

A New Reaction-Separation Unit: The Simulated Moving Bed Reactor

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Abstract: Process intensification is one of the most promising tools for improving current technologies. This requires dealing in most cases with complex systems where many different and often interacting physico-chemical phenomena take place simultaneously. Continuous reactive chromatography, implemented through the simulated moving bed reactor technology, represents a novel example of such an intensified process. In this case, only a detailed description of the selective polymer swelling and reaction kinetics enables the modeling and the understanding of the behavior of the chemical production process. The optimization of the unit reveals its major economic limitation to arise from the sorptive properties of the currently available stationary phase. Based on a proper understanding of the unit operation, it is possible to design new stationary phases, tailor-made for specific reacting systems, which allow the performance of the process to be significantly improved.

Keywords: Catalyst design · Esterification · Reactive chromatography · Simulated moving bed reactor · Sulfonated resins

Introduction

The integration of reaction and separation of the corresponding products in one single unit allows, in addition to obvious savings in equipment costs, significant improvements in process performance, particularly in the case of equilibrium limited reactions. Typical examples include condensations, esterifications, transesterifications, etherifications and others. By separating the reaction products, the equilibrium limitation can in fact be overcome and the conversion can be driven to completion in a single pass in the unit. Currently, the industrial application of such multifunctional units is substantially limited to reactive distillation, which however is not suitable for com-

plex molecules that are difficult to evaporate, such as those typically of interest in the fine chemical and pharmaceutical industries. An interesting alternative is the integration of chemical reaction and adsorptive separation into one single unit, *i.e.* reactive chromatography.

The underlying principle is a continuous process in which a reactive fluid is contacted with a solid adsorbent phase in a counter-current manner, as shown for example in Fig. 1 for the case of a reversible reaction $A \rightleftharpoons B + C$. Here, the solid phase is passing at a constant flow rate from top to bottom through the unit, while the carrier fluid or eluent, E, is introduced to the unit at the bottom and is proceeding in the opposite direction with respect to the solid phase. The two feed streams for the eluent and the reactant and the two withdrawal streams, *i.e.* the extract and the raffinate, divide the unit into four sections, as indicated in Fig. 1. As the reactant, A, is fed to the central part of the unit, the chemical reaction takes place, and the product species are formed. The more strongly adsorbing component, *i.e.* B in this example, is carried downwards by the solid phase and can be withdrawn in the extract stream, while the less retained species, C, moves in the direction of the fluid flow towards the raffinate outlet. Before being recy-

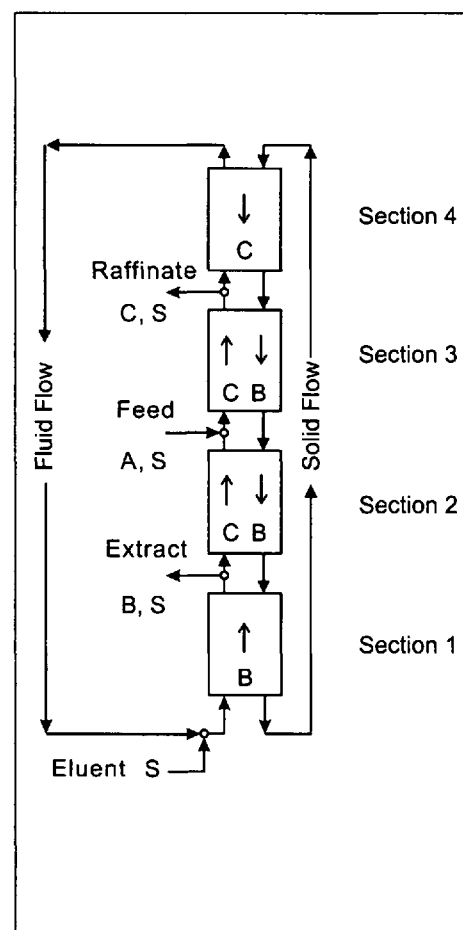


Fig. 1. Process scheme for a true counter-current chromatographic (TCC) reactor

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cluded, both the solid and the fluid phase are regenerated in sections 1 and 4, respectively. If the solid and fluid flow rates are properly adjusted, reactant A is completely consumed within the two central sections of the unit, and both products can be withdrawn at high purity with the extract and raffinate streams.

The practical implementation of this so-called true counter-current (TCC) unit is difficult due to the movement of the solid, while an equivalent unit can easily be realized by simply redesigning the TCC unit with reference to an observer moving with the solid phase. This leads to the simulated moving bed (SMB) unit, where a certain number of fixed beds are connected in series to form a closed loop, and the counter-current movement of the solid and liquid phase is simulated by periodically shifting the fluid inlets and outlets in the direction of the fluid flow. An example of a laboratory SMB reactor is shown in Fig. 2. It is worth noting that the non-reactive, *i.e.* purely separative, version of this unit has attained in the last few years significant success in industry, particularly with reference to chiral separations (see [1] for a review). Several projects in our group contributed to the success of this new technology: modeling and design of SMBs [2], development of laboratory units in the liquid [3], gas [4] and supercritical [5] phase, and the development of a general procedure for the scale-up of an industrial process from simple laboratory information [6].

Design of Simulated Moving Bed Reactors

A key aspect for this technology to be competitive is the proper design of the operating conditions, which due to the complexity of the unit requires the development of appropriate simulation models. Design procedures have been recently developed, starting from the so-called triangle theory developed earlier for non-reactive SMBs, and applied as a demonstration system to the synthesis of methyl acetate from methanol and acetic acid [7]. As packing material a commercially available sulfonated poly(styrene-divinylbenzene) resin was used, which acts simultaneously as a selective sorbent with respect to the reaction products (with higher selectivity for the more polar species) and as a catalyst, due to its acidic groups.

The starting point for the successful design of the unit is a proper understanding of the adsorption equilibria, governing the partitioning of all the involved chemical species between solid (q_i^{eq}) and fluid phase (c_i), and the reaction kinetics. This requires the formulation of multi-component adsorption equilibrium models and of kinetic models based on the mass action rate law in terms of sorbed phase concentrations (q_i). On this basis, a detailed mathematical model describing the dynamic behavior of a single chromatographic column under reactive conditions was developed (Eqn. (1)):

$$\begin{aligned} \varepsilon \frac{\partial c_i}{\partial t} + u_j \frac{\partial c_i}{\partial z} &= \varepsilon_b D \frac{\partial^2 c_i}{\partial z^2} - (1 - \varepsilon^*) k_m (q_i^{eq} - q_i) \\ \frac{\partial q_i}{\partial t} &= k_m (q_i^{eq} - q_i) + v_i r \end{aligned} \quad (1)$$

where mass transfer (k_m) and axial dispersion (D) were properly accounted for. From this, the complete model of the SMB reactor can be obtained. However, due to the complexity of these models, the optimization of the SMBR process based on extensive numerical simulations alone, remains rather time consuming and an approximate solution has to be devised which can provide a detailed understanding of the interplay between the operating parameters and the process performance. For this all the dissipative phenomena in Eqn. (1) can be neglected leading to a system of first order hyperbolic partial differential equations, which in some cases are amenable to analytical solution for the TCC configuration, but in general show that the dimensionless ratios between the fluid and the solid flow rate in each section of the unit (m_j , $j = 1..4$), together with the dimensionless residence times or Damköhler numbers in the two central sections (Da_j), are the dimensionless parameters governing the performance of the unit [7]. In particular, the representation of the unit's operating point within the parameter plane defined by the flow rate ratios in the two central sections (m_2 , m_3) for a given residence time (constant Da_2 , Da_3) allows to quickly and accurately predict the performance of the unit. In particular, triangle-shaped operating regions adjacent to the diagonal are identified within which each operating point leads to the complete conversion of the reactant and complete separation of the products. In order to verify the reliability of these theoretical results, the boundaries of these regions computed through numerical simulations have been compared with the experimental data for a laboratory SMB reactor as shown in Fig. 3 [8].

Based on this mathematical analysis of the SMB reactor, its potential with respect to other competitive technologies for different reacting systems can be

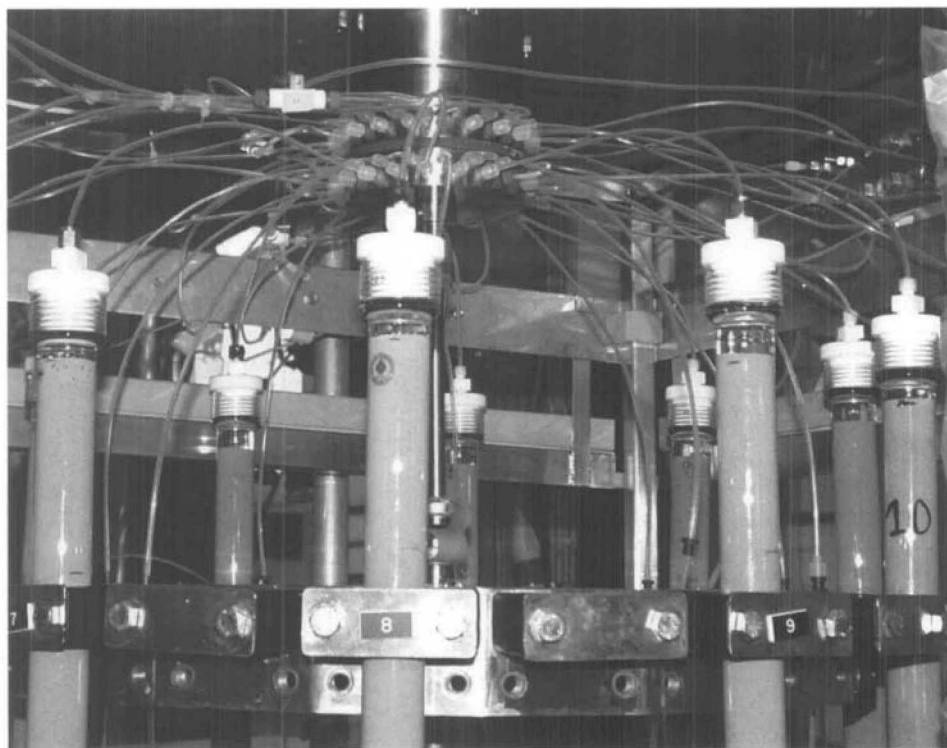


Fig. 2. Simulated moving bed (SMB) reactor. The glass columns containing the stationary phase are attached to a rotating table and connected to the mobile part of a rotating valve (upper center of the picture), while the feed and withdrawal streams are connected to the stationary part of the valve above the mobile one. After a specified time interval, the table with the columns and the mobile part of the valves move clockwise by one position in order to simulate the solid movement.

identified. It is found that in the case of most esterification reactions, including the examined model system, the achievable productivity of the process is satisfactory, but the consumption of the eluent (methanol in this case), which is used not only as reactant but also as desorbent, is too large and constitutes the major limitation to the economy of the process. However, this eluent consumption is determined by the sorptive properties of the resin, and in particular by its affinity to the reaction products, *i.e.* water and methyl acetate, as compared to the eluent, *i.e.* methanol. Therefore a significant improvement in the process performance can be achieved by properly designing the sorptive properties of the resin, while maintaining a sufficient acidic character to properly catalyze the esterification reaction.

Improving Process Performance by Catalyst Design

Considering the hydrophobicity of the resin's polymeric backbone, its affinity towards polar species, in particular water, arises from the highly polar sulfonic acid moieties. Accordingly, a reduction in the concentration of these groups allows for a reduction of the resin selectivity for the more polar species, and thus offers a benefit with respect to the solvent consumption. At the same time the catalytic activity of the resin, though, is affected detrimentally, leading to losses in process productivity. A proper design of the resin's sulfonic acid site density therefore has to find the best compromise between sorptive properties and catalytic activity. Several techniques are currently available for catalyst design (see [9] for a review), but let us focus now only on the concentration of sulfonic groups in the resin, maintained constant through the entire resin particle.

The rational development of such design procedures requires proper mathematical models describing the equilibrium inter-phase partitioning of the reacting species, which explicitly take into account the acid site concentration. One possible approach is the application of an extension to Flory's theory of gel elasticity [8], that is by modeling the sorbed phase as a semi-permeable, elastic membrane. In short, the activity of the *i*-th species within the gel phase (a_i) is given by

$$\ln a_i = 1 + \ln v_i - \sum_{j=1}^{N+1} \frac{\tilde{V}_j}{\tilde{V}_j} v_j + \sum_{j=1}^{N+1} \chi_{ij} v_j - \sum_{j=1}^{N+1} \sum_{k=1}^{j-1} \frac{\tilde{V}_j}{\tilde{V}_j} v_j v_k \chi_{kj} + \eta \tilde{V}_i \left(v_p^{1/3} - \frac{1}{2} v_p \right) \quad (2)$$

Eqn. (2) where v_i denotes the volume fraction of species *i* in the gel phase and is related to the sorbed amounts (q_i). The first two terms on the right hand side of Eqn. (2) represent the entropic contribution, the third and fourth the enthalpic contribution, where the binary interactions between the various species and with the polymer are represented by the parameter χ_{ij} , and χ_{iP} , respectively, and the last term describes the contribution of the elasticity of the polymer backbone (η). In the presence of water the dissociation of the sulfonic acid sites within the gel phase has also to be accounted for.

By experimentally investigating resins carrying different amounts of sulfonic sites equally distributed throughout the polymer particle, proper correlations linking the interaction parameters χ_{iP} to the acid site concentration can be obtained, thus establishing a tool to describe the sorption behavior of these resins as a function of the concentration of sulfonic groups.

With respect to the application of SMB reactors in the model system under examination, a substantial decrease in the resins' affinity towards water, with at the same time an improved interaction between polymer and methyl acetate, has been obtained for resins with reduced sulfonic acid site density. As an example, the phase diagram for the sorptive behavior of binary mixtures of water and methanol is shown in Fig. 4 for resins of three different acid site densities. The decreasing affinity of the resin towards water is evidenced by the decrease in the initial slope of the data for water mole fractions approaching zero, as well as by the fact that the intersection of the data with the diagonal moves towards lower values of water mole fraction. For all three resins,

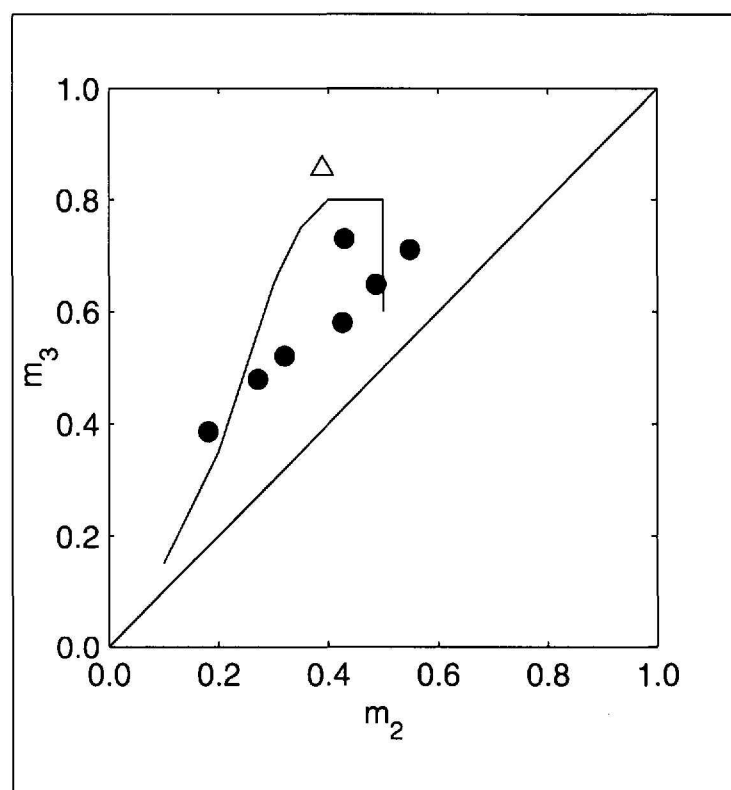


Fig. 3. Performance of a SMB reactor for methyl acetate synthesis as represented in the flow rate ratios (m_2 - m_3)-parameter plane, for a given residence time; solid symbols: complete conversion of acetic acid, extract purity 100%, raffinate purity >90%; open symbol: incomplete conversion; the curved solid line envelopes the region of operating conditions where complete conversion is predicted by the model (see [8] for details).

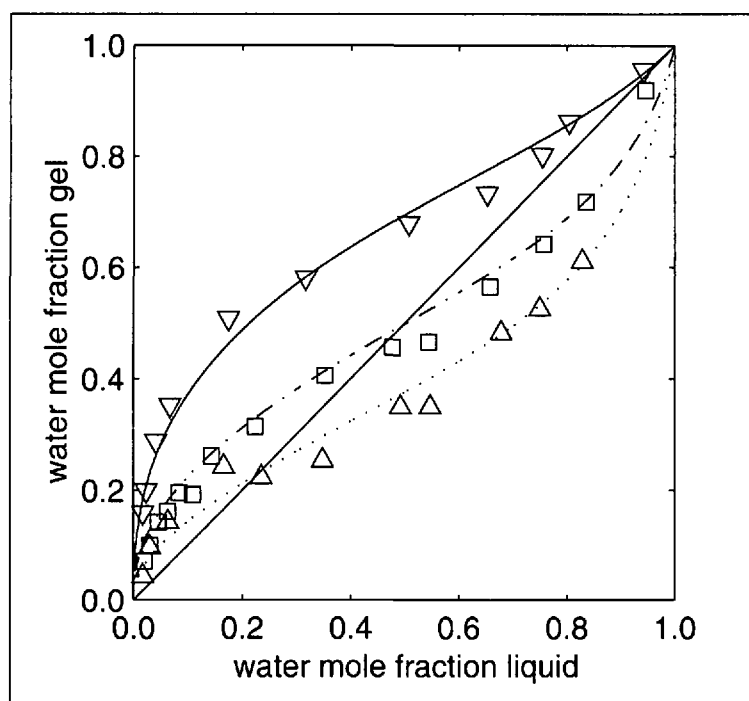


Fig. 4. Equilibrium partitioning of binary mixtures of water and methanol on sulfonated poly(styrene-DVB) resins of different acid site density: 5.0 (∇ , —), 2.4 (—, -), and 0.8 10^{-3} mol/g (Δ , ...); lines represent predictions based on the extended Flory model [8].

the extended Flory model is able to well describe the experimental data.

These results show that by reducing the acid loading of the resin, water regeneration can be significantly facilitated and in the context of the SMB operation the eluent consumption can be substantially decreased. On the other hand, the productivity of the process remains sufficiently high, since such acid concentration reduction leads to only modest losses in the catalytic activity of the resin [8]. This effect has, however, also to be accounted for in developing a complete procedure for determining the best acid loading level for the operation of the SMB reactor.

Conclusions

SMB reactors represent an efficient process alternative in the manufacture of temperature sensitive products, such as drugs and natural products. The reliability of this process has been demonstrated in this work where suitable design procedures have been developed based on appropriate mathematical models. It is found that significant improvements in the economical performance of these units can be obtained by the proper design of the adsorbent-catalyst to be used in the SMB reactor. When considering sulfonated polymer resins, this means to identify the best acidic loading, and possibly radial distribution of the sulfonic

groups in the resin particle, with respect to the performance of the unit in terms of productivity and purity of the extract and raffinate streams. This should be tailor-made for each specific reacting system, which requires a detailed understanding of the involved adsorption equilibria and reaction kinetics, based on appropriate mathematical models.

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