.370 ^a	0.316
Keq2	2.296 ^a	2.556	2.296 ^a	2.545
Keq3	-	-	1.176 ^a	1.143

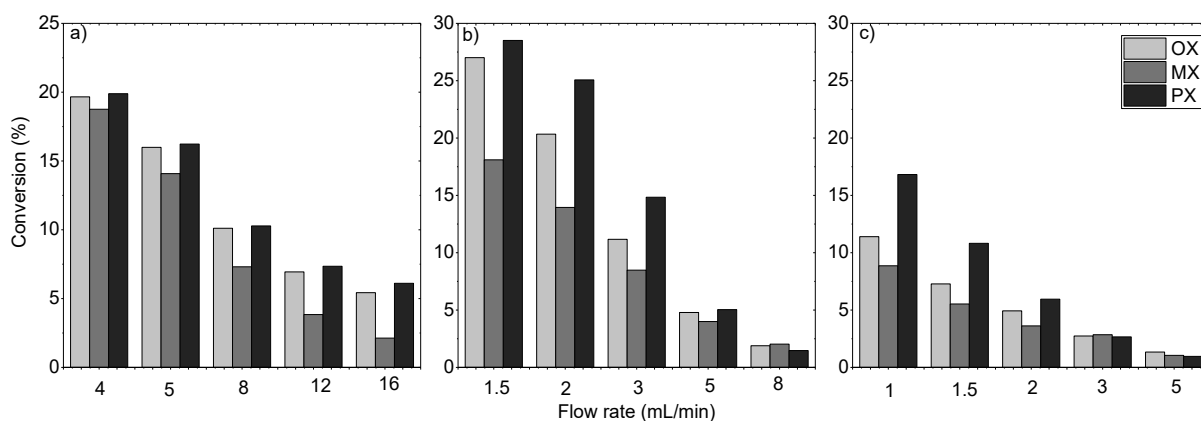
^a $k_2=k_1 \cdot \text{Keq1}$; $k_4=k_3 \cdot \text{Keq2}$; $k_5=k_6 \cdot \text{Keq3}$. Linear with equilibrium and triangular with equilibrium mean the models combined with the thermodynamic equilibrium equations proposed by Gonçalves and Rodrigues.

Table B16 The kinetic parameters of xylene isomerization on BEA35 at 453 K with the corresponding 95% confidence limit

Parameter	Linear - Equilibrium from Literature	Linear	Triangular - Equilibrium from Literature	Triangular
$k_1 \times 10^8$ (m ³ /kg s)	2.6 ± 0.3	2.6 ± 0.3	2.4 ± 0.3	2.6 ± 0.3
$k_2 \times 10^8$ (m ³ /kg s)	-	0.9 ± 0.3	-	0.9 ± 0.3
$k_3 \times 10^8$ (m ³ /kg s)	1.59 ± 0.13	1.25 ± 0.31	1.52 ± 0.12	1.23 ± 0.30
$k_4 \times 10^8$ (m ³ /kg s)	-	3.7 ± 0.3	-	3.7 ± 0.3
$k_5 \times 10^8$ (m ³ /kg s)	-	-	-	0.10 ± 0.30
$k_6 \times 10^8$ (m ³ /kg s)	-	-	0.2 ± 0.2	0.11 ± 0.31
Keq1 ^b	0.363 ^a	0.346	0.363 ^a	0.346
Keq2 ^b	2.325 ^a	2.960	2.325 ^a	3.008
Keq3 ^b	-	-	1.184 ^a	1.100

^a $k_2=k_1 \cdot \text{Keq1}$; $k_4=k_3 \cdot \text{Keq2}$; $k_5=k_6 \cdot \text{Keq3}$. Linear with equilibrium and triangular with equilibrium mean the models combined with the thermodynamic equilibrium equations proposed by Gonçalves and Rodrigues.

B.7 Conversion of xylene isomers on BEA35

**Figure B2** Comparison of the conversions of pure xylenes over BEA35 at different flow rates and temperature a) 493 K, b) 473 K, c) 453 K

B.8 External and internal mass-transfer resistances of EB disproportionation on BEA35

Table B17 External mass-transfer results of EB disproportionation on BEA35 at 493 K

Flow rate mL/min	R_{obs} (mol/g s)	Re	D_m (m ² /s)	k_f (m/s)	Ca
16.00	1.33×10^{-6}	12	1.33×10^{-8}	7.05×10^{-5}	0.0013
12.00	1.22×10^{-6}	9	1.33×10^{-8}	6.42×10^{-5}	0.0013
10.00	1.87×10^{-6}	7	1.33×10^{-8}	6.05×10^{-5}	0.0022
8.00	2.19×10^{-6}	6	1.34×10^{-8}	5.63×10^{-5}	0.0029
5.00	1.75×10^{-6}	4	1.34×10^{-8}	4.83×10^{-5}	0.0029

Table B18 Internal mass-transfer results of EB disproportionation on BEA35 at 493 K

Flow rate mL/min	D_e (m ² /s)	$\eta\phi^2$	Sphere	
			ϕ	η
16.00	1.09×10^{-9}	4.08×10^{-2}	0.20	0.98
12.00	1.09×10^{-9}	3.78×10^{-2}	0.20	0.98
10.00	1.10×10^{-9}	6.05×10^{-2}	0.25	0.96
8.00	1.10×10^{-9}	7.45×10^{-2}	0.28	0.96
5.00	1.10×10^{-9}	6.24×10^{-2}	0.25	0.96

B.9 Products distribution of EB disproportionation on BEA35

Table B19 Products distribution of EB disproportionation reaction at several temperatures

Temp. (K)	Flow rate (mL/min)	Conversion (%)	Products (mol/L)					PDEB /DEB	Bz/DEB
			Bz	EB	PDEB	MDEB	ODEB		
453	1.50	13.18	0.544	7.084	0.197	0.252	0.018	0.421	1.163
	2.00	11.40	0.464	7.229	0.268	0.252	0.016	0.500	0.865
	3.00	10.24	0.423	7.325	0.224	0.181	0.011	0.539	1.016
	5.00	4.91	0.208	7.760	0.127	0.070	0.000	0.645	1.055
	8.00	0.65	0.032	8.107	0.018	0.006	0.000	0.736	1.291
473	3.00	14.70	0.595	6.960	0.224	0.347	0.033	0.371	0.984
	5.00	8.01	0.331	7.506	0.139	0.173	0.014	0.426	1.017
	8.00	4.71	0.193	7.776	0.094	0.094	0.006	0.485	1.002
	12.00	3.05	0.128	7.911	0.070	0.054	0.000	0.566	1.035
	16.00	1.89	0.079	8.006	0.049	0.028	0.000	0.637	1.011
493	5.00	18.18	0.744	6.676	0.303	0.408	0.032	0.408	1.002
	8.00	14.20	0.586	7.001	0.243	0.310	0.024	0.421	1.014
	10.00	9.68	0.395	7.370	0.166	0.210	0.017	0.422	1.005
	12.00	5.28	0.217	7.730	0.092	0.114	0.010	0.427	1.006
	16.00	4.31	0.179	7.809	0.076	0.092	0.008	0.430	1.018

B.10 Results analysis of EB-TOL (equal mass ratio) transalkylation

Table B20 Product distribution for equal mass ratio EB-TOL transalkylation reaction

Temperature (K)	Feed (mol/L)		Flow rate (mL/min)	Products (mol/L)				
	EB	TOL		EB	Bz	TOL	DEB	EMB
493	4.086	4.715	3.00	3.288	0.554	4.409	0.247	0.307
			5.05	3.522	0.393	4.500	0.164	0.221
			8.06	3.705	0.260	4.581	0.112	0.142
			12.3	3.846	0.160	4.463	0.070	0.084
			16.3	3.995	0.067	4.680	0.031	0.030
473	4.099	4.700	1.50	3.193	0.649	4.320	0.249	0.392
			1.97	3.311	0.557	4.387	0.221	0.328
			3.03	3.565	0.364	4.505	0.160	0.203
			5.00	3.833	0.175	4.615	0.083	0.091
			8.09	3.985	0.075	4.663	0.035	0.034
453	4.102	4.696	1.01	3.359	0.515	4.417	0.217	0.294
			1.61	3.609	0.330	4.532	0.152	0.177
			2.06	3.763	0.225	4.589	0.109	0.114
			2.98	3.917	0.120	4.648	0.059	0.058
			5.05	4.013	0.057	4.676	0.028	0.026

^aEMB, Ethylmethylbenzene; DEB, Diethylbenzene.

Table B21 Proportion of EB and TOL involved in each reaction in equal mass ratio EB-TOL transalkylation reaction experiments

Temp. (K)	Feed (mol/L)		Flow rate (mL/min)	EB	EB in	EB in	TOL
	EB	TOL		Conversion (%)	disproportionation (%)	transalkylation (%)	conversion (%)
493	4.086	4.715	3.00	19.53	57.00	43.00	6.49
			5.05	13.80	59.75	40.25	4.57
			8.06	9.31	61.31	38.69	2.85
			12.3	5.87	62.63	37.37	1.71
			16.3	2.22	67.34	32.66	0.75
473	4.099	4.700	1.50	22.10	55.99	44.01	8.07
			1.97	19.22	57.45	42.55	6.66
			3.03	13.03	61.22	38.78	4.15
			5.00	6.49	64.66	35.34	1.81
			8.09	2.79	67.34	32.66	0.77
453	4.102	4.696	1.01	18.07	59.61	40.39	6.00
			1.61	11.95	63.23	36.77	3.56
			2.06	8.21	65.63	34.37	2.35
			2.98	4.46	67.12	32.88	1.10
			5.05	2.10	68.61	31.39	0.51

B.11 Results analysis of EB-TOL (various mass ratio) transalkylation

Table B22 Products distribution for various mass ratio feed mixtures in the EB-TOL transalkylation reaction at 493 K

Feed (mol/L)		Flow rate (mL/min)	Products (mol/L)				
EB	TOL		EB	Bz	TOL	DEB	EMB
2.506	6.543	3.06	2.155	0.279	6.348	0.069	0.202
		5.12	2.275	0.182	6.422	0.045	0.129
		8.07	2.346	0.125	6.460	0.031	0.089
		12.14	2.396	0.089	6.479	0.022	0.064
		16.30	2.430	0.062	6.505	0.017	0.037
3.253	5.678	3.00	2.693	0.408	5.447	0.127	0.266
		5.05	2.884	0.282	5.494	0.098	0.176
		8.06	3.027	0.178	5.555	0.060	0.112
		12.3	3.098	0.119	5.593	0.042	0.079
		16.3	3.146	0.083	5.622	0.030	0.051
5.692	2.857	3.11	4.288	0.890	2.502	0.512	0.364
		5.16	4.832	0.528	2.668	0.327	0.197
		8.09	5.160	0.319	2.753	0.208	0.111
		12.00	5.340	0.209	2.792	0.136	0.070
		16.13	5.450	0.141	2.818	0.092	0.044

^aEMB,Ethylmethylbenzene;DEB,Diethylbenzne.

Table B23 Proportion of EB and TOL involved in each reaction in various mass ratio EB-TOL mixtures at 493 K

Feed (mol/L)		Flow rate (mL/min)	EB	EB in	EB in	TOL
EB	TOL		Conversion (%)	disproportionation (%)	transalkylation (%)	conversion (%)
2.506	6.543	3.06	13.97	40.50	59.50	2.99
		5.12	9.22	41.12	58.88	1.85
		8.07	6.39	41.14	58.86	1.27
		12.14	4.37	40.58	59.42	0.98
		16.30	3.03	47.86	52.14	0.59
3.253	5.678	3.00	17.20	48.90	51.10	4.07
		5.05	11.36	52.79	47.21	3.24
		8.06	6.96	51.86	48.14	2.16
		12.30	4.77	51.21	48.79	1.50
		16.30	3.29	53.92	46.08	0.99
5.692	2.857	3.11	24.66	73.80	26.20	12.42
		5.16	15.11	76.79	23.21	6.61
		8.09	9.35	78.89	21.11	3.66
		12.00	6.19	79.45	20.55	2.29
		16.13	4.24	80.73	19.27	1.38

B.12 Kinetic constants and activation energies of EB disproportionation

Table B24 Estimated parameters for the EB disproportionation reaction, second order, considering only the results from pure ethylbenzene experiments and considering all the experiments including EB-TOL mixtures at 95% confidence limit

Experiment data	Pure EB	Pure EB and EB-TOL mixture
Temperature	$k_1 \times 10^{12}$ (m ⁶ /kg s mol)	$k_1 \times 10^{12}$ (m ⁶ /kg s mol)
493 K	15.5 ± 1.6	15.2 ± 0.6
473 K	6.8 ± 0.5	6.8 ± 0.3
453 K	3.6 ± 0.4	3.6 ± 0.2
$E_{a,1}$ (kJ/mol)	68 ± 7	66 ± 3
$k_{0,1} \times 10^{12}$ (m ⁶ /kg s mol)	7.4 ± 0.5	7.2 ± 0.2

Table B25 Kinetic constants considering EB disproportionation as first- and second-order reaction and EB-TOL transalkylation as second order calculated at 493 K with estimated activation energy and kinetic constant at centered temperature

Reaction	EB disproportionation as first order	EB disproportionation as second order
EB disproportionation	8.45×10^{-8} (m ³ /kg s)	1.42×10^{-12} (m ⁶ / kg s mol)
EB-TOL transalkylation	8.29×10^{-12} (m ⁶ / kg s mol)	1.31×10^{-12} (m ⁶ / kg s mol)

B.13 Analytical solution for EB disproportionation and EB-TOL transalkylation

On the basis that both reactions are second order

Dividing the mass balances for EB and TOL gives:

$$\frac{dC_{EB}}{dC_{TOL}} = \frac{k_1}{k_2} \frac{C_{EB}}{C_{TOL}} + 1 \quad (\text{B8})$$

This is a first order linear differential equation, the solution is given by:

$$C_{EB} = \frac{C_{TOL}}{1 - k_1/k_2} + A \cdot C_{TOL}^{k_1/k_2} \quad (\text{B9})$$

where A is the integration constant and $k_1 \neq k_2$. A is obtained evaluating the function at feed conditions ($C_{F,EB}$ and $C_{F,TOL}$), giving:

$$A = \frac{1}{C_{F,TOL}^{k_1/k_2}} \left(C_{F,EB} - \frac{C_{F,TOL}}{1-k_1/k_2} \right) \quad (B10)$$

Substituting A and rearranging:

$$\frac{C_{EB}}{C_{TOL}} = \frac{1}{1-k_1/k_2} + \frac{C_{TOL}^{k_1/k_2-1}}{C_{F,TOL}^{k_1/k_2}} \left(C_{F,EB} - \frac{C_{F,TOL}}{1-k_1/k_2} \right) \quad (B11)$$

Diving the mass balances for DEB and EMB gives:

$$\frac{dC_{DEB}}{dC_{EMB}} = \frac{k_1}{k_2} \frac{C_{EB}}{C_{TOL}} \quad (B12)$$

Substituting the result from the previous mass balance and taking into account that $C_{TOL} = C_{F,TOL} - C_{EMB}$, the mass balance gives:

$$\frac{dC_{DEB}}{dC_{EMB}} = \frac{k_1}{k_2} \left(\frac{1}{1-k_1/k_2} + \frac{(C_{F,TOL}-C_{EMB})^{k_1/k_2-1}}{C_{F,TOL}^{k_1/k_2}} \left(C_{F,EB} - \frac{C_{F,TOL}}{1-k_1/k_2} \right) \right) \quad (B13)$$

The differential equation can be solved by the separation of variables method, after rearranging gives:

$$\frac{C_{DEB}}{C_{EMB}} = \frac{k_1/k_2}{1-k_1/k_2} - \frac{1}{C_{F,TOL}^{k_1/k_2-1}} \left(\frac{C_{F,EB}}{C_{F,TOL}} - \frac{1}{1-k_1/k_2} \right) \left[\frac{(C_{F,TOL}-C_{EMB})^{k_1/k_2} - C_{F,TOL}^{k_1/k_2}}{C_{EMB}} \right] \quad (B14)$$

On the basis that EB disproportionation is first order

Diving the mass balances for EB and TOL gives:

$$\frac{dC_{EB}}{dC_{TOL}} = \frac{k_1}{k_2} \frac{1}{C_{TOL}} + 1 \quad (B15)$$

Solving through separation of variables:

$$\frac{C_{EB}}{C_{TOL}} = \frac{k_1}{k_2} \frac{1}{C_{TOL}} \ln \left(\frac{C_{TOL}}{C_{F,TOL}} \right) + \left(1 - \frac{C_{F,TOL}}{C_{TOL}} \right) + \frac{C_{F,EB}}{C_{TOL}} \quad (B16)$$

Diving the mass balances for DEB and EMB gives:

$$\frac{dC_{DEB}}{dC_{EMB}} = \frac{k_1}{k_2} \frac{1}{C_{TOL}} \quad (B17)$$

Taking into account that $C_{TOL} = C_{F,TOL} - C_{EMB}$ and solving through the separation of variables method gives:

$$\frac{C_{DEB}}{C_{EMB}} = -\frac{k_1}{k_2} \frac{1}{C_{EMB}} \ln \left(\frac{C_{F,TOL} - C_{EMB}}{C_{F,TOL}} \right) \quad (B18)$$

B.14 Predicted and experimental data comparison at 493 K for EB-TOL transalkylation

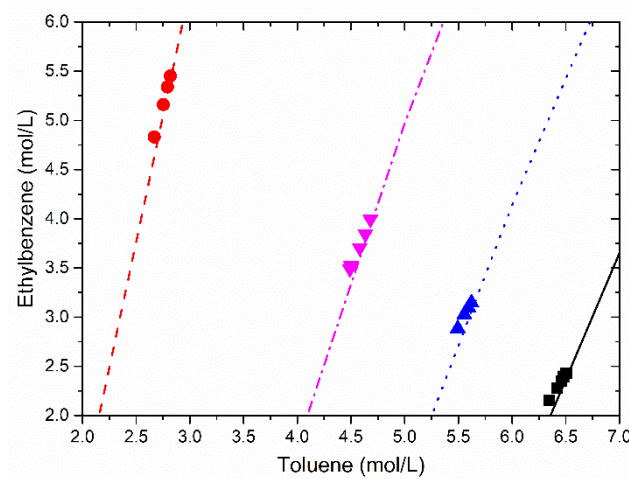


Figure B3 Reactants comparison of simulation (lines) and experimental (markers) values of EB and TOL at 493 K based on EB disproportionation as first order reaction
(■30%EB+70%TOL, ▲40%EB+60%TOL, ▼50%EB+50%TOL, ●70%EB+30%TOL)

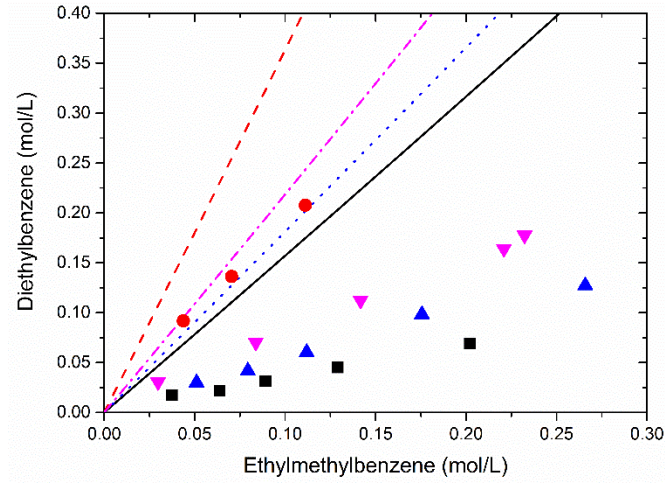


Figure B4 Products comparison of simulation (lines) and experimental (markers) values of DEB and EMB at 493 K based on EB disproportionation as first order reaction (■30%EB+70%TOL, ▲40%EB+60%TOL, ▼50%EB+50%TOL, ●70%EB+30%TOL)

B.15 Surface excess from Everett equation

Equation from Everett² for binary systems based on the surface excess:

$$\frac{x_1 x_2}{M_t \Delta x_1} = \frac{1}{M_s} \left(x_1 + \frac{1}{\alpha - 1} \right) \quad (\text{B19})$$

where x_1 and x_2 are the mole fractions of each species (i.e., the aromatic compound and *i*-octane respectively) in equilibrium with the adsorbent; M_t is the initial total mole by mass of adsorbent, mol/kg; Δx_1 is the variation of the aromatic compound; M_s is the adsorption capacity of the aromatic compound, mol/kg; and α is the selectivity of the aromatic compound over *i*-octane.

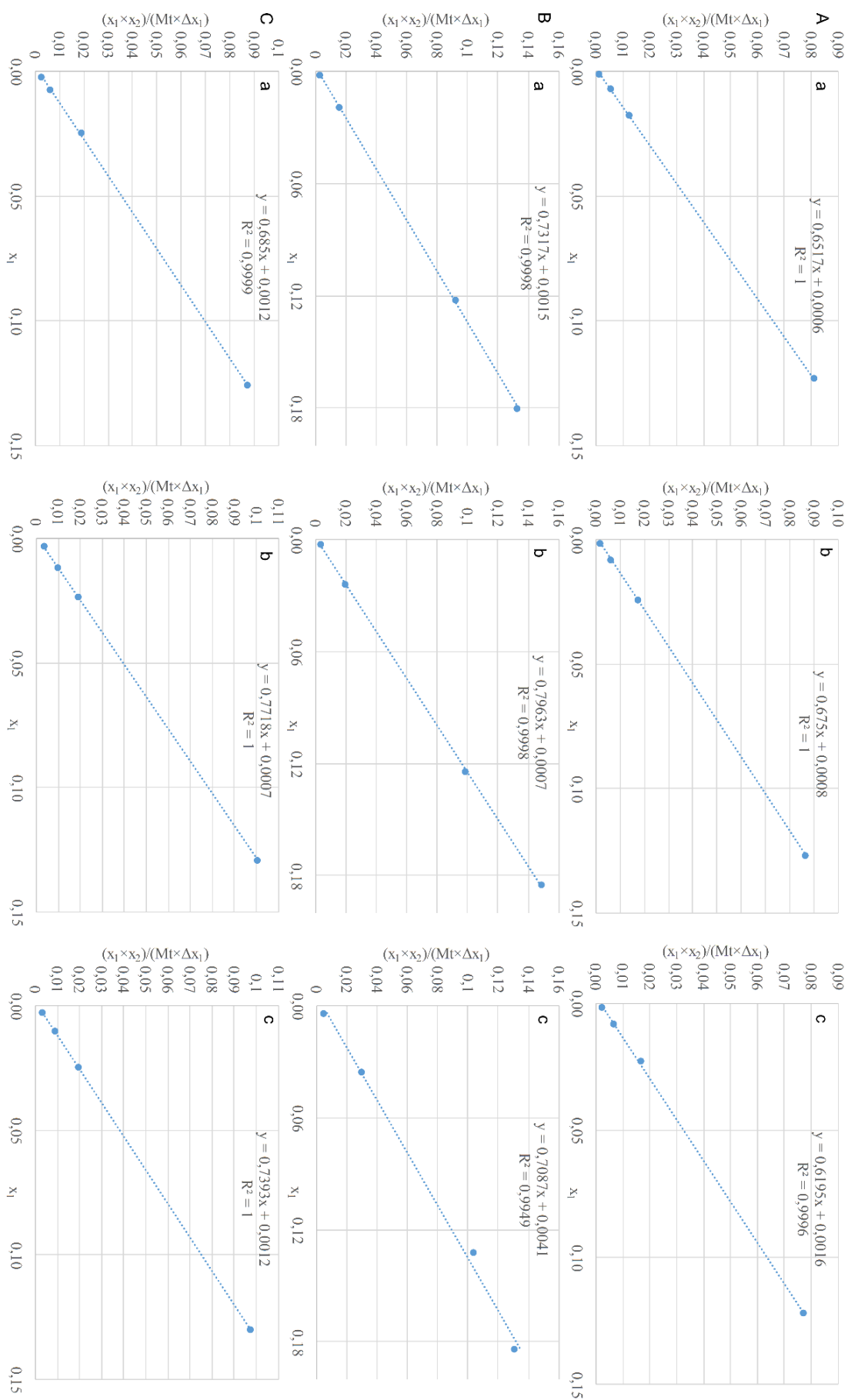


Figure B5 Surface excess plot for A) *p*-xylene, B) *m*-xylene, C) *o*-xylene at a) 450 K, b) 483 K, and c) 513 K

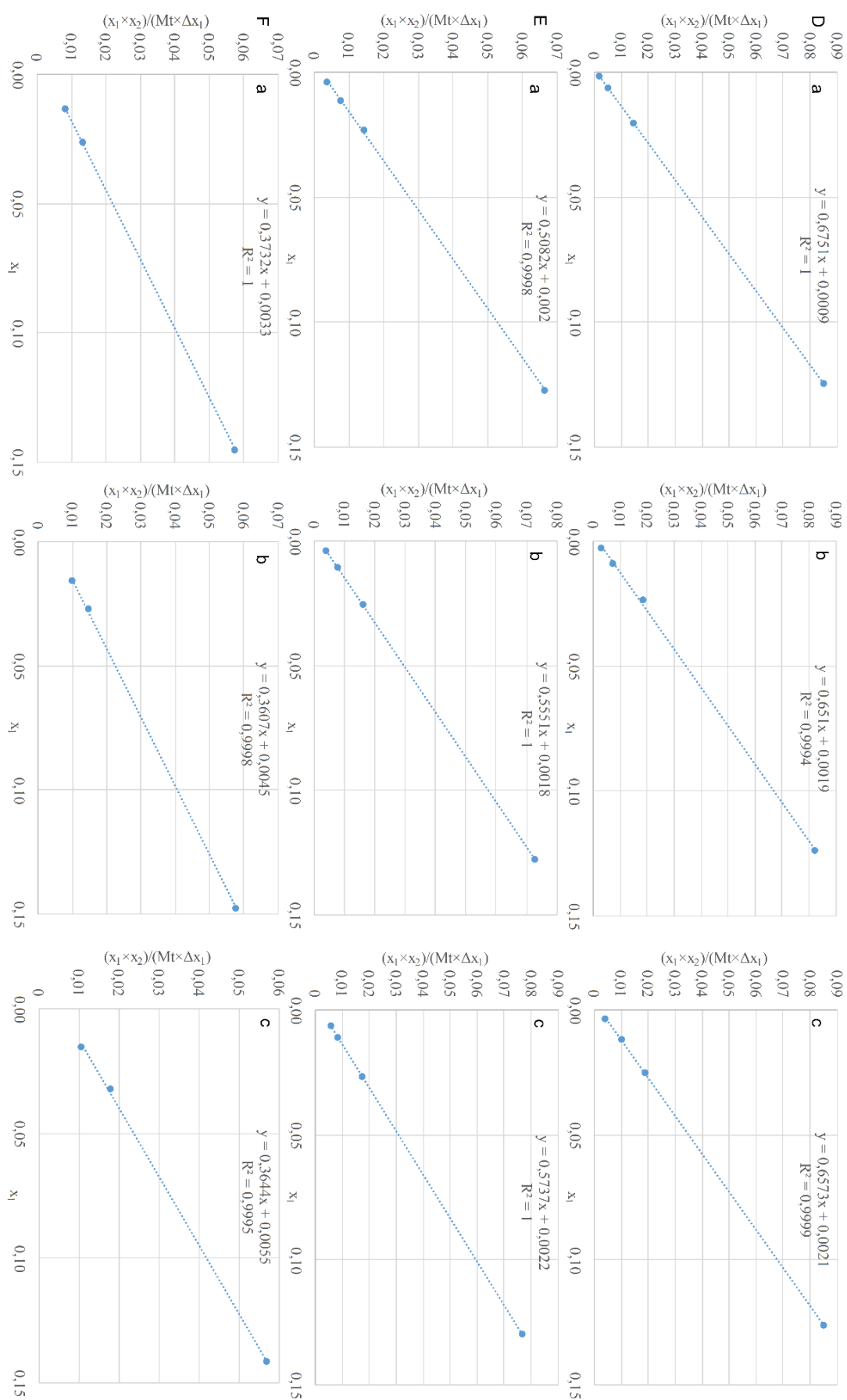


Figure B6 Surface excess plot for D) ethylbenzene, E) toluene, F) benzene at a) 450 K, b) 483 K, and c) 513 K

B.16 Adsorption results of *p*-xylene, *m*-xylene, *o*-xylene, ethylbenzene, toluene, and benzene**Table B26** Adsorption results of *p*-xylene (PX)

Temp. (K)	PX (wt%)	C (mol/L)	q(mol/kg)
450	15	0.771	1.523
	5	0.107	1.432
	3.5	0.042	1.329
	2	0.006	0.882
483	15	0.795	1.469
	5	0.148	1.386
	3.5	0.049	1.328
	2	0.009	0.896
513	15	0.763	1.583
	5	0.138	1.361
	3.5	0.050	1.279
	2	0.010	0.808

Table B27 Adsorption results of *m*-xylene (MX)

Temp. (K)	MX (wt%)	C (mol/L)	q(mol/kg)
450	20	1.142	1.359
	15	0.763	1.327
	5	0.116	1.239
	2	0.011	0.751
483	20	1.175	1.243
	15	0.776	1.260
	5	0.146	1.233
	2	0.016	0.757
513	20	1.171	1.412
	15	0.830	1.278
	5	0.216	1.192
	2	0.024	0.831

Table B28 Adsorption results of *o*-xylene (OX)

Temp. (K)	OX (wt%)	C (mol/L)	q(mol/kg)
450	15	0.790	1.442
	5	0.150	1.315
	3.5	0.046	1.235
	2	0.015	0.969
483	15	0.812	1.287
	5	0.144	1.252
	3.5	0.071	1.229
	2	0.019	0.964
513	15	0.818	1.336
	5	0.149	1.269
	3.5	0.062	1.186
	2	0.017	0.845

Table B29 Adsorption results of ethylbenzene (EB)

Temp. (K)	EB (wt%)	C (mol/L)	q(mol/kg)
450	15	0.780	1.466
	5	0.124	1.399
	3.5	0.037	1.204
	2	0.010	0.840
483	15	0.774	1.504
	5	0.144	1.265
	3.5	0.055	1.232
	2	0.016	0.876
513	15	0.791	1.484
	5	0.152	1.314
	3.5	0.072	1.186
	2	0.022	0.884

Table B30 Adsorption results of toluene (TOL)

Temp. (K)	TOL (wt%)	C (mol/L)	q(mol/kg)
450	15	0.808	1.912
	5	0.141	1.618
	3.5	0.068	1.470
	2	0.024	1.128
483	15	0.812	1.757
	5	0.156	1.589
	3.5	0.065	1.378
	2	0.023	0.992
513	15	0.823	1.692
	5	0.163	1.531
	3.5	0.067	1.296
	2	0.037	1.043

Table B31 Adsorption results of benzene (Bz)

Temp. (K)	Bz (wt%)	C (mol/L)	q(mol/kg)
450	15	0.944	2.528
	5	0.160	1.972
	3.5	0.081	1.648
483	15	0.960	2.559
	5	0.166	1.851
	3.5	0.094	1.590
513	15	0.917	2.484
	8.5	0.425	2.175
	5	0.197	1.802
	3.5	0.094	1.459

B.17 Langmuir constants of each component

Table B32 Adsorption equilibrium constants of *p*-xylene, *m*-xylene, *o*-xylene, ethylbenzene, toluene, and benzene between 450 and 513 K

Component	b_i (L/mol)		
	450 K	483 K	513 K
<i>p</i> -Xylene	241	166	124
<i>m</i> -Xylene	129	96	76
<i>o</i> -Xylene	158	117	92
Ethylbenzene	140	96	71
Toluene	72	51	39
Benzene	20	16	13

B.18 Heat of adsorption from binary mixtures

Enthalpy change for a binary mixture from Everett²:

$$\Delta H - (x_1\Delta H_1^0 + x_2\Delta H_2^0) = \frac{x_1x_2}{x_1 + \frac{1}{\alpha-1}}(\Delta H_1^0 - \Delta H_2^0) \quad (\text{B20})$$

where α is the selectivity of the aromatic compound over *i*-octane, and ΔH_1^0 and ΔH_2^0 are the heats of immersion of the solid in the two pure liquids. As it was already proven, $\alpha \gg 1$, in almost all cases $x_1 \gg 1/(\alpha-1)$, therefore:

$$\Delta H = x_2\Delta H_1^0 - x_2\Delta H_2^0 + (x_1\Delta H_1^0 + x_2\Delta H_2^0) = x_2\Delta H_1^0 + x_1\Delta H_1^0 = \Delta H_1^0 \quad (\text{B21})$$

The enthalpy change is equal to the heat of immersion in the pure liquid (in this case, the corresponding aromatic). On the other hand, for very low concentrations, $x_1 \approx 1/(\alpha-1)$ and $x_2 \approx 1$, therefore:

$$\begin{aligned} \Delta H &= \frac{x_2}{2}(\Delta H_1^0 - \Delta H_2^0) + x_1\Delta H_1^0 + x_2\Delta H_2^0 = \left(x_1 + \frac{x_2}{2}\right)\Delta H_1^0 + \frac{x_2}{2}\Delta H_2^0 \\ &= \frac{1}{2}(\Delta H_1^0 + \Delta H_2^0) \end{aligned} \quad (\text{B22})$$

B.19 Heat of adsorption from liquid phase vs heat of adsorption from gas phase

When comparing heats of adsorption from liquid phase with heats of adsorption from gas phase one cannot neglect the heat of vaporization of the species. Let us denote the enthalpy in gas phase, liquid phase and adsorbed phase by H^g , H^l and H^a , respectively and assume that the enthalpy of the adsorbed phase H^a is the same when the adsorbed molecules come from gas or liquid phase following a statement from Ruthven³ : “there is no difference in principle between adsorption from liquid and vapor phase since, thermodynamically, the adsorbed phase concentration in equilibrium with a liquid must be precisely the same as that which is in equilibrium with the saturated vapor”. We also know that “since enthalpy is a point function the total change for a process is governed solely by the terminal conditions, and not by the path followed”⁴. From **Figure B7**, it follows that adsorption enthalpy from gas phase $H^a - H^g$ (path 1) is equal to enthalpy of condensation $H^l - H^g$ (path 2) plus adsorption enthalpy from liquid phase (path 3), i.e., $H^a - H^g = H^l - H^g + H^a - H^l$ or $\Delta H_{ads,g} = \Delta H_{cond} + \Delta H_{ads,l}$.

In the above equation the three terms are negative; if we call heat of adsorption from gas phase $Q_{ads,g} = -\Delta H_{ads,g}$ and $Q_{ads,l} = -\Delta H_{ads,l}$ heat of adsorption from liquid phase, we see that the difference $Q_{ads,g} - Q_{ads,l}$ is the heat of condensation (or vaporization). The change of state from vapor needs to be considered (at fixed temperature, pressure must be changed to go from gas to liquid). More rigorous calculations are given in the paper by Builes et al.⁵.

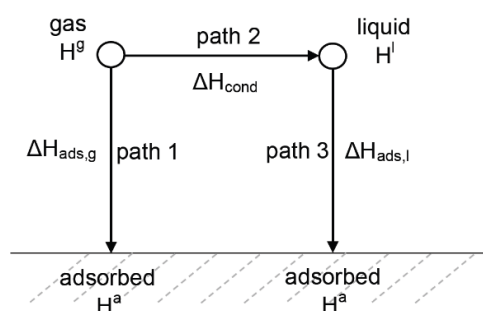


Figure B7 Sketch of adsorption from gas phase and from liquid phase

B.20 Objective functions description

Table B33 Minimization of desorbent consumption (DC)

Objective function	kg of desorbent per kg of PX in the extract $\min_{\alpha} \left\{ \frac{Q_D C E_D}{Q_X C_{PX,1}^{out}} \right\}$ Q_D is the volumetric flow rate of desorbent, m³/h; Q_X is the volumetric flow rate of extract, m³/h; $C_{PX,1}^{out}$ is the mass concentration of PX in the bulk phase at the end of zone I, kg/m³; $C E_D$ is the mass concentration of the desorbent stream, kg/m³.		
Constraints	Purity of extract $\geq 70\%$ Maximum pressure drop/bed ($\Delta P_{max}/bed$) ≤ 35 kPa Minimum recovery $\geq 90\%$ Purity of raffinate $\geq 95\%$		
Fixed variables	Q_F Feed flow rate m³/h $N_{col}^{zone I}$ Number of beds in zone I $N_{col}^{zone II}$ Number of beds in zone II $N_{col}^{zone IV}$ Number of beds in zone IV T Temperature K		
Decision variables (α)	φ	Adsorbent/(adsorbent+catalyst) volume ratio	[0, 1]
	Q_D	Volumetric flow rate of desorbent	m ³ /h [80, 2000]
	Q_R	Volumetric flow rate of raffinate	m ³ /h [50, 600]
	Q_1^{in}	Volumetric flow rate at the beginning of zone I	m ³ /h [100, 3000]
	t_s	Switching time	s [30, 180]

Table B34 Maximization of productivity

Objective function	kg/h of PX in the extract per m ³ of (adsorbent + catalyst) $\max_{\alpha} \left\{ \frac{Q_X C_{PX,1}^{out}}{\pi L \left(\frac{D}{2}\right)^2 N_{col} (1 - \varepsilon)} \right\}$ Q_X is the volumetric flow rate of desorbent, m³/h; $C_{PX,1}^{out}$ is the mass concentration of PX in the bulk phase at the end of zone I, kg/m³; L is the length of each bed, m; D diameter of each bed, m; N_{col} is the total number of beds; ε is the bed porosity.		
Constraints	Purity of extract $\geq 70\%$ Maximum pressure drop/bed ($\Delta P_{max}/bed$) ≤ 35 kPa Minimum recovery $\geq 90\%$ Purity of raffinate $\geq 95\%$		
Fixed variables	Q_F Feed flow rate m ³ /h $N_{col}^{zone I}$ Number of beds in zone I $N_{col}^{zone II}$ Number of beds in zone II $N_{col}^{zone IV}$ Number of beds in zone IV T Temperature K DC Desorbent consumption kg/kg		
Decision variables (α)	φ	Adsorbent/(adsorbent+catalyst) volume ratio	[0, 1]
	Q_D	Volumetric flow rate of desorbent	m ³ /h [80, 2000]
	Q_R	Volumetric flow rate of raffinate	m ³ /h [50, 600]
	Q_I^{in}	Volumetric flow rate at the beginning of zone I	m ³ /h [100, 3000]
	t_s	Switching time	s [30, 180]

Table B35 Minimization of energy consumption per kg/h of PX produced

Objective function	Energy (GJ) per kg/h of high content PX from extract distillation $\min_{\alpha} \left\{ \frac{E_{distil.} + \Delta E_{HX}}{XCol.F_{bottom}x_{PX}} \right\}$ $E_{distil.}$ is the energy consumed in the distillation columns, GJ; ΔE_{HX} is the difference in energy consumed in the heater exchangers, GJ; $XCol.F_{bottom}$ is the mass flow rate of the bottom of the extract distillation column, kg/h; and x_{PX} is the mass fraction of PX.		
Constraints	Purity of extract $\geq 70\%$ Maximum pressure drop/bed ($\Delta P_{max}/bed$) ≤ 35 kPa Minimum recovery $\geq 97\%$ Purity of raffinate $\geq 95\%$		
Fixed variables	Q_F T	Feed flow rate m ³ /h Temperature K	
Decision variables (α)	φ Q_D Q_R Q_I^{in} t_s $N_{col}^{zone I}$ $N_{col}^{zone II}$ $N_{col}^{zone IV}$	Adsorbent/(adsorbent+catalyst) volume ratio Volumetric flow rate of desorbent Volumetric flow rate of raffinate Volumetric flow rate at the beginning of zone I Switching time Number of beds in zone I Number of beds in zone II Number of beds in zone IV	[0, 1] m ³ /h [80, 2000] m ³ /h [50, 600] m ³ /h [100, 3000] s [30.180] [2, 14] [2, 14] [2, 6]

Table B36 Maximization of profit

Objective function	Value of the high content PX minus the cost for fuel oil, cooling water, and the cost for energy consumed in heat exchangers $\max_{\alpha} \{X_{Col} F_{bottom} 1.196 - E_{CW} 0.354 - E_{FO} 14.2 - \Delta E_{HX} \beta\}$ $X_{Col} F_{bottom}$ is the mass flow rate of the bottom of the extract distillation column, kg/h; the price of that stream (high content PX) is 1.196USD/kg; E_{CW} is the energy required for the condenser, GJ; E_{FO} is the energy for the reboiler, GJ; ΔE_{HX} is the difference in energy consumed in the heater exchangers, GJ; and β depends on the value of ΔE_{HX} (if cooling is needed, β equals to the price of cooling water 0.354USD/GJ; if heating is needed, β equals to the price of fuel oil 14.2USD/GJ).		
Constraints	Purity of extract $\geq 70\%$ Maximum pressure drop/bed ($\Delta P_{max}/bed$) ≤ 35 kPa Minimum recovery $\geq 97\%$ Purity of raffinate $\geq 95\%$		
Fixed variables	Q_F	Feed flow rate m ³ /h	
Decision variables (α)	φ	Adsorbent/(adsorbent+catalyst) volume ratio	[0, 1]
	Q_D	Volumetric flow rate of desorbent	m ³ /h [80, 2000]
	Q_R	Volumetric flow rate of raffinate	m ³ /h [50, 600]
	Q_I^{in}	Volumetric flow rate at the beginning of zone I	m ³ /h [100, 3000]
	t_s	Switching time	s [30, 180]
	$N_{col}^{zone I}$	Number of beds in zone I	[2, 14]
	$N_{col}^{zone II}$	Number of beds in zone II	[2, 14]
	$N_{col}^{zone IV}$	Number of beds in zone IV	[2, 6]
	T	Temperature	K [450, 573]

B.21 Minimum desorbent consumption for various configurations at 453 K and 513 K for the four cases

Table B37 Minimization of desorbent consumption for several configurations at 513 K and 453 K for case A (feed not involving EB; Bz as desorbent)

Temp., K	Configuration	Q _D , m ³ /h	Q _R , m ³ /h	Q _X , m ³ /h	Q ₁ , m ³ /h	ts, s	PR, kg/h m ³	DC, kg/kg	ΔP _{max} /bed, kPa
513	3-5-14-2	818	139	769	1300	61	63	34.2	31
	4-6-12-2	770	137	723	1247	61	63	32.2	29
	5-6-11-2	747	136	700	1223	61	63	31.2	29
	6-6-10-2	734	136	688	1207	62	63	30.7	28
	7-4-11-2	730	140	679	1214	61	63	30.5	28
453	3-5-14-2	674	98	656	962	85	63	33.0	24
	4-6-12-2	624	97	607	910	85	63	30.8	23
	5-6-11-2	600	97	583	886	85	63	29.6	22
	6-6-10-2	586	96	570	872	85	63	29.6	21
	7-4-11-2	580	99	561	870	85	63	28.6	21

Table B38 Minimization of desorbent consumption for several configurations at 513 K and 453 K for case B (feed involving EB; Bz as desorbent)

Temp., K	Configuration	Q _D , m ³ /h	Q _R , m ³ /h	Q _X , m ³ /h	Q ₁ , m ³ /h	ts, s	PR, kg/h m ³	DC, kg/kg	ΔP _{max} /bed, kPa
513	3-5-14-2	877	164	803	1382	60	54	42.6	34
	4-6-12-2	819	160	748	1318	60	54	39.7	32
	5-6-11-2	792	159	722	1288	60	54	38.4	31
	6-6-10-2	776	158	708	1269	61	54	37.7	30
	7-4-11-2	774	165	698	1279	60	54	37.5	31
453	3-5-14-2	803	128	755	1132	79	54	46.0	31
	4-6-12-2	730	125	685	1055	80	54	42.0	28
	5-6-11-2	695	125	650	1020	80	54	39.8	27
	6-6-10-2	675	124	631	998	80	54	38.6	26
	7-4-11-2	668	129	619	999	79	54	38.0	26

Annex B

Table B39 Minimization of desorbent consumption for several configurations at 513 K and 453 K for case C (feed not involving EB; TOL as desorbent)

Temp., K	Configuration	Q _D , m ³ /h	Q _R , m ³ /h	Q _X , m ³ /h	Q _I , m ³ /h	ts, s	PR, kg/h m ³	DC, kg/kg	ΔP _{max} /bed, kPa
513	2-6-14-2	185	70	204	450	71	63	8.1	10
	4-7-11-2	168	69	188	434	71	63	7.4	9
	5-6-11-2	166	69	186	433	71	63	7.4	9
	6-6-10-2	165	69	185	431	71	63	7.3	9
	7-4-11-2	166	71	184	435	70	63	7.3	9
453	2-6-14-2	134	59	155	312	95	63	7.0	8
	4-7-11-2	119	58	141	299	95	63	6.5	8
	5-6-11-2	117	58	139	298	95	63	6.4	8
	6-6-10-2	116	58	138	296	95	63	6.2	8
	7-4-11-2	116	59	137	298	94	63	6.1	8

Table B40 Minimization of desorbent consumption for several configurations at 513 K and 453 K for case D (feed involving EB; TOL as desorbent)

Temp., K	Configuration	Q _D , m ³ /h	Q _R , m ³ /h	Q _X , m ³ /h	Q _I , m ³ /h	ts, s	PR, kg/h m ³	DC, kg/kg	ΔP _{max} /bed, kPa
513	2-6-14-2	195	78	207	462	71	54	9.9	10
	4-7-11-2	177	77	190	444	71	54	9.0	9
	5-6-11-2	175	77	187	443	71	54	9.0	9
	6-6-10-2	173	77	186	440	71	54	8.9	9
	7-4-11-2	174	79	184	444	70	54	8.9	9
453	2-6-14-2	154	68	166	340	91	54	8.9	9
	4-7-11-2	136	67	149	323	91	54	7.9	8
	5-6-11-2	134	67	147	322	91	54	7.7	8
	6-6-10-2	132	67	145	320	91	54	7.6	8
	7-4-11-2	133	68	145	323	90	54	7.7	8

B.22 Energy consumption at different temperatures for the four cases

Table B41 Energy consumption in condenser and reboiler at different temperatures for the four cases

Case A				Case B				Case C				Case D			
Temp. K	R.Col GJ/h	X.Col GJ/h		Temp. K	R.Col GJ/h	X.Col GJ/h		Temp. K	R.Col GJ/h	X.Col GJ/h		Temp. K	R.Col GJ/h	X.Col GJ/h	
Condenser				Condenser				Condenser				Condenser			
460	18.48	225.19		470	27.62	244.51		450	15.59	99.92		460	19.58	108.47	
480	20.91	225.70		490	29.22	239.78		470	16.22	99.73		480	20.11	107.24	
500	23.59	227.59		510	31.17	236.82		490	17.06	102.46		500	21.12	108.52	
520	25.39	231.58		530	33.34	236.70		510	18.04	107.52		520	22.17	111.90	
Reboiler				Reboiler				Reboiler				Reboiler			
460	20.98	255.70		470	31.34	277.51		450	16.16	103.60		460	20.30	112.50	
480	23.73	256.34		490	33.15	272.23		470	16.81	103.44		480	20.84	111.24	
500	26.78	258.53		510	35.36	268.95		490	17.69	106.29		500	21.89	112.59	
520	28.82	263.13		530	37.81	268.90		510	18.70	111.55		520	22.96	116.10	
Total			Total	Total			Total	Total			Total	Total			Total
460	39.46	480.89		470	58.96	522.03		450	31.76	203.52		460	39.87	220.97	
480	44.64	482.04		490	62.37	512.01		470	33.03	203.17		480	40.95	218.48	
500	50.37	486.12		510	66.53	505.77		490	34.75	208.76		500	43.01	221.11	
520	54.21	494.70		530	71.15	505.60		510	36.74	219.07		520	45.13	228.00	

B.23 Composition of the raffinate and the extract streams for the four cases at different temperatures

Table B42 Composition of the raffinate and the extract streams in molar fraction for the four cases

Temp. K	Case A					Case B					Case C					Case D				
	460	480	500	520		470	490	510	530		450	470	470	510		460	480	500	520	
Feed, kmol/h	695.7	754.9	820.5	864.3		933.7	972.1	1019.2	1071.5		356.2	363.0	374.2	387.5		413.7	420.3	432.1	445.5	
R.Col																				
EB	0.000	0.000	0.000	0.000		0.067	0.066	0.066	0.064		0.000	0.000	0.000	0.000		0.142	0.148	0.150	0.153	
PX	0.006	0.006	0.005	0.005		0.004	0.004	0.004	0.004		0.007	0.012	0.017	0.020		0.005	0.008	0.011	0.012	
MX	0.395	0.366	0.338	0.323		0.264	0.253	0.240	0.228		0.761	0.742	0.716	0.687		0.590	0.575	0.552	0.532	
OX	0.077	0.069	0.062	0.057		0.052	0.048	0.044	0.041		0.150	0.142	0.138	0.136		0.115	0.112	0.105	0.100	
TOL	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000		0.082	0.104	0.129	0.157		0.146	0.156	0.181	0.203	
Bz	0.522	0.559	0.595	0.615		0.613	0.629	0.646	0.663		0.000	0.000	0.000	0.000		0.002	0.001	0.001	0.000	
PDEB	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000	
PEMB	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000	
Feed, kmol/h	5816.7	5830.9	5881.4	5987.8		6397.0	6263.1	6177.7	6170.4		1403.0	1402.0	1437.9	1504.4		1538.8	1518.8	1532.7	1571.1	
X.Col																				
EB	0.000	0.000	0.000	0.000		0.002	0.002	0.001	0.001		0.000	0.000	0.000	0.000		0.009	0.007	0.006	0.004	
PX	0.025	0.024	0.024	0.024		0.019	0.020	0.020	0.020		0.105	0.105	0.102	0.097		0.082	0.083	0.083	0.081	
MX	0.006	0.006	0.006	0.005		0.003	0.003	0.003	0.003		0.025	0.025	0.023	0.021		0.013	0.014	0.014	0.014	
OX	0.004	0.005	0.005	0.005		0.003	0.003	0.004	0.004		0.019	0.021	0.021	0.021		0.014	0.015	0.016	0.017	
TOL	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000		0.851	0.849	0.854	0.861		0.880	0.880	0.881	0.884	
Bz	0.965	0.965	0.965	0.966		0.973	0.972	0.972	0.972		0.000	0.000	0.000	0.000		0.001	0.000	0.000	0.000	
PDEB	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000	
PEMB	0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000		0.000	0.000	0.000	0.000		0.001	0.001	0.000	0.000	

B.24 Comparison of the simplified model against commercial software Aspen Plus for the four cases

Table B43 Comparison of the simplified model against commercial software Aspen Plus for case A (feed not involving EB; Bz as desorbent)

	Raffinate distillation column Heavy key: MX; Light key: Bz			Extract distillation column Heavy key: PX; Light key: Bz		
	Feed	This work	Aspen RadFrac	Feed	This work	Aspen RadFrac
		Top	Top		Top	Top
Temp. K		363	364		363	364
Bz	0.522	0.999	0.999	0.965	0.999	0.999
PX	0.006	0.000	0.000	0.025	0.001	0.001
MX	0.395	0.001	0.001	0.006	0.000	0.000
OX	0.077	0.000	0.000	0.005	0.000	0.000
		Bottom	Bottom		Bottom	Bottom
Temp. K		441	441		441	441
Bz		0.001	0.001		0.001	0.001
PX		0.013	0.013		0.691	0.697
MX		0.825	0.825		0.177	0.171
OX		0.161	0.160		0.131	0.130
Actual reflux		0.694	0.694		0.334	0.334
N stages		-	23		-	15
Feed stage		-	12		-	6
Condenser (GJ/h)		18.5	18.5		225	226
Reboiler (GJ/h)		21.0	20.7		256	221

Table B44 Comparison of the simplified model against commercial software Aspen Plus for case B (feed involving EB; Bz as desorbent)

	Raffinate distillation column Heavy key: EB; Light key: Bz			Extract distillation column Heavy key: PX; Light key: Bz		
	Feed	This work	Aspen RadFrac	Feed	This work	Aspen RadFrac
		Top	Top		Top	Top
Temp. K		363	364		363	364
Bz	0.646	0.999	0.998	0.972	0.999	0.999
EB	0.066	0.001	0.001	0.001	0.000	0.000
PX	0.004	0.000	0.000	0.020	0.001	0.001
MX	0.241	0.000	0.001	0.003	0.000	0.000
OX	0.044	0.000	0.000	0.004	0.000	0.000
		Bottom	Bottom		Bottom	Bottom
Temp. K		440	441		440	441
Bz		0.001	0.001		0.001	0.002
EB		0.184	0.185		0.047	0.045
PX		0.011	0.010		0.689	0.697
MX		0.680	0.679		0.126	0.122
OX		0.124	0.124		0.137	0.135
Actual reflux		0.576	0.576		0.312	0.312
N stages		-	20		-	14
Feed stage		-	10		-	6
Condenser (GJ/h)		31.2	31.2		237	237
Reboiler (GJ/h)		35.4	33.6		269	232

Table B45 Comparison of the simplified model against commercial software Aspen Plus for case C (feed not involving EB; TOL as desorbent)

	Raffinate distillation column			Extract distillation column		
	Heavy key: MX; Light key: TOL			Heavy key: PX; Light key: TOL		
	Feed	This work	Aspen RadFrac	Feed	This work	Aspen RadFrac
		Top	Top		Top	Top
Temp. K		395	397		395	397
TOL	0.082	0.999	0.982	0.851	0.999	0.998
PX	0.007	0.000	0.000	0.105	0.001	0.002
MX	0.761	0.001	0.017	0.025	0.000	0.000
OX	0.150	0.000	0.000	0.019	0.000	0.000
		Bottom	Bottom		Bottom	Bottom
Temp. K		441	442		441	441
TOL		0.001	0.002		0.001	0.006
PX		0.008	0.008		0.699	0.696
MX		0.828	0.827		0.171	0.170
OX		0.163	0.163		0.129	0.129
Actual reflux		15.452	15.452		1.542	1.542
N stages		-	60		-	39
Feed stage		-	16		-	17
Condenser (GJ/h)		15.6	15.6		99.9	101
Reboiler (GJ/h)		16.2	16.2		104	99.8

Table B46 Comparison of the simplified model against commercial software Aspen Plus for case D (feed involving EB; TOL as desorbent)

	Raffinate distillation column			Extract distillation column		
	Heavy key: EB; Light key: TOL			Heavy key: PX; Light key: TOL		
	Feed	This work	Aspen RadFrac	Feed	This work	Aspen RadFrac
		Top	Top		Top	Top
Temp. K		394	396		395	397
Bz	0.001	0.008	0.007	0.000	0.000	0.000
TOL	0.156	0.991	0.987	0.880	0.999	0.998
EB	0.148	0.001	0.003	0.008	0.000	0.000
PX	0.008	0.000	0.000	0.083	0.001	0.002
MX	0.574	0.000	0.003	0.014	0.000	0.000
OX	0.112	0.000	0.000	0.015	0.000	0.000
EMB	0.000	0.000	0.000	0.001	0.000	0.000
PDEB	0.000	0.000	0.000	0.000	0.000	0.000
		Bottom	Bottom		Bottom	Bottom
Temp. K		441	441		441	441
Bz		0.000	0.000		0.000	0.000
TOL		0.001	0.001		0.001	0.006
EB		0.175	0.175		0.063	0.061
PX		0.009	0.009		0.692	0.690
MX		0.682	0.681		0.113	0.112
OX		0.133	0.133		0.124	0.124
EMB		0.000	0.000		0.004	0.005
PDEB		0.000	0.000		0.001	0.002
Actual reflux		8.263	8.263		1.437	1.437
N stages		-	60		-	40
Feed stage		-	20		-	20
Condenser (GJ/h)		20.1	20.0		107	107
Reboiler (GJ/h)		20.8	20.8		111	105

B.25 Energy consumption under the objective function of maximum profit for the four cases

Table B47 Energy consumption under the objective function of maximum profit for the four cases

	R.Col Condenser GJ/h	R.Col Reboiler GJ/h	R.Col Total GJ/h	X.Col Condenser GJ/h	X.Col Reboiler GJ/h	X.Col Total GJ/h
Case A						
bothlow	26.27	29.82	56.09	261.01	296.48	557.49
R.high_200	32.78	35.38	68.16	259.07	294.29	553.36
X.high_200	29.54	33.53	63.08	267.84	307.92	575.77
Case B						
bothlow	33.67	38.18	71.85	242.26	275.16	517.42
R.high_200	41.33	45.01	86.34	239.63	272.19	511.82
X.high_200	52.93	60.03	112.96	247.61	285.29	532.91
Case C						
bothlow	60.04	62.18	122.22	265.70	275.79	541.50
R.high_100	75.55	76.04	151.59	263.39	273.40	536.79
X.high_100	64.25	66.54	130.79	293.05	305.71	598.75
Case D						
bothlow	61.06	63.19	124.25	252.00	261.69	513.70
R.high_100	93.08	94.20	187.28	249.17	258.77	187.28
X.high_100	80.75	83.56	164.32	279.03	291.36	570.39

B.26 Nomenclature

C_i , molar concentration of component i , mol/L

Ca , Carberry number

C_b , bulk reactant concentration, mol/L

D_{AA} , self-diffusion coefficient, m²/s

DC, desorbent consumption, kg/kg

D_e , effective diffusion coefficient, m²/s

D_m , molecular diffusivity, m²/s

$E_{a,j}$, activation energy of reaction j , kJ/mol

H, enthalpy, kJ/mol

K, Boltzmann constant, m² kg/s² K

k_f , mass transfer coefficient, m/s

k_j , kinetic constant of reaction j ($j=1,2,3,4,5,6$), m³/kg s

$k_{0,j}$, kinetic constant of reaction j ($j=1,2,3,4,5,6$) at centered temperature T_0 , m³/kg s

M_t , initial total mole by mass of adsorbent, mol/kg

M_s , adsorption capacity of the aromatic compound, mol/kg

$\tilde{N}_A$, Avogadro number, mol⁻¹

PR, productivity, kg/h of PX per m³ of solid

Q , flow rate, mL/min

Q_{ads} , heat of adsorption, kJ/mol

R_{obs} , observed reaction rate, mol/g s

S_p , particle surface, m²

T, temperature, K

$\tilde{V}_A$, molar volume of the compound, m³/mol

V_p , particle volume, m³

x_i , mole fractions of species i

W_c , mass of catalyst, g

Greek letters

α , selectivity of the aromatic compound over *i*-octane

τ , tortuosity factor

ε_p , particle porosity

ρ_p , particle density, g/L

η , effectiveness factor

ϕ , Thiele modulus

μ_A , viscosity of the pure compound, kg/m s

Superscripts and subscripts

0, heat of immersion

1, zone I

a, adsorbed phase

ads, adsorption

D, desorbent

g, gas phase

in, in the feed

l, liquid phase

out, in the effluent

R, raffinate

X, extract

Abbreviations

Bz, benzene

EB, ethylbenzene

EMB, ethylmethylbenzene

F, feed

MX, *m*-xylene

OX, *o*-xylene

PDEB, *p*-diethylbenzen

PEMB, *p*-ethylmethylbenzene

PX, *p*-xylene

R.Col, raffinate distillation column

TOL, toluene

X.Col, extract distillation column

B.27 References

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