SIMULATED MOVING BED REACTOR PROCESSES FOR THE INDUSTRIAL PRODUCTION OF BUTYL ACRYLATE

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Abstract

The present work aims the development of alternative processes to produce 50,000 ton/year of butyl acrylate with an assay of 99.5%, taking advantage of the potential of the simulated moving bed reactor (SMBR) technology. In a first approach, a SMBR unit was used to simultaneously synthesize and separate the reaction products together with a distillation column to purify butyl acrylate and a pervaporation module to recycle the desorbent (butanol). Compared to the current industrial process the number of unit operations was reduced as the energy consumption was decreased significantly. An additional process was design in which a fixed bed reactor was introduced before the SMBR to extend the reactants conversion. This modification resulted in a significant improvement of the overall process performance, leading to an increase in the productivity of approximately 40% and in a decrease of the energy demand around 30%.

Keywords

Butyl Acrylate, Simulated Moving Bed Reactor, Process Intensification

Introduction

Butyl acrylate is an important building block for the chemical industry; however, its conventional production process is very complex and energy demanding. It comprises a series of two homogeneously catalyzed reactors operating at temperatures above 100 ºC and three distillation columns to purify the product.

Multifunctional reactors have demonstrated to be one of the most effective process intensification strategy to overcome the constraints of equilibrium limited reactions as the esterification reaction for the synthesis of butyl acrylate. Hence, Niesbach et al. (2013) suggested the use of a reactive distillation column as an interesting alternative to the conventional butyl acrylate production process. In fact, the authors reported a reduction of 10% in the total process cost and, if a decanter was coupled with the reactive distillation column, the costs would decrease over 35%. Despite the advantages of these processes, the existence of multiple azeotropes and the high risk of polymerization at the operating temperature might hindered its industrial implementation. Our proposal to overcome these issues is the use of a simulated moving bed reactor (SMBR) in this process (using Amberlyst-15 as catalyst/adsorbent), since this multifunctional reactor has successfully been applied to the synthesis of similar esters (Pereira et al., 2009).

Results and Discussion

To develop a SMBR process one must have accurate fundamental reaction and adsorption data. For the studied system this information is available in the open literature and reports that the reaction rate follows a Langmuir-Hinshelwood-Hougen-Watson mechanism (Ostaniewicz-Cydzik et al., 2014) and the multicomponent adsorption can be described by a competitive Langmuir model (Constantino et al., 2015). Considering this, a mathematical model (similar to the described by Pereira et al. (2009)) was developed and experimentally validated. The optimization of the SMBR units within this work was performed based on an initial guess obtained through the equilibrium theory followed by the determination of the reactive-separation regions using the previously mentioned model.

By setting as goal the design of an industrial process capable of producing 50,000 ton/year of butyl acrylate (capacity reported for the BASF plant located in Freeport, Texas) with a purity of 99.5%, it was possible to dimension the SMBR. The unit should then be constituted by 12 columns, with 0.62 m length and a radius of 2.23 m each. Moreover, as previous investigations (Constantino et al., 2015) have reported, high residence times are required to reach the esterification reaction equilibrium conversion at 363 K hence, a SMBR with an enlarged reactive zone must be adopted. Considering a 2-4-4-2 configuration, an equimolar feed mixture of butanol and acrylic acid and using pure butanol as eluent, at optimal conditions, these SMBR presents a productivity of 7.2 $kg \cdot L_{ads}^{-1} \cdot day^{-1}$ and an eluent consumption of 27.5 $L \cdot kg_{Prod}^{-1}$. At this point two complementary separation units were dimensioned and added to the process, as presented in Figure 1: a distillation column to separate the remaining reactants from the butyl acrylate of the raffinate stream to get the purified product; a pervaporation module to remove water from the extract stream and recycle butanol as eluent.

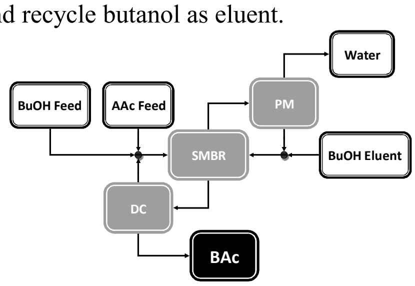

Figure 1. Flowsheet for the SMBR based process.

The estimated energy consumption for this process is approximately 1.8$MJ \cdot kg_{Prod}^{-1}$. A value similar value was estimated for the reactive distillation processes reported in the literature (Niesbach et al., 2013).

As previously stated, the limitations imposed by the reaction kinetics severely affect the reactive-separation regions, since low acrylic acid conversions will lead to the contamination of the raffinate stream. Accordingly, an adjustment was made to the previous process consisting in the introduction of a fixed bed reactor before the SMBR as shown in Figure 2. To keep the same annual production capacity this fixed bed reactor should be 2m long and have a radius of 3.6m. At the outlet of the reactor an acrylic acid conversion of 62% is achieved (a value close to the equilibrium conversion) and this mixture is subsequently fed to the SMBR where the conversion of the reactants proceeds and the target product is purified. As a consequence of the introduction of the fixed bed reactor the productivity increases by 40% and the energy consumption decreases approximately 30%. This data evidences that this process represents a competitive and environmental friendly alternative for the production of butyl acrylate.

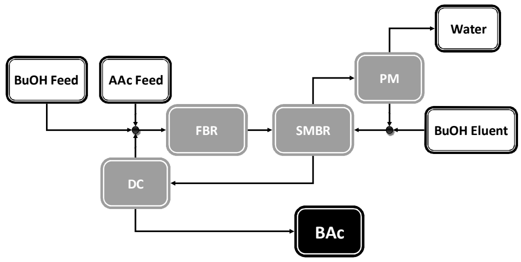

Figure 2. Flowsheet for the coupled Fixed Bed Reactor – SMBR based process.

Conclusions

This work demonstrated the feasibility of the synthesis of butyl acrylate in a SMBR packed with Amberlyst-15. A maximum productivity of 7.2 $kg \cdot L_{ads}^{-1} \cdot day^{-1}$ was achieved with an eluent consumption of 27.5 $L \cdot kg_{Prod}^{-1}$. Based on this results, a plant was designed to produce 50,000 ton/year of butyl acrylate (>99.5%) by combining the SMBR with a distillation column and a pervaporation module for the purification of the product and recycling the eluent, respectively. The overall performance of the process was similar to the presented for reactive distillation based processes reported in the open literature. However, the addition of a fixed bed reactor before the SMBR enhanced the productivity, which increased by 40%, and reduced the energy consumption by approximately 30%.

Acknowledgments

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References

Constantino, D., Pereira, C., Faria, R., Ferreira, A., Loureiro, J. Rodrigues, A. (2015). Synthesis of butyl acrylate in a fixed-bed adsorptive reactor over Amberlyst 15. *AIChE Journal*, 61, 1263-1274.

Niesbach, A., Kuhlmann, H., Keller, T., Lutze, P., Górak, A. (2013). Optimisation of industrial-scale n-butyl acrylate production using reactive distillation. *Chem. Eng. Sci.*, 100, 360-372.

Ostaniewicz-Cydzik, A., Pereira C., Molga, E., Rodrigues, A. (2014). Reaction Kinetics and Thermodynamic Equilibrium for Butyl Acrylate Synthesis from n-Butanol and Acrylic Acid. *Ind. Eng. Chem. Res.*, 53, 6647-6654.

Pereira, C., Zabka, M., Silva, V., Rodrigues, A. (2009). A novel process for the ethyl lactate synthesis in a simulated moving bed reactor (SMBR). *Chem. Eng. Sci.*, 64, 3301-3310.