



Process intensification in a photocatalytic membrane reactor: Analysis of the techniques to integrate reaction and separation



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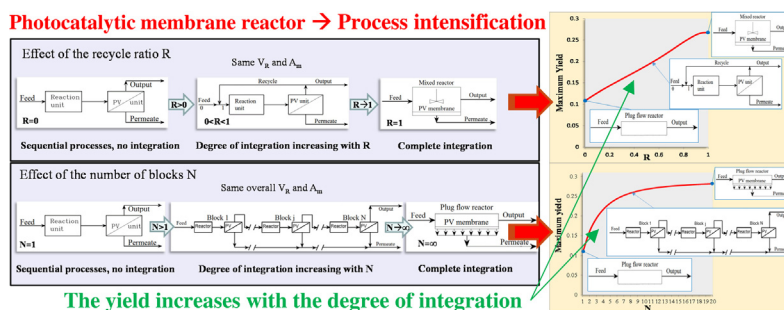
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HIGHLIGHTS

- Separate units for reaction and separation give higher degrees of freedom.
- Design and optimization can take advantage of the higher degrees of freedom.
- The case study for process intensification is the photocatalytic synthesis of aromas.
- Process intensification depends on the degree of integration of the processes.
- Alternative schemes for the coupling of reaction and separation are possible.

GRAPHICAL ABSTRACT



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ABSTRACT

Different methods to integrate reaction and separation in a membrane reactor are studied in the present work, with the aim being to highlight the pros and cons of the different alternatives and the effects of the intervening parameters. The coupling of the two processes can take place inside a single apparatus or using separate units. If a single apparatus is utilized, the coupling is more direct, but separate units offer higher degrees of freedom for the design with more opportunities to optimize the system without constraints. However, when using separate units, the integration of the two unit operations depends largely on the parameters intervening in the coupling procedure. These parameters are the recycle ratio, R , if a recycle stream is used to backmix part of the exiting stream, or the number, N , of blocks if the volume of the reaction and the membrane area are fractionated into multiple reaction–separation blocks. The possibility of different combinations of these two basic methods is also presented.

The case study to illustrate the effect of the various parameters (R , N , the Damköhler number and the Péclet number) and to find the proper operating conditions is the photocatalytic green synthesis of an aromatic aldehyde, which is recovered from the reaction solution by a pervaporation process to avoid further oxidation. The results show that process intensification is the result of appropriately choosing the reaction system and operating conditions because these factors may substantially increase the yield.

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1. Introduction

Membrane reactors represent a particular case of the coupling of a reaction with a separation process in a multifunctional reactor.

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In many applications, process intensification [1–6] is the result of the concurrent action of these two processes because significant benefits are obtained in comparison with the same unit operations in series. Therefore, the interest and the research about membrane reactors is increasing because the benefits ultimately make more convenient and sustainable processes possible, which are currently the key objectives of the chemical industry. The mechanisms of the intensification can vary, but most of them are operative only if the two processes are effectively integrated [7], or, in other words, if the degree of sequential operation is minimized.

In theory, the most direct way to combine the two unit operations is to carry out the reaction and the separation inside the same apparatus because in a single apparatus only mass and heat transport may limit the effectiveness of the coupling. However, this choice requires stringent compatibility between the processes both for the operating conditions and for the fluid dynamics requirements. Moreover, coupling the reaction and separation in a unique apparatus implies a reduction in the degrees of freedom [8], which reduces the opportunities to enhance the process during the design of the system because the optimization of the intervening parameters is partially constrained. For instance, in membrane reactors, a fundamental parameter, which has to be optimized, is the ratio, δ , of the rate of separation to the rate of the reaction [9–12]. This parameter is proportional to the ratio of the membrane area to the reactor volume (or to the catalyst mass), which is the alternative dimensional parameter adopted by some researchers [13–17] in membrane reactors. It is obvious that in a single apparatus or in a catalytic membrane, this ratio cannot be freely varied [9,18] because of technical and practical restrictions.

The utilization of distinct units, one for the reaction and one for the separation, surmounts these problems and, for this reason, this solution has been widely adopted in many membrane reactors. Nonetheless, in this case, the attention is focused on the “degree” of the integration because the connection in series makes it possible for the processes to operate to some extent sequentially rather than simultaneously. It is strange that this aspect has been largely disregarded until now because the final performances of the integrated process depend largely on the parameters intervening in the procedure of coupling the reaction with the separation as is shown in the analysis carried out in the present work.

The most common way to combine the reaction and separation while maintaining them in distinct units is to connect the two units by a recycle stream to create a loop between the apparatuses. In this case, the recycle ratio is the relevant parameter that the degree of the integration depends on [9,12]. However, in the current work, it is demonstrated that the utilization of a recycle stream is not the only solution that can achieve the integration of the processes. Actually, it is possible to adopt new alternative configurations, which, through optimization of the parameters, can lead to a substantial enhancement of the yield. The analysis of these old and new solutions is the subject of the present work with the aim being to investigate the possible improvement of the process.

The fundamentals presented here are general so that they can be applied to any membrane reactor. They will be illustrated for the specific case of consecutive reactions in a pervaporation membrane reactor for the photocatalytic green synthesis of an aromatic aldehyde.

2. Methods

An integrated process consists of the combination of different unit operations that operate concurrently [7]. In specific applications, there are significant benefits from this coupling. For example, the conversion of a reversible reaction can be improved by

continuously removing at least one product while it is formed. In this way, the rate of the reverse reaction is substantially reduced. In consecutive reactions, the direct recovery of the intermediate valuable product from the reacting solution prevents further degradation of this product. The simultaneity of the processes is fundamental to get these results because the expected benefits can be achieved only if the product is recovered while it is formed and before it is affected by the reverse or by the consecutive reaction. In theory, the most direct way to achieve simultaneity is to carry out the reaction and the separation inside the same apparatus because it is sufficient to abate the mass transfer limitations. However, as it was stated in the introduction, different drawbacks restrict the utilization of a single unit to carry out both the reaction and separation. The use of separate units for the reaction and separation is the remedy for these problems, but in this case, it is necessary to ensure the simultaneity of the two unit operations, which is obtained only if both processes operate with virtually the same solution.

So, in the following analysis, the conditions that must be met to obtain a high degree of integration between the reaction and separation with separate units are identified for different configurations.

For a membrane reactor, it has been shown [9,12] that, no matter what layout is adopted, the behavior of the system depends on the following relevant parameters:

- the Damköhler number $Da = \frac{\tau}{t_r} = \frac{R(C_{S0})}{V_r} \frac{V_r}{V_0}$, i.e., the ratio of the characteristic process time to the characteristic reaction time,
- $\delta = \frac{t_r}{t_{sep}} = \frac{C_{S0} \dot{V}_{permeate}}{R(C_{S0}) V_r} = \frac{C_{S0} A_m \dot{m}''/\rho}{R(C_{S0}) V_r} = \frac{1}{Da Pe}$, i.e., the ratio of the characteristic reaction time to the characteristic separation time, where $Pe = \frac{V_0}{\dot{V}_{permeate}} = \frac{V_0}{A_m \dot{m}''/\rho} = \frac{t_{sep}}{\tau}$ is the Péclet number ($1 \leq Pe \leq \infty$), as it is usually defined in membrane processes [19,20], and
- the enrichment factor of chemical S_i , $\beta_i = \frac{C_{i,permeate}}{C_{i,upstream}}$ with $i = 1 \dots N_c$

where C_{S0} is a reference value of the reactant concentration, A_m is the membrane area, \dot{m}'' is the mass flux of the permeate, ρ is the density of the condensed permeate, R is the reaction rate, \dot{V}_0 is the volumetric flow rate of the feed to the system, $\dot{V}_{permeate}$ is the volumetric flow rate of the permeate, V_r is the reactor volume, $\tau = V_r/\dot{V}_0$ is the average residence time in the reactor, and t_r and t_{sep} are the characteristic times of the reaction and of the membrane separation, respectively.

To illustrate how the integration mechanisms between the reaction and separation take place in membrane reactors, the case of reactions in series was analyzed. Even though this is a specific example, the adopted approach and the conclusions drawn can be extended in general to any membrane reactor.

The case study analyzed the partial oxidation by photocatalysis of a substrate to produce an aromatic aldehyde. The kinetics of the relevant reactions and the performances of the membrane, which are used to recover the produced aldehyde, are known from previous studies, but until now no systematic study on the different possibilities of integrating the membrane separation and the reaction and on the parameters affecting this coupling has been performed. This photocatalytic production has been recently investigated because it represents an interesting route for the green synthesis of fine chemicals [21–23]. In fact, photocatalysis has been shown to oxidize organic compounds in mild conditions (ambient temperature and atmospheric pressure) without using chemical additives and resorting to a radiative source (possibly the sun) for the energy demand. However, the valuable aldehyde, which is produced by the partial oxidation of the substrate, is

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