

## PermSMBR - A new hybrid technology: application on a green fuel production

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### Introduction

Diesels have to further reduce their emissions to meet the everyday more severe emission legislations. The use of oxygenated biofuels offers the possibility of reducing emissions dramatically, mainly particulate matter emission, without causing serious penalties on NO<sub>x</sub>, unburned hydrocarbon (UHC) and carbon monoxide (CO) emissions. Acetals are recognized as green fuels to be blended in diesel[1], as the acetaldehyde dibutyl acetal (DBE). The DBE synthesis involves equilibrium limited reaction between butanol and acetaldehyde (renewable chemicals) catalysed in acid medium, having water as by-product. The conversion of this reaction is limited by the chemical equilibrium and in order to obtain higher DBE yields it is necessary to shift the reaction towards products formation. Therefore, the use of multifunctional technologies, where reaction and separation take place into a single unit, will be valuable for the DBE production, since by removing one of the products from the reaction zone (usually the water), the equilibrium limitation can be overcome and the conversion can be driven to completion. One of the most important multifunctional technologies is the Simulated Moving Bed Reactor (SMBR), which was already successfully applied for the synthesis of acetals [2-4]. This technology has several advantages, as the ones wellknown for reactive separation processes; however, it also suffers from some drawbacks, as products dilution with the desorbent, which needs to be then separated and recycled to the SMBR unit, and the necessity of using very pure raw materials. In order to overcome these issues, a new hybrid technology, the Simulated Moving Bed Membrane Reactor (PermSMBR), in which the SMBR is integrated with membranes, was recently developed (Figure 1) [5-6]. In the PermSMBR, the products are not only separated by adsorption but also through the perm selective membranes.

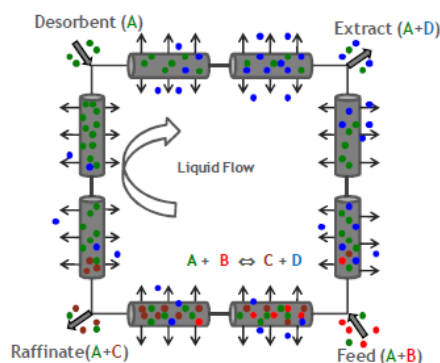


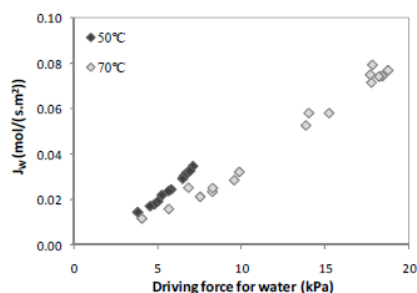
Figure 1: Schematic representation of a PermSMBR unit.

In this work, the DBE production will be implemented using the PermSMBR technology. In order to do that as well for improving the performance of the overall PermSMBR process it is needed a clear and quantitative understanding on kinetic reaction, adsorption and permeation performance. In previous works [7-8] a detailed kinetic and adsorption study was carried out for the DBE system using a heterogeneous ion exchange resin, the Amberlyst 15-wet, that acts as catalyst and selective adsorbent to water. In this work, the pervaporation process using commercial microporous silica water selective membranes (from Pervatech BV) was studied. A mathematical model was developed and applied in order to evaluate the PermSMBR performance and compare it with the one of the SMBR.

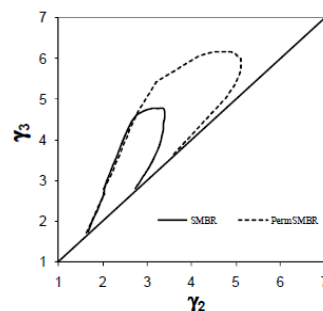
### Results and Discussion

In the absence of mass transfer limitations, the membrane performance was evaluated experimentally, at different compositions and at two temperatures, 50°C and 70°C, measuring the flux of each species in binary (water/butanol) and quaternary mixtures (water/butanol/acetaldehyde/DBE). In order to describe the permeation molar flux of each component through the membrane the solution-diffusion model [9] was applied:  $J_i = \frac{D_i}{l} (p_i - p_{i,perm})$ . In Figure 2, the water flux is plotted as a function of the water driving force for all the experiments at which the water content has been varied, at 50°C and 70°C. A linear pattern is observed, indicating a water permeance of  $4.43 \cdot 10^{-6}$  mol/(Pa.s.m<sup>2</sup>) @ 50°C and  $3.93 \cdot 10^{-6}$  mol/(Pa.s.m<sup>2</sup>) @ 70°C.

Regarding the remaining species, it was found that the butanol permeances are  $9.84 \cdot 10^{-9}$  mol/(Pa.s.m<sup>2</sup>) @ 50°C and  $6.48 \cdot 10^{-9}$  mol/(Pa.s.m<sup>2</sup>) @ 70°C, the acetaldehyde flux is negligible (permeance:  $7.9 \cdot 10^{-16}$  mol/(Pa.s.m<sup>2</sup>) @ 70°C), and that 1,1-DBE does not permeate through the membrane.



**Figure 2:** Water flux as a function of water driving force for different water contents on binary mixtures (water/butanol) and quaternary mixtures (acetaldehyde, butanol, 1,1-DBE and water).



**Figure 3:** Reactive/separation region for the SMBR and PermSMBR processes.

The permeation, kinetic and adsorption data were used in developed mathematical models to simulate the SMBR and PermSMBR processes for the DBE production. In Figure 3, the reactive/separation regions are presented for both processes at 50°C, calculated imposing a 95% criteria for DBE purity and for acetaldehyde conversion. In the PermSMBR, it is possible to process a higher feed flowrate (34.9 mL/min) than in the SMBR (29 mL/min), which represents an increase of about 21% in the DBE productivity that is accompanied by a considerable reduction in the butanol consumption.

Depending on the permeable product, the most/less adsorbed, it is possible to remove the extract/raffinate stream, leading to a PermSMBR with just 3 sections (PermSMBR-3s). In this case, the membranes are selective to water, and therefore, the PermSMBR unit was simplified from 4 to 3 sections, eliminating the extract stream. For the PermSMBR-3s it was noticed that at 50°C the permeation through the membranes was overloaded and the criteria of 95% purity was not achieved for a significant DBE productivity. Therefore, the PermSMBR-3s was evaluated at a higher temperature (70°C), in order to increase the water flux through the membranes, being now possible to obtain the same productivity that in the PermSMBR with 4 sections (64 kgDBE·Lresin<sup>-1</sup>·day<sup>-1</sup>), but with a desorbent consumption of just 0.21 LButanol/kgDBE, which is 90% smaller than the one needed in the PermSMBR at 50°C. The best performance obtained on the PermSMBR-3s, as well as, on the SMBR and PermSMBR processes is presented in Table 1.

**Table 1:** Performance parameters for SMBR and PermSMBR technologies.

	SMBR (50 °C)	PermSMBR (50 °C)	PermSMBR-3s (70 °C)
PR (kg <sub>DBE</sub> ·L <sub>resin</sub> <sup>-1</sup> ·day <sup>-1</sup> )	53.15	64.15	70.97
DC (L <sub>Butanol</sub> /kg <sub>DBE</sub> )	2.69	2.15	0.42

## Conclusions

The PermSMBR proved to be more effective than the SMBR having higher productivities and lower desorbent consumptions, for the same DBE purity and acetaldehyde conversion. The use of the PermSMBR with just 3 sections further improved the DBE production, decreasing drastically the butanol consumption as desorbent. The PermSMBR-3s is operated at higher temperature (70°C); however, besides the significant reduction on the desorbent consumption, in this operating mode, it is also eliminated one subsequent separation unit, since there will be no extract stream to be treated, contrarily to the SMBR and PermSMBR with 4 sections. The PermSMBR is a very interesting technology for the production of acetals, leading to higher productivities, less diluted products, and lower downstream costs associated to the separation units.

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