

## Process Intensification

### Liquid Phase Sorption Enhanced Reaction Process

#### Simulated moving bed reactor: green fuels and additives production

**KEYWORDS:** Simulated moving bed reactor / Multifunctional reactors / Heterogeneous catalysis / Process intensification / Green fuels

**Simulated Moving Bed Reactors (SMBRs) have emerged as a promising technology for the production of green fuels and additives, offering a unique integration of reaction and separation steps in a single unit. This report explores the application of SMBRs in the synthesis of biofuels and additives, focusing on key processes such as Butyl Acrylate production, 1,1-Diethoxybutane synthesis, the synthesis of sulfonated polymer resins by the reaction of styrene and trimethylolpropane triacrylate, and n-Propyl Propionate production and separation. The report underscores the versatility of SMBRs in the production of biofuels and additives, emphasizing their role in the transition towards greener and more sustainable energy production.**

#### Introduction

Biofuels and additives derived from biomass have been pointed out as reliable and sustainable solutions to address environmental challenges associated with fossil fuels. Despite their promise, the synthesis of these products faces significant limitations, mainly due to the low efficiency of the technologies employed and the thermodynamic limitations of chemical reactions or product separations.

Process Intensification techniques, particularly reactive separation technologies, offer potential solutions. Among these, one of the most promising technologies for the production of Biofuels and additives is the Simulated Moving Bed Reactor (SMBR), an extension of the Simulated Moving Bed separation unit where the chromatographic columns were converted into chromatographic reactors, combining chromatographic columns with fixed bed reactors. The stationary phase of the SMBR may be hybrid materials with both catalytic and adsorptive properties or mixtures of adsorbent and catalysts in each column, or even performing the reaction and separation steps in independent columns of the SMBR.

The SMBR basic configuration and operating principles mirror the well-studied SMB; however, sections II and III acquired a new function: to convert the reactants as they are introduced within the unit through the feed stream. The products will be separated as they are formed within these sections, while sections I and IV remain responsible for the regeneration of the solid and liquid phases, respectively. For reactive systems involving two or more reactants, one of them is usually used as desorbent. Fig.1 presents a schematic representation of the SMBR operating mode and internal concentration profiles.

The different affinity of each compound towards the SMBR stationary phase is the reason for their distinct distribution throughout the unit and the consequent ability of this technology to displace the thermodynamic equilibrium of the chemical reaction. The efficiency and flexibility of this technology are closely related to the advances observed in materials sciences that contributed to the development of numerous commercially available catalysts and adsorbents.

SMBRs have been considered an extremely efficient technology for the production of bio-derived fuels and additives, which include the production of biodiesel and several oxygenated additives obtained from bioethanol (1,1-diethoxyethane (DEE) and 1,1-diethoxybutane (DEB)) and glycerol (GEA).

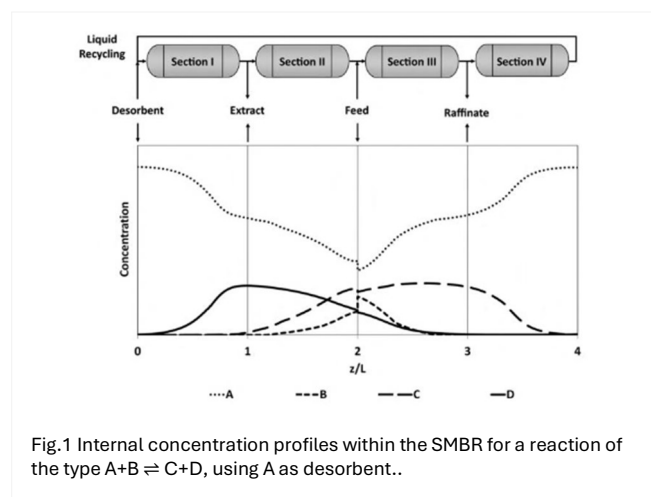


Fig.1 Internal concentration profiles within the SMBR for a reaction of the type  $A+B \rightleftharpoons C+D$ , using A as desorbent..

These additives, primarily oxygenated compounds, result from reversible reactions with moderate equilibrium conversions, namely acetalization, transesterification, esterification, transesterification, and etherification reactions. Among the potential oxygenated compound families previously mentioned, acetals in particular gain significance due to their performance as fuel additives, including the ability to increase the octane number, reduce the particulate and exhaust gases emissions and improve the fuel fluid properties; and the possibility of producing them almost exclusively from renewable resources such as bioethanol or bioglycerol.

#### Current Development

SMBR technology was studied for several systems, and the most recent advances will be presented herein.

#### Synthesis of Sulfonated Polymer Resins:

This study aimed to synthesize sulfonated polymer resins based on styrene and trimethylolpropane triacrylate (TMPTA) and evaluate their catalytic efficiency in glycerol acetylation. A factorial design was used, with two factors, three levels, and three replicates of the center point. The factors were cross-linker percentage (YTMPA) and cross-linker feed time (TTMPA). Ion-exchange capacity, swelling index, and catalytic efficiency were analyzed to characterize each resin. Lower cross-linker percentages resulted in higher catalytic efficiencies, as expected. Resins synthesized with 2, 6, and 10% TMPTA had mean catalytic efficiencies of 215, 176, and 121, respectively. Statistical and kinetic models were developed to represent the experimental results and support the development of strategies to improve resin formulation and synthesis conditions. TMPTA feed time at low and high levels positively influenced catalytic efficiency; the result is attributed to the micro- and macrostructure of resins. This finding was corroborated by the kinetic constants provided by the model.

#### 1,1-Diethoxybutane synthesis

The synthesis of acetals in the liquid phase involves a reversible reaction between a monohydric alcohol and an aldehyde, catalyzed in an acidic medium, producing water as a by-product. Ethanol or bioethanol derived from biomass, is a main candidate for acetal synthesis.

Butanal reacts with ethanol to produce DEB and water, in this case over Amberlyst-47, an acidic resin acting as both catalyst and adsorbent. Ethanol serves also as the desorbent, facilitating DEB purification.

DEB production via SMBR was designed and optimized by extending the fixed bed column model, which showed good agreement with the experimental data. From this SMBR model, the optimum switching time was found to be 2.4 min, and the ratio of liquid flowrate over the solid flowrate in section I, section II, section III, and section IV of the SMBR was found to be 4.24, 1.77, 3.03 and 1.35, respectively. Under those conditions, the productivity was 19.8 kg of DEB per liter of adsorbent per day, and the desorbent consumption was 6.1 L of ethanol per kg of DEB. The results were obtained with a minimum purity of the extract and raffinate of 97%.

Reactive distillation units and membrane reactors have been reported in the open literature as the most efficient multifunctional reactors for the synthesis of DEB; however, the results attained for the SMBR revealed that adsorption-based reactive processes can outperform the technologies previously proposed for the synthesis of this acetal. Since this process involves a thermodynamically limited exothermic reaction, it will take advantage of the lower operating temperatures typically associated with chromatographic separations (due to the exothermic nature of the adsorption). SMBR can reach complete limiting reactants conversion at 303 K, while the remaining state-of-the-art technologies typically do not overcome 50% to 70%, because their operating temperature is above 343 K. Also, this method does not have issues with azeotropes compared to distillation.

#### Butyl Acrylate synthesis:

Butyl Acrylate is a significant acrylic monomer with diverse industrial applications. Different process intensification strategies to overcome the equilibrium conversion by the continuous removal of water (by-product) using chromatographic (adsorption) and pervaporation techniques.

A full SMBR process showed a very competitive production capacity of 51,500 tons of Butyl Acrylate per year, recycling almost all the n-butanol used as eluent. A reaction conversion of 99.8% was obtained at cyclic steady state, with a final product purity of 99.7 mol.%.

A novel process design was investigated for the synthesis of butyl acrylate at an industrial scale, by coupling two reactors: a fixed-bed reactor with a SMBR, which achieved a reaction conversion of 99.5 % and a production capacity of 30 % higher (67,000 tons of Butyl Acrylate per year) than the conventional SMBR with a similar energy consumption ( $1.9 \times 10^3$  kJ per kg Butyl Acrylate).

From the industrial point of view, SMBR-based processes seem to be one of the most attractive due to their key economic indicators, presenting an economic potential of 30,500 €/year, which is approximately three times higher than the remaining processes.

#### n-Propyl Propionate Synthesis:

The synthesis of n-Propyl Propionate (ProPro) holds significant industrial potential, with applications ranging from solvents for paints and inks to additives in food and perfumes. However, the current production route faces challenges, particularly in downstream purification, prompting the exploration of alternative solutions such as chromatographic separation. Experimental studies in a fixed bed unit using Amberlyst 46 resin demonstrated the feasibility of this approach. Adsorption equilibrium isotherms and Langmuir model parameters were determined, contributing to the development and validation of a phenomenological model for the process. Notably, the model's uncertainties were thoroughly characterized, extending to predictions, enabling the estimation of parameters with fewer experiments.

The results were extended for the design and optimization of an SMBR process. The results demonstrate that the unit is capable of producing the n-Propyl Propionate with high purity and conversion, over 99 %. Furthermore, the productivity associated with its low consumption of eluent and its operation at significantly lower temperatures provides evidence that the SMBR may be an efficient and competitive route to produce n-Propyl Propionate. Moreover, the swarm optimization method here used showed to be a powerful optimization tool while simultaneously providing deep information about the SMBR process feasible operating region.

#### **Future Perspectives**

For butyl acrylate synthesis the deactivation of the catalyst/adsorbent must be investigated.

For 1,1-Diethoxybutane Synthesis, now that the system has been optimized, the modeling results will be validated experimentally.

The production of n-Propyl Propionate will be experimentally validated in an SMB unit. After that, the system will be optimized to increase productivity and decrease eluent consumption, based on optimization algorithms implemented in gPROMS software.

#### **Related Sustainable Development Goals**



#### **Outputs**

##### **Selected Publications**

- [1] R. Faria *et al.*, Intensification of Biobased Processes 55, 145 (2018)
- [2] D. Constantino *et al.*, Chemical Engineering and Processing-Process Intensification 142, 107563 (2019)
- [3] I. Nogueira *et al.*, Computers & Chemical Engineering 119, 371-382, (2018)
- [4] I Nogueira *et al.*, Computers & Chemical Engineering 128, 164-173 (2019).
- [5] W. Godoy *et al.*, Catalysts 13, 181 (2023)
- [6] J. Spitters. *et al.*, Processes 9, 189 (2021)
- [7] L. Aguiar *et al.*, Industrial & Engineering Chemistry Research 60, 6101-6110 (2021)

#### **Team**

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## Liquid Phase Sorption Enhanced Reaction Process

### Simulated Moving Bed Reactor: Glycerol Valorisation

**KEYWORDS:** Process Intensification / Adsorption / Glycerol Valorisation/ Alcohols / Green Chemistry / Simulated Moving Bed Reactor

The Simulated Moving Bed Reactor (SMBR) is a sorption-enhanced reactive technology that has been successfully applied to the synthesis of several organic compounds, due to its ability to overcome the thermodynamic limitations associated with reversible reactions. To deal with the global glycerol glut consequence of biodiesel production, Solketal arises as a promising fuel additive due to improving the quality of the fuel. Besides, reinserting solketal in the biodiesel production chain complies with the Circular Economy model, which is of great economic and environmental interest. Solketal synthesis in the Conventional SMBR, however, is limited due to the high characteristic diffusion times of the species, the low reactants conversion, and the low adsorption selectivity between acetone and solketal. The Multifeed SMBR is a non-conventional operating strategy that can improve the performance of the SMBR, particularly for systems in which none of the reactants can be used as desorbent. Within this strategy, it was possible to reach a productivity of over 10  $\text{kg}_{\text{Solk}} \text{L}_{\text{Ads}}^{-1} \text{day}^{-1}$ , with desorbent consumptions below 6  $\text{L}_{\text{Desorbent}} \text{kg}_{\text{Prod}}^{-1}$ , while for a conventional unit, this is barely possible. Moreover, it led to a reduction in desorbent consumption of 85%.

#### Introduction

With global biodiesel production growing as never seen before, encouraged by government policies, fiscal incentives, and emissions laws to control air pollution, there has been the collateral effect of generating massive amounts of crude glycerol, a by-product from the biodiesel industry. The positive effect of minimizing CO<sub>2</sub> emissions using biofuels is jeopardized by the fact that the waste generated by this industry represents an enormous environmental disadvantage.

The strategy of viewing “waste as a resource” led the scientific community to propose numerous processes that use glycerol as raw material (Fig 1). Nonetheless, many of the reactions for the valorisation of glycerol have low equilibrium constants; therefore, they are thermodynamically limited. To obtain high conversion yields, it is necessary to shift the reaction in favor of product formation by either removing one of the products or by adding one of the reactants in excess.

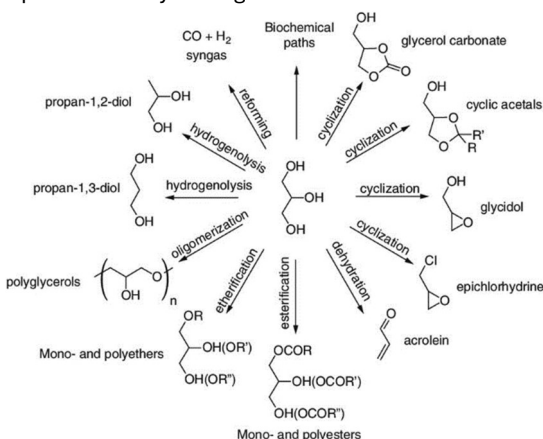


Fig 1. Glycerol valorization reactions

This is the case of Solketal, the product of the reaction of glycerol and acetone, a promising fuel additive capable of

enhancing fuel octane number and oxidation stability, diminishing particle emissions and gum formation, and enhancing properties at low temperatures. For solketal synthesis, equimolar amounts of glycerol and acetone react, forming water as a by-product. To overcome the mentioned thermodynamic limitation, we propose developing the process in the SMBR, a sorption-enhanced Process Intensification (PI) strategy that improves the efficiency of reactive systems by combining separation by adsorption and chemical reaction using a hybrid stationary phase with catalytic activity and adsorption selectivity between the products. This way, by adsorbing one of the reaction products, the reaction equilibrium shifts towards product formation.

In the Conventional SMBR (Fig. 2), a feed stream composed of a reactive mixture is inserted in a four-section unit, with a synchronous time switch ( $t^*$ ) and constant flow rates. Unlike most SMBR processes, for solketal synthesis, none of the reactants can be used as desorbent, due to miscibility issues. For this reason, an SMBR with multiple feed (Multifeed – Fig. 2) streams was implemented and optimized for the first time to produce solketal. In this alternative SMBR, acetone, and glycerol are fed by independent feed streams and the counter-current contact between the reactants shall increase the limiting reactant conversion, as well as the products concentration.

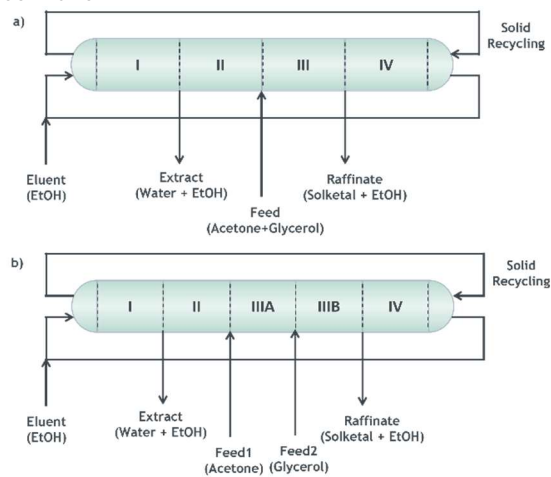


Fig. 2. Schematic drawing of a) SMBR and b) Five-section SMBR.

#### Current Development

To implement a Process Intensification strategy in the SMBR, it is necessary to gather the adsorption equilibrium data and the reaction thermodynamic and kinetic data. Then, implementing the process in the Fixed-bed adsorptive reactor because it is the elementary unit of the SMBR. In this step, the mathematical model developed with the data from the previous steps is validated. Then, the process can finally be transitioned to the more complex unit. Before validating experimentally, ideally, optimizations are performed to find the set of operation conditions that leads to the best performance parameters.

The screening of commercial catalysts showed that the acid ion-exchange resin Amberlyst-35 has the highest activity. As for the solvent selection, the methodology applied in this work,

which was specifically developed for integrated reactive-adsorptive processes, identified ethanol as the most suitable solvent for this system.

Chemical equilibrium data was gathered for temperatures ranging from 303 to 323 K. The standard enthalpy and Gibbs free energies were found to be  $-20.1 \pm 1.1$  kJ mol<sup>-1</sup> and  $1.4 \pm 0.3$  kJ mol<sup>-1</sup>, respectively. The experimental results revealed that the reaction kinetics behavior could be accurately described by the Langmuir–Hinshelwood–Hougen–Watson (LHHW) reaction rate law, considering the presence of internal mass-transfer resistances. The model considers the surface reaction between the adsorbed reactants that leads to the formation of water as the rate-determining step. The activation energy value estimated for the reaction was  $69.0 \pm 6.6$  kJ mol<sup>-1</sup>, which is within the range of values reported in the open literature for similar reactive systems. A value of  $14.4 \pm 3.1$  was estimated for the adsorption equilibrium constant.

Then, the adsorption equilibrium data isotherms for all the compounds of the process were determined at 313 K through a frontal analysis methodology, and the results were fitted through a competitive multicomponent Langmuir model. It was possible to conclude that water was the most adsorbed compound while solketal was the least.

Then, solketal was synthesized by reacting glycerol with acetone (in the presence of ethanol) in a fixed bed adsorptive reactor packed with Amberlyst-35. The potential for implementing sorption-enhanced reactive processes was experimentally demonstrated since the conversion values transiently attained during the solketal synthesis process were approximately 30% above the equilibrium values. A study on the influence of the temperature on the conversion led to conclude that at higher temperatures, the sorption enhancement is higher due to the better mass transfer and favored selectivity. Nonetheless, there was only a marginal difference in the maximum conversion for both temperatures and the steady state conversion is higher for 303 K, as expected for exothermic reactions. The mathematical model developed with the fundamental reaction and equilibrium data was successfully validated in this step.

When transitioning solketal synthesis to the SMBR technology, the results were not encouraging, once the system reached a productivity of only  $0.15$  kg<sub>Solk</sub> L<sub>Ads</sub><sup>-1</sup> day<sup>-1</sup>, with desorbent consumptions below  $6$  L<sub>Desorbent</sub> kg<sub>Prod</sub><sup>-1</sup>. This is a consequence of the high characteristic diffusion times of the species, the low reactants conversion, and the low adsorption selectivity between acetone and solketal, which dramatically limited the performance of the process, making its practical implementation unfeasible.

As an alternative, the Multifeed SMBR was developed, consisting of an SMBR unit in which acetone and glycerol were fed through independent feed ports. Since acetone was the least retained reactant, its feed port was placed near the extract collection port, while the glycerol feed stream was introduced in the unit between the acetone feed port and the raffinate collection point. In this way, a counter-current contact between the reactant concentration bands was promoted inside the reactor, which allowed the development of the first continuous chromatographic process for the production of solketal. The main SMBR design variables, including all sectional flow rates, the configuration, and the solid phase velocity, were optimized through a methodology developed for this particular purpose. Under optimal conditions, the maximum productivity of the Multifeed SMBR reached over  $10$  kg<sub>Solk</sub> L<sub>Ads</sub><sup>-1</sup> day<sup>-1</sup>, with desorbent consumptions below  $6$  L<sub>Desorbent</sub> kg<sub>Prod</sub><sup>-1</sup>.

## Future Perspectives

The experimental validation of Solketal synthesis in the SMBR is fundamental for validating and adjusting the mathematical model and the optimization methodology developed under the scope of these studies.

For validating the SMBR as a competitive industrial production route for solketal, it is also necessary to perform the scale-up of the processes and to perform a careful economical analysis, maybe even assuming the reduction of the production costs as the objective function for optimizing the operational conditions of the SMBR.

The potential applications of the SMBR are several, therefore, other products with higher aggregated value may be produced within this unit. Also, non-conventional operating strategies are still rarely studied for the reactive simulated moving bed, so there is still plenty of room in the open literature for alternative processes to be proposed and developed.

## Related Sustainable Development Goals



### Outputs

#### Master Dissertations

- [1] Bruno Alexandre Carvalho de Castro, Development of hierarchical zeolites, MIEQ, FEUP, 2020
- [2] Carolina Joana Vieira Viveiros, Development of hierarchical zeolites for the valorization of glycerol, MIEQ, FEUP, 2022

#### Selected Publications

- [1] M.N. Moreira *et al.*, Ind. Eng. Chem. Res. 58, 17746–17759 (2019)
- [2] M.N. Moreira *et al.*, Ind. Eng. Chem. Res. 59, 2805–2816 (2020)
- [3] J.T.S. Gomes *et al.*, Results Chem. 2, 100063 (2020)
- [4] I. Corrêa *et al.*, Sustain. Chem. 2, 286–324 (2021)
- [5] R.P. V. Faria *et al.*, Ind. Eng. Chem. Res. 61, 14531–14545 (2022)
- [6] I. Corrêa *et al.*, Ind. Eng. Chem. Res. Process. 61, 4017–4030 (2022)

#### Team

**Alírio E. Rodrigues** Emeritus Professor; **Ana M Ribeiro** Assistant Professor; Rui P. V. Faria Junior Researcher; Jonathan C. Gonçalves Junior Researcher; Isabella Corrêa *Ph.D.* Student; Miguel N. Moreira, Project Researcher; Bruno Castro *M.Sc.* Student; Carolina Viveiros *M.Sc.* Student

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## Process Intensification

# Liquid Phase Sorption Enhanced Reaction Process

## Simulated Moving Bed Reactor: Isomerization and separation of Xylene Isomers

**KEYWORDS:** Xylenes / Simulated Moving Bed Reactor / Isomerization / Adsorption / Zeolites

The isomerization of xylenes was studied over different zeolites (MFI, BEA, MOR) with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. These experiments were performed between 453 and 513 K at 2.1 MPa to guarantee liquid-phase conditions. Mordenite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 40 exhibited the best performance.

The adsorption of xylenes was studied in the absence of water to assess the adsorption equilibrium properties.

The Langmuir model was applied to describe the adsorption equilibrium data and the estimated parameters predicted very well the equilibrium in the adsorbent.

### Introduction

Xylenes are a group of aromatic compounds widely used in the chemical industry, as its isomers, *ortho* (*o*), *meta* (*m*), and *para* (*p*), are used as intermediates of various compounds. Regardless of the raw material used, the production of xylenes generally results in an equilibrium mixture of isomers.

The separation of xylene isomers is considered one of the seven world-changing separations and the complexity of this separation is related to their similar physicochemical properties, preventing their separation by conventional methods, such as distillation. The most valuable isomer, *p*-xylene, can be recovered by adsorption, in a SMB unit. Normally, for the separation of *p*-xylene from the other  $\text{C}_8$  aromatics, the solid phase of the SMB unit is a faujasite-type zeolite, X or Y, exchanged with alkali and/or alkaline earth metal ions, such as barium or potassium.

### Current Development

The kinetics of xylene isomerization was studied over two beta zeolites with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of 35 (BEA35) and 38 (BEA38). The isomerization reactions were carried out under the following conditions: 513, 493, 473, and 453 K at 2.1 MPa in the liquid phase. It was verified that all reactions were in the kinetic-controlled regime. Kinetic constants were estimated with four different models; two of them were based on the xylene isomerization thermodynamic equilibrium from the literature. The linear reaction scheme, which does not consider the direct conversion between *p*- and *o*-xylene, presented a better fit to the experimental values. A 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. Finally, activation energies over the two catalysts, estimated through the Arrhenius equation, presented similar values.

The isomerization of xylenes was also studied in the liquid phase at 513 K over three MFI-type, two MOR-type, and one BEA-type zeolite with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios. The catalysts were characterized through several techniques to assess their textural and acidic properties. The experiments consisted of 3 ml/min ( $5 \times 10^{-8} \text{ m}^3/\text{s}$ ) of *m*-xylene fed to a fixed-bed column at 2.1 MPa to maintain liquid-phase conditions for 25-30 h. MFI-type zeolites showed high selectivity towards *p*-xylene and long stability, but *m*-xylene conversions were below 5%. Large-pore zeolites exhibited significantly higher conversion but faster deactivation due to secondary reactions. MOR-type zeolite with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 40 showed the best performance with a *m*-xylene conversion of 45.3% with only 1.9% of secondary products.

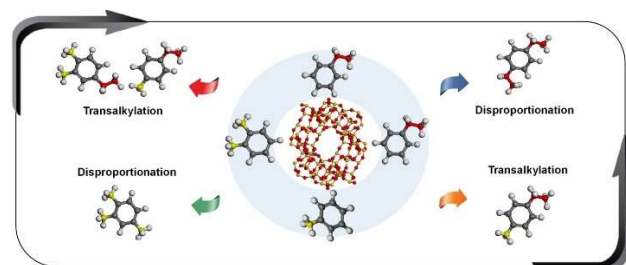


Fig 1. Xylene isomerization and side reactions within zeolite catalysts.

The isomerization reaction may occur simultaneously with side reactions such as transalkylation, where toluene and trimethylbenzenes or even benzene and tetramethylbenzenes can be formed. An experimental and parametric behavior study of disproportionation and transalkylation between  $\text{C}_8$  aromatics and toluene was carried out over the mono-functional acid Beta zeolite with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 35 (BEA35). The experiments 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; therefore, the kinetics of both reactions were estimated. Both reactions were verified to be second-order with no signs of competition for the adsorption sites under the studied conditions. Additionally, ethylbenzene disproportionation and ethylbenzene-toluene transalkylation, undergo through a deethylation-ethylation mechanism, the activation energies were 66 and 57 kJ/mol respectively. Furthermore, the existence of parallel reactions, as well as the feed concentration, showed no effect on the *p*-diethylbenzene selectivity. Selectivity towards the *para*-isomer was observed only at very low conversions. Finally, an analytical solution was developed for the system showing excellent agreement with the experimental data.

The adsorption of  $\text{C}_6$ - $\text{C}_8$  aromatics was investigated at higher temperatures than normally used in the industry in the absence of water to assess the adsorption equilibrium properties under conditions that can be suitable for a simulated moving-bed reactor for the production of *p*-xylene. Batch experiments were conducted on a dry Ba-exchanged zeolite X at various temperatures in the liquid phase. Pseudo-single-component adsorption equilibrium isotherms from binary mixtures with *i*-octane were obtained based on the adsorbed amount with different initial concentrations. The Langmuir model was applied to describe the adsorption equilibrium data. The estimated parameters predicted very well the equilibrium in the adsorbent.

A Simulated Moving Bed Reactor (SMBR), comprising a homogeneous mixture of adsorbent and catalyst, can overcome the equilibrium constraints in the production of *p*-xylene (PX). In this proposal, toluene and benzene were respectively considered as desorbent in the process. The arrangement of columns and optimum operating conditions such as switching time and flow rates that lead to maximum *p*-xylene productivity and minimum desorbent consumption were determined. Several constraints, including maximum pressure drop per bed and purity, were considered. Additionally, the operating temperature was optimized for the first time taking

into account the energy consumption within the associated distillation columns; the heat integration involving the distillation columns was also discussed. Finally, toluene showed better performance than benzene as desorbent. For the best case studied, the optimized temperature was 540 K. Moreover, an increase of about 25% in the recovery of PX, compared to the conventional Simulated Moving Bed, was obtained.

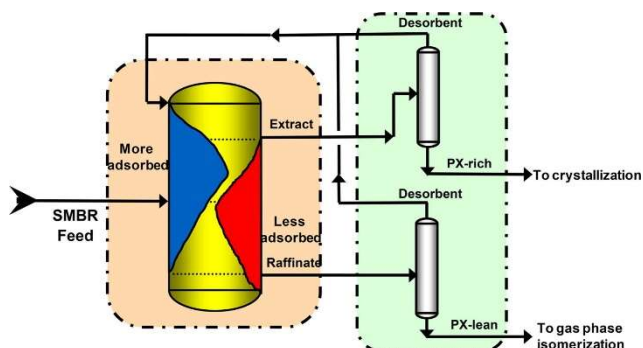


Fig 2. SMBR unit scheme.

The minimum cross diameter of organic species is highly important in catalyst and adsorbent design. In the aromatics industry, the size of the desired compound is the cornerstone of the commonly known shape-selective processes. In spite of the paramount importance of the said sizes, information in the literature is scarce and inconsistent. A thorough methodology was developed using the commercial software ChemBio3D Ultra. The minimum cross diameter of 21 aromatic compounds was calculated including benzene, toluene, ethylbenzene, xylene isomers, ethyltoluene isomers, diethylbenzene isomers, ethylxylene isomers, and trimethylbenzene isomers.

The global *p*-xylene market has demonstrated positive growth thanks to increasing demand for polyester fibers in the textile industry. Additionally, the chemical process becomes a target for energy efficiency; thus, process improvement and intensification have increasingly gained the attention of the scientific community. This article summarizes the advances in the production and separation of xylene isomers. An overview of the aromatics complex is displayed followed by a detailed description of the *p*-xylene production and separation processes. It summarizes the improvement of the catalysts, adsorbents, advanced materials; processes that strengthen the performance of the existing units, membrane-based processes, and alternative sources in past years. Special attention is given to the Simulated Moving Bed technology for separation; the flushing strategies and model development studies are also addressed. Attention has also been given to the process intensification and the unit combination with other aromatic technologies. A brief review of the latest results of Simulated Moving Bed Reactor and heat integration is also included. In summary, process intensification and integration are promising to save energy and costs, and it also allows flexibility within the feeds and intermediate products, maximizing the advantages of each process.

## Future Perspectives

Development of a Simulated Moving Bed Reactor (SMBR) process for the production of *p*-xylene, employing a hybrid particle composed of both the adsorbent and the catalyst that will be used in a sorption-enhanced reactive process to maximize the isomers conversion and the selectivity towards *p*-xylene. The adsorbent is a faujasite-type zeolite exchanged with both barium and potassium, and the catalyst is zeolite mordenite.

## Related Sustainable Development Goals



## Outputs

### PhD Theses

- [1] Qian Shi, New Processes and Adsorbents for *p*-Xylene production, PDEQB, FEUP, 2019
- [2] Bruno Alexandre Carvalho de Castro, Simultaneous Adsorption and Reaction of Xylenes, PDEQB, FEUP, ongoing

### Master Dissertations

- [1] Marcelo F.T. Oliveira, Xylene isomerization studies over acid catalysts in the liquid phase, MIEQ, FEUP, 2019

### Selected Publications

- [1] Q. Shi et al., *Ind. Eng. Chem. Res.* 57, 5568–5579, (2018)
- [2] Q. Shi et al., *Appl. Catal. A-Gen* 562, 198–205 (2018)
- [3] J. C. Gonçalves et al., *Chem. Eng. Technol.* 42, 1169–1173 (2019)
- [4] Q. Shi et al., *Chem. Eng. Technol.* 42, 2410–2418 (2019)
- [5] Q. Shi et al., *Chem. Eng. Sci.* 225, 115802 (2020)
- [6] Q. Shi et al., *Chem. Eng. Process.* 169, 108603 (2021)
- [7] J. C. Gonçalves et al., *The Canadian Journal of Chemical Engineering* 100, 3367–3380 (2021)

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## Process Intensification

# Liquid Phase Sorption Enhanced Reaction Process

## PermSMBR: Production of Acetals and Esters

**KEYWORDS:** Organic compounds / Hybrid processes / Membranes / Sorption enhanced reaction / Adsorption

**Chemicals derived from equilibrium-limited reactions represent a huge challenge mainly from the process sustainability point of view. Usually, high temperatures are required to reach reasonable kinetic rates and interesting yields. Therefore, other alternatives must be investigated to attain competitive yields from the industrial point of view, reducing the energy required through process intensification strategies. In this work, a novel approach is presented by combining pervaporation and sorption-enhanced reactive processes, the simulated moving-bed membrane reactor (SMBR), also known as PermSMBR. Butyl acrylate takes special advantage of such a process because its kinetics is limited and it is sensitive to high temperatures.**

### Introduction

Over the last decades, PI is a subject that has been explored in chemical engineering research, being the key to finding new paths towards more sustainable processes allowing a more efficient answer to the market demand for some products of industrial interest. Multifunctional reactors, where reaction and separation steps are integrated into a single equipment, usually known as reactive separations, are one of the most relevant examples of PI. This concept leads to smaller, cleaner, and more energy-efficient processes since the reaction and separation take place simultaneously. Furthermore, it allows overtaking the equilibrium limitations by removing one of the products continuously, which improves the reaction conversion.

The PermSMBR is a novel multifunctional reactor that emerged from the integration of the SMB technology with hydrophilic membranes, also known as a simulated moving bed membrane reactor. According to the literature, this new hybrid technology enables improved water removal in a continuous process, using different separation techniques simultaneously (adsorption and pervaporation). It was investigated for acetals and green solvents production leading to higher productivity and lower eluent consumption than SMBR.

As a case study for validating the PermSMBR, Butyl Acrylate (BAC) was selected due to the numerous global market studies that have predicted a considerable growth in its demand for long forecast periods. BAC is usually obtained from an esterification reaction between acrylic acid (AAc) and n-butanol having water as by-product. However, its conventional production involves a complex multistage process with homogeneous catalysis. Therefore, the downstream separation represents high operating and investment costs. Besides, the reaction kinetics is limited, but it cannot rely on high temperatures to improve the performance, as it is sensitive to it. The PermSMBR is known to improve the process performance while operating in mild conditions.

### Current Development

To develop a PI technology based on the membrane SMBR, initially, the dynamic study of the BAC synthesis in a fixed-bed membrane reactor (FBMR) must be performed, since this is the elementary unit of the PermSMBR. The experiments were performed using Amberlyst-15 ion exchange resin (A-15) simultaneously as a catalyst and as an adsorbent and a hydrophilic pervaporation membrane, for which experimental

pervaporation data are measured in the absence of reaction using a pilot scale unit. In this step, one determines the best operating conditions required to implement a PermSMBR process. Furthermore, a mathematical model able to describe the synthesis of BAC in an FBMR is developed and validated by reactive adsorption experiments conducted under different operating conditions.

A similar procedure is followed to develop the process in a conventional SMBR for comparison purposes. The synthesis of BAC in an SMBR is numerically investigated by developing a mathematical model taking into account the kinetic and multicomponent adsorption equilibrium data previously determined. The experimental BAC synthesis in a pilot scale SMBR unit (LICOSEP) is also performed for validation of the mathematical model. With the model validated, an optimization study is performed to determine the ideal operating conditions and the resultant data enables to proceed to the scale-up of the unit (SMBR) to industrial scale (IS) assessing its viability, and comparing it with other alternative processes proposed in the open literature.

The resultant composition profiles were analyzed showing great performance parameters, a reaction conversion of 99.5 % was obtained with extract and raffinate purities of 99.3 % and 99.8 %, respectively. The effects of configuration and switching time on the performance parameters were studied, concluding that the ideal parameters are 3.1 min as switching time and 2-4-4-2 as the configuration of the SMBR.

Finally, the PermSMBR process study for BAC synthesis is numerically investigated under different operating parameters, and the ideal operating conditions are described. For that, a complex mathematical model is developed considering all pervaporation, adsorption, and kinetic data used in the FBMR study. An optimisation study is carried out by studying different configurations and the respective performance is evaluated. The PermSMBR unit is scaled up to the industrial scale to assess its feasibility and to compare it with SMBR performance.

An optimization study was performed by studying the effect of the switching time and the ratios between the liquid and solid velocities in the critical PermSMBR sections (sections 1 and 4). Further optimization was attained by reducing the unit from 4 to 3 sections eliminating the extract stream (3-section integrated PermSMBR). The maximum performance of the reactor was achieved with a configuration 4-6-2 (columns per section) and a switching time of 4.0 min at 363 K. Comparatively to the SMBR performance, the productivity increased 36% and the desorbent consumption was reduced 98%.

Concerning the scale-up of the PermSMBR, the most suitable scenario comprises the use of a distillation column top stream as part of the feed solution to the PermSMBR-3s unit (Figure 1), leading to a recovery of 100% of n-butanol. Hence, the productivity increased 49% and the desorbent consumption reduced by 56% compared to the SMBR at the same scale and after eluent recovery.

A brief economic analysis also proved the viability of the PermSMBR for BAC production, once its marked reference price was reduced by 36% following this production strategy.

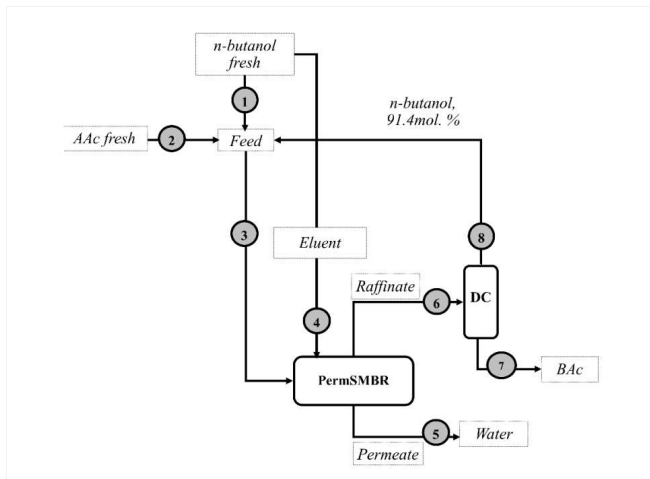


Fig 1. Configuration for eluent recycle using the top stream of the distillation column as part of the feed solution to the PermsMBR-3s unit

### Future Perspectives

Although promising results were attained with the different SMBR-based process intensification strategies proposed by this work for the synthesis of butyl acrylate, there is still a long way to go toward a real sustainable and competitive industrial process. Some topics must be deeply investigated to clarify some assumptions and/or complement some research lines that can lead to a better understanding of the results obtained. Hence, some suggestions for future work are:

- i) The deactivation of the catalyst/adsorbent must be investigated since it is known that the economic viability of a process depends, among several factors, on the catalyst life cycle. Moreover, tests of membrane stability in long-term operation are recommended to check the materials compatibility (including catalyst and membrane coating);
- ii) Experimental runs must be performed in the pervaporation membrane reactor (single unit) under batch conditions in order to validate the mathematical model developed;
- iii) As mentioned previously, the influence of the resin shrinking combined with the high viscosity of the eluent used (n-butanol) on the SMBR performance can be mitigated by using special fixed-bed columns with dynamically adjustable pistons in order to avoid the creation of voids in the bulk during the operation. This can help to reduce the dispersion observed in the concentration profiles inside the reactor, increasing its performance. In this way, experimental runs, using these sorts of columns in the SMBR at pilot scale unit should be performed and the dispersion effect re-evaluated; Another alternative would be to perform some adaptations to the unit in order to mitigate the dispersion generated by the recycling line;
- iv) Additionally, SMBR design can be optimized using an objective function based on annual profit maximization, for instance, using more advanced optimization tools (genetic algorithms, particle swarm optimization, etc.).
- v) Finally, a study of alternative process integration configurations considering different downstream units can be investigated.

### Related Sustainable Development Goals



### Outputs

#### PhD Theses

[1] Dânia Sofia Martins Constantino, Process Intensification for Butyl Acrylate Synthesis based on Sorption-Enhanced Reaction and Pervaporation-based Hybrid Processes, PDEQB, FEUP, 2019.

#### Selected Publications

- [1] D.S.M. Constantino *et al.*, Ind. Eng. Chem. Res. 59, 7, 2817–2827 (2020)
- [2] D.S.M. Constantino *et al.*, J. Adv. Manuf. Process. 2:e10048 (2020)
- [3] D.S.M. Constantino *et al.*, Ind. Eng. Chem. Res. 60, 46, 16747–16755 (2021)

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