New sorption enhanced reaction technologies (SMBR and PermSMBR) for the production of diesel blends and green solvents

CARLA S.M. PEREIRA, ALÍRIO E. RODRIGUES*
*Corresponding author
Universidade do Porto, LSRE - Laboratory of Separation and Reaction Engineering - Associate Laboratory LSRE/LCM
Faculdade de Engenharia, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

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ABSTRACT
Chromatographic reactors, where reaction and separation processes are combined into single equipment, are a way of achieving better energy efficiency, productivity improvement and lower solvent consumption. In this perspective two innovative technologies are presented: the Simulated Moving Bed Reactor (SMBR) and the recently developed Simulated Moving Bed Membrane Reactor (PermSMBR). Potential applications for these technologies are addressed and their performance for the synthesis of some important oxygenates, such as acetals (1,1-diethoxyethane, 1,1-dibutoxyethane, 1,1-dimethoxyethane) used on diesel blends and ethyl lactate used as green solvent. Future challenges are highlighted.

INTRODUCTION
Traditionally, compounds involving equilibrium limited reactions (as acetals, esters, ethers, among others) are synthesized in a batch reactor fed with excess of one of the reactants and followed by various separation units (mainly energy-intensive distillation steps) in order to recover the desired product, to remove the by-product(s), and to recycle the unconverted reactants to the reactor, which represents high costs (Figure 1). Process intensification, regarding the integration of reaction and separation steps into a single unit, provides the most feasible engineering solution for sustainable synthesis of this type of compounds since the products are separated as they are formed overcoming by this way the equilibrium conversion, leading to higher yields and purities of the final products. In particular, chromatographic reactors have arisen substantial interest in the chemical engineering research and industry. The simplest way of operating a chromatographic reactor is in batch mode, which was patented in the early 1960s (1, 2). However, due to the drawbacks associated with a batch process such as low yields and high product dilution, over the last 40 years, research has been focused on the development of continuous chromatographic reactors. In this framework, two interesting technologies can be spotted for the sustainable production of oxygenated compounds: the Simulated Moving Bed Reactor (SMBR) and the Simulated Moving Bed Membrane Reactor (PermSMBR).

SMBR concept
The SMBR is implemented in the well-known, but non-trivial, Simulated Moving Bed (SMB) equipment patented in 1961 by Universal Oil Products (UOP)(3) and commercialized for a number of large-scale separations in petrochemical industries (Parex, Molex, Olex) and sugar industry (Sarex). It consists in a set of fixed bed columns arranged in a closed circuit and packed with an adsorbent with catalytic properties or a mixture of adsorbent and catalyst particles. The SMBR standard configuration comprises two inlet streams (feed and desorbent) and two outlet streams (extract and raffinate), which are continuously moved from one bed to the next one, at regular time intervals called the switching time, in the fluid direction. By this way a counter current contact between the solid and liquid phases is simulated. If the feed comprises two reactants (A and B), in which, say A, is used as desorbent, and A and B react to give two products, C and D, the latter being more adsorbed than the former, then a mixture of D+A is obtained in the extract and a mixture of C+A is obtained in the raffinate. This is the SMBR principle. The inlet/outlet streams divide the unit into four different sections, each one with a fixed number of columns and having a specific role: section I, between desorbent and extract nodes, where the solid is regenerated by desorption of the most adsorbed product [D] using the desorbent [A]; section II, between the extract and feed nodes and section III, between the feed and raffinate nodes, where the reaction takes place and the formed products are separated; section IV, between the raffinate and desorbent nodes, where the desorbent [A], before being recycled to section I, is regenerated by adsorption of the less retained product [C]. In Figure 2, a schematic representation of a SMBR unit is presented.
SUSTAINABILITY/GREEN CHEMISTRY

APPLICATIONS

**SMBR applications**

The SMBR is particularly interesting when the species involved in the production of the desired product exhibit small volatility differences, are non-volatile or are sensitive to temperature, as it uses differences in the adsorptivity of the different components involved rather than differences in their volatility as is the case of Reactive Distillation.

Diethylacetal or 1,1-diethoxyethane (DEE) synthesis is one of the best examples where the use of the SMBR seems the best choice, since the reactive mixture involved in the production of DEE exhibits three binary azeotropes (ethanol/water, ethanol/DEE and DEE/water) and one ternary aze trope (ethanol/water/DEE). Indeed, the DEE synthesis via SMBR technology was the first process that uses an SMB based technology for the production and separation of acetal by means of ion-exchange acid resins (5, 6). An SMB unit was used for technology demonstration and consisted in 12 columns packed with the ion exchange resin Amberlyst-15 (A15). This resin has the ability to act simultaneously as catalyst and selective adsorbent to water (by-product on DEE synthesis). Ethanol, which is one of the reactants, was also used as desorbent and, therefore, it was fed in the desorbent stream and in mixture with acetaldehyde in the feed stream. Water is the most adsorbed species onto the A15 resin while DEE is the less adsorbed one, and thus water and DEE were obtained in the extract and raffinate streams, respectively, both diluted into the desorbent (ethanol). Almost complete conversion of acetaldehyde (99.8%) and 99% pure DEE (ethanol free basis) were obtained (5). The ethanol from the extract can be dehydrated in a commercial membrane process with purity of 99% and recycled to the SMBR, representing a 50% reduction in energy costs when compared with traditional distillation processes. DEE from the raffinate can be separated by distillation, obtaining pure DEE and an azeotropic mixture of ethanol/DEE which can be recycled to the SMBR, avoiding the use of solvents to break the azeotrope and the associated solvent distillation costs. In Figure 5 a schematic representation of a SMBR based production plant for DEE synthesis is shown.

PermSMBR concept

The PermSMBR is a recently developed hybrid technology (4) that combines the SMBR with membranes. Its principle of operation is similar to the one of the SMBR; however, in the PermSMBR, each column contains a set of tubular membranes that are permeable to one of the reaction products - integrated PermSMBR (Figure 3) or each SMBR column is followed by a membrane module - coupled PermSMBR (Figure 4). Depending on the configuration, the solid (catalyst with adsorptive properties) or the mixture of solids (catalyst and adsorbent) are packed in the membranes (integrated PermSMBR) or in the columns (coupled PermSMBR). Besides, another stream is collected: the permeate stream that combines all the flows removed through the membranes. The permeate is rich in the product for which the membranes are selective. As in the SMBR, the typical PermSMBR contains 4 sections with the same functions as the ones previously described; however, in the PermSMBR case the permeable product is continuously removed in all sections, enhancing the solid/desorbent regeneration (section I/section IV) and the reaction conversion (section II and III). Depending on the system, different membrane processes can be applied as microfiltration, ultrafiltration, vapour permeation, pervaporation, among others.

These promising results led to the implementation (by our group) of the SMBR technology for the production of other acetals, 1,1-dimethoxyethane (DME) (7) and 1,1-dibutoxyethane (DBE) (8), and an ester, ethyl lactate (9). The products were selected due to their potential applications. Acetals have found to be promising oxygenates to be used on diesel blends due to...
their ability to reduce emissions, mainly of particulate matter, without causing serious penalties on nitrogen oxide (NOx), unburned hydrocarbon and carbon monoxide emissions and keeping or even improving the cetane number. Particularly, DEE has shown interesting results when blended into diesel fuel: 10% of DEE added to diesel has reduced the particulate matter and NOx emissions by 34.6% and 3.2%, respectively, from fuel combustion, decreasing additionally the net contribution of CO2 emissions by 6.4%[10]. 20% (V/V) DBE blended with a commercial diesel increased its cetane number from 55 to 58[11]. Ethyl lactate is an important green solvent that could replace a range of environment-damaging halogenated and toxic solvents[12]. Some industry experts suggest that ethyl lactate could replace the traditional solvents by more than 80% of their applications[13]. However, this is probably highly inflated, since ethyl lactate is a high boiling polar protic solvent[14] and there are applications where non-polar, aprotic and/or lower boiling point solvents are required.

The production by SMBR, for all the mentioned compounds, was experimentally validated, which demonstrates the reliability of this technology for the production of green fuels and solvents (an important and emerging market). In the open literature, other SMBR applications can be found as for instance the production of bisphenol-A[15], methyl acetate[16], fructose[17], MTBE[18] among others. However, to the best of our knowledge, the SMBR is not yet an established technology from the industrial point of view as is the case of the SMBR for the production of active pharmaceutical ingredients (APIs), sugars and xylenes.

The major SMBR limitation is, for the most of the studied systems, the high desorbent consumption, which is caused by the high affinity of the resins used towards water. High desorbent consumptions to regenerate the resin in section I leads to more diluted products that obviously increases the costs associated with the subsequent separation units to obtain the products with the desired purity. One way of overcome the high resin affinity to water is decreasing its sulfonic groups; however, it should be kept in mind that this procedure decreases the catalytic activity detrimentally affecting the productivity. Moreover, the selectivity between the product/product and between the reactant-product can also be affected jeopardizing the efficiency of the SMBR tasks in the sections 2, 3 and 4[19]. All these effects should be considered when re-designing the resin properties in order to have the best SMBR performance. The use of new materials with potentially better characteristics for both reaction and adsorption might be an alternative that should be explored, as carbon-based catalysts. The use of two solids (catalysts/adsorbents) can also be an option. These solutions (tailor made resins, new materials, ...) will lead to more competitive SMBR based processes which, together with the easy scale up of this type of units will certainly motivate the SMBR industrial implementation.

PermSMBR applications
The PermSMBR by combining two separation processes (adsorption and membranes) with reaction has the potential to produce at a higher yield and purity a product C and a by-product D obtained by: (1) equilibrium-limited reactions (as example A+B <-> C+D), where conversions of 100% can be achieved due to displacement of the equilibrium by continuous removal of the products (D in the extract, C in the raffinate and additionally one of them is also collected in the raffinate by using an appropriate membrane); (2) parallel and sequential reactions (as example A+B ->C; B+C- >D), where the selectivity to component C is enhanced by using a selective membrane to component C, therefore C is collected both in raffinate and retentate, and D is collected in extract.

The PermSMBR technology was not yet experimentally tested. However, its integrated concept (Figure 2) was theoretically evaluated for the synthesis of ethyl lactate (EL), DEE and DBE, using mathematical models that strongly rely on experimental data (the SMBR for the production of EL, DEE and DBE, and the pervaporation performance of the compounds involved in their synthesis were already experimentally assessed)[20, 21]. In all cases, the PermSMBR reveals a high performance with high productivity and low solvent consumption which proves this technology potential for the sustainable synthesis of oxygenated compounds even when compared with other intensified processes. For example, for an EL productivity of about 16 KgEL/(Lresin·day), at 50°C, the SMBR ethanol consumption is 165 % higher than that of the PermSMBR. A reactive distillation process at 128°C (bottom temperature) requires a larger amount of ethanol by 152 % than the PermSMBR at 70°C, for a productivity of about 41 KgEL/(Lresin·day)[20]. When compared with the SMBR, in addition to the lower solvent consumption that leads to higher purity of the products, the major PermSMBR advantage is that it is possible (and most of the times convenient) to, depending on the permeable product (if it is the most or the less adsorbed), eliminate the extract or the raffinate stream, which means that one less separation step will be required within the overall flowsheet. For instance, in the DBE production, water selective membranes were employed and so it was possible to eliminate the extract stream (Figure 6). Besides one less stream to be treated (to separate the product and recycle the desorbent) this led to a significant reduction on the solvent consumption: 77 % less consumption of n-butanol used as desorbent when compared with the PermSMBR operated with both extract and raffinate streams[21].

In tables 1 and 2, a summary of the best performance parameters obtained for both SMBR and PermSMBR technologies, at 50°C and 70°C, respectively, is presented, for all the studied systems. In overall, the PermSMBR leads to a better performance than that of the SMBR; however, at 50°C, the improvement is more evident for the production of EL and DEE. At 70°C, a larger amount of water is removed through the selective membranes (due to the higher driving force), which (as expected) enhances the PermSMBR performance. Moreover, this large quantity of water removal by the membranes allows eliminating the extract stream. Therefore, in spite of the temperature increase from 50 to 70°C, the overall downstream separation costs will be significantly lower, and thus the PermSMBR operated without extract stream (PermSMBR-3s) seems to be the most feasible PermSMBR configuration for the production of these oxygenated compounds.

![Figure 6. PermSMBR process scheme for DBE production.](image-url)
sense that the concept was already proved and tested for the production of different oxygenates through lab prototypes although not yet implemented at industrial scale.

REFERENCES AND NOTES


CONCLUSIONS

Both SMBR and PermSMBR technologies are interesting options for the sustainable synthesis of oxygenated compounds involving equilibrium limited reactions. The PermSMBR leads to better results, but it requires higher capital and operational costs. An economical evaluation must be done in order to assess if the higher productivities and lower solvent (desorbent) consumptions compensate the higher investment when compared with the SMBR. Besides, the PermSMBR is a young technology and its proof-of-concept is still missing, which is crucial in order to demonstrate its feasibility. One of the PermSMBR major challenges is the development of stable membranes under acidic conditions, which might be overcome by using the coupled set-up instead of the integrated one. The SMBR is a mature technology in the