

A New Process Re-Intensification Strategy for Butyl Acrylate Production

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1. Introduction

Chromatographic reactors and reactive distillation are among the most common multifunctional reactors applied for equilibrium-limited reactions, as the esterification reaction for the butyl acrylate synthesis. Indeed, performing reaction and separation steps simultaneously in the same equipment enable to shift the equilibrium conversion by continuously removing one of the reaction products. Moreover, this process intensification strategy leads to design, safety and energy efficiency enhancements when compared with the conventional processes (reaction followed by separation). Apart from its thermodynamic limitations, the reaction between acrylic acid and n-butanol presents a very slow kinetics [1] and a high risk of polymerization [2], which is further promoted by the high temperatures used in reactive distillation, for instance. In this way, several studies have been performed aiming to find alternative processes to the conventional one, which comprises a homogeneous catalysed multistage process using two reactors and three distillation columns for the recovery of the reactants and the purification of the desired product [3]. However, most of them are based on reactive distillation technology.

According to our previous work [4], it is known that pervaporation significantly improves the reaction conversion by continuous water permeation under isothermal conditions. Therefore, the integration of reactive-adsorption technologies with hydrophilic membranes can be an attractive solution for the synthesis of butyl acrylate since water can be continuously removed by adsorption and permeation. Meanwhile, a recent technology involving a pervaporation-based hybrid cyclic process, also known as PermSMBR (simulated moving bed membrane reactor), was already applied for the synthesis of similar esters [5], showing a very promising performance. Its operating principle is very similar to the simulated moving bed reactor comprising packed membranes instead fixed-bed columns. The major difference between this technologies is the integration of reaction with two separation techniques (chromatography and pervaporation) leading to a more effective process with lower desorbent requirements.

In summary, the objective of this work was to study, for the first time, the PermSMBR technology for the synthesis of butyl acrylate at industrial scale and compare its performance with other alternatives presented in open literature.

2. Materials and Methods

In order to study the PermSMBR technology, a suitable choice of the membrane and catalyst/adsorbent materials is crucial. In this case, Amberlyst-15 ion exchange resin and commercial tubular inorganic membranes were considered. A mathematical model was developed and implemented in gPROMS software taking into account reaction, adsorption and pervaporation fundamental data available in the literature [1, 4, 6]. The PermSMBR was optimized in order to maximize the BAc productivity and minimize the consumption of butanol, simultaneously used as eluent and reactant in the process. The optimization was based on the determination of the respective reactive-separation regions.

3. Results and Discussion

Several simulations were performed considering different operating parameters and the respective reactive separation regions were determined. Through the optimization procedure it was possible to conclude that the maximum operating point was reached considering 3 sections PermSMBR unit, with a configuration of 4-6-2 (packed membrane modules per section) resulting from the elimination of the extract stream since water is removed by permeation through the membranes along the reactor. Afterwards, a distillation column was considered as downstream unit, for raffinate stream treatment purposes, for the process integration study at industrial scale with an eluent recovery strategy, which comprises the use of the distillation column top stream as part of the feed solution of the 3-sections integrated PermSMBR unit leading to 100 % n-butanol (eluent) recovery.

A comparison of the performance parameters attained in this work with those obtained in the process intensification strategies presented in open literature can be observed in Table 1. Although the enhanced SMBR (fixed-bed reactor coupled with a SMBR unit) allows to achieve higher productivity, PermSMBR- 3 sections is the process that presents the lowest eluent consumption (with a reduction of 56 % and 60 % relatively to the conventional SMBR and enhanced SMBR, respectively) and the lowest energy requirement per kg of product, since it is able to remove water more effectively.

Table 1. Performance parameters resulting from different process intensification strategies with eluent recovery at industrial scale.

Process	Conventional SMBR [7]	Enhanced SMBR [8]	PermSMBR- 3 sections
Butyl Acrylate Purity (%)	99.7	99.5	99.6
Productivity ($\text{kg}_{\text{BAC}} \cdot (\text{L}_{\text{ads}}^{-1} \cdot \text{day}^{-1})$)	7.25	11.8	10.7
Eluent Consumption ($\text{L}_{\text{n-butanol}} \cdot \text{kg}_{\text{BAC}}^{-1}$)	1.00	1.11	0.44
Energy Consumption ($\times 10^3$) ($\text{kJ} \cdot \text{kg}_{\text{BAC}} \cdot \text{Y}^{-1}$)	1.80	1.85	1.18

3. Conclusions

A novel process intensification approach for the synthesis of butyl acrylate was investigated focusing on a pervaporation and sorption enhanced reaction based cyclic processes, the Simulated Moving Bed Membrane Reactor, also known as PermSMBR.

After the process integration study and eluent recovery at industrial scale, PermSMBR- 3 sections demonstrated to be the most effective process, presenting the lowest eluent consumption and energy requirement per kg of product (butyl acrylate).

References

- [1] A.M. Ostaniewicz-Cydzik, C.S.M. Pereira, E. Molga, A.E. Rodrigues, *Ind. Eng. Chem. Res.* 53 (2014) 6647-6654.
- [2] A. Niesbach, J. Daniels, B. Schröter, P. Lutze, A. Górak, *Chem. Eng. Sci.* 88 (2013) 95-107.
- [3] A. Niesbach, R. Fuhrmeister, T. Keller, P. Lutze, A. Górak, *Ind. Eng. Chem. Res.* 51 (2012) 16444-16456.
- [4] D.S.M. Constantino, R.P.V. Faria, A.M. Ribeiro, J.M. Loureiro, A.E. Rodrigues, *Ind. Eng. Chem. Res.* (2017).
- [5] V.M.T.M. Silva, C.S.M. Pereira, A.E. Rodrigues, *AIChE J.* 57 (2011) 1840-1851.
- [6] D.S.M. Constantino, C.S.M. Pereira, R.P.V. Faria, A.F.P. Ferreira, J.M. Loureiro, A.E. Rodrigues, *AIChE J.* 61 (2015) 1263-1274.
- [7] D.S.M. Constantino, C.S.M. Pereira, R.P.V. Faria, J.M. Loureiro, A.E. Rodrigues, *Chem. Eng. Process.* 97 (2015) 153-168.
- [8] D.S.M. Constantino, R.P.V. Faria, C.S.M. Pereira, J.M. Loureiro, A.E. Rodrigues, *Ind. Eng. Chem. Res.* 55 (2016) 10735-10743.