

Simulated moving bed process with cyclic modulation of the feed concentration

Henning Schramm^{a,*}, Malte Kaspereit^a, Achim Kienle^{a,b}, Andreas Seidel-Morgenstern^{a,b}

^aMax-Planck-Institut Dynamik Komplexer Technischer Systeme, Sandtorstrasse 1, D-39106 Magdeburg, Germany

^bOtto-von-Guericke-Universität Magdeburg, Universitätsplatz 2, D-39106 Magdeburg, Germany

Abstract

The improvement of the simulated moving bed (SMB) process based on the introduction of a cyclic modulation of the feed concentration is described. It is demonstrated that such a feed concentration gradient during the shifting cycle can improve the performance significantly. The productivity and the product concentrations can be increased while simultaneously the solvent consumption can be decreased compared to the conventional SMB process with constant feed parameters.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Simulated moving bed chromatography; Preparative chromatography; Feed concentration gradient; Cyclic modulation

1. Introduction

Preparative chromatographic separation processes are increasingly applied in the pharmaceutical industry, in biotechnology or for the purification of fine chemicals.

Traditionally, chromatographic separations are performed discontinuously, i.e., an amount of a feed mixture is injected periodically into a solvent stream and carried through a chromatographic column. The separation is based on different affinities of the components to be separated with a solid stationary phase. Because of high solvent consumption, dilution of the products and low productivity, new continuous chromatographic separation processes were de-

veloped. The concept of the simulated moving bed (SMB) was introduced several decades ago [1] and has been up to now applied to solve a large number of separation problems.

In the SMB process, the continuous separation of a binary mixture is enabled by a simulated counter-current flow between a liquid and a solid-phase. In Fig. 1 the classical SMB scheme is shown. The unit consists of a number of chromatographic columns connected in series. A liquid solvent stream circulates in the apparatus. Two inlet nodes (feed and solvent) and two outlet nodes (extract and raffinate) define four distinct separation zones. Synchronous switching of the inlet and outlet nodes by one column in the direction of the fluid flow “simulates” a movement of the solid-phase. If the switching time and the flow-rate of the liquid phase are chosen properly, the stronger adsorbed component A moves in the direction of the extract port. Simultaneously, the weaker adsorbed component B moves in the

*Corresponding author. Fax: +49-391-6110-543.

E-mail address: schramm@mpi-magdeburg.mpg.de (H. Schramm).

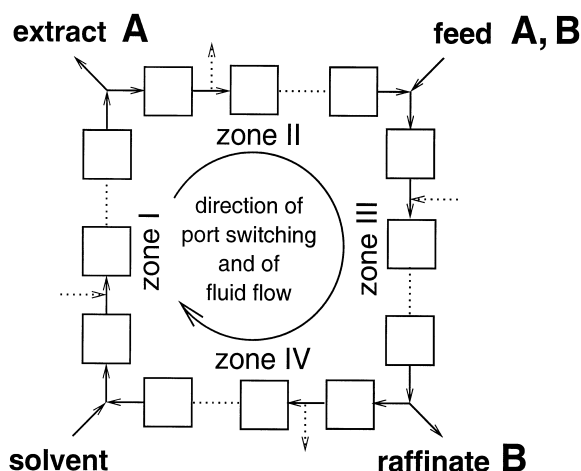


Fig. 1. Simulated moving bed process for the separation of components A and B.

direction of the liquid flow and can be withdrawn at the raffinate port.

In contrast to the classical concept in which the SMB process is operated with constant inlet and outlet flow-rates and feed concentrations, recently the operation of SMB processes was improved by variations of operating parameters during the switching intervals. Kearney and Hieb [2] patented an operating mode, where all flow-rates in the process are varied during the switching intervals. Kloppenburg and Gilles [3] calculated optimal flow-rate profiles by numerical optimization and pointed out the potential to decrease the solvent consumption significantly. A closer inspection of their suggestions reveals that the feed flow characteristics influence the separation performance most. Consequently, recently a new operation strategy exploiting a variable feed flow-rate was described by Morbidelli and Mazzotti [4]. For this variant of the SMB process the term “PowerFeed” was coined.

In this context in particular also the so-called “VariCol” process must be mentioned which is based on asynchronous switching strategies. This type of switching varies the lengths of the four distinct SMB zones during the switching intervals. It was demonstrated (e.g., Refs. [5,6]) that with this strategy the same performance as in the conventional case can be achieved with less columns.

As concerns operation strategies exploiting variable flow-rates, there is the disadvantage of alternat-

ing loads of the pumps causing a reduced life time and higher fault probability. For processes with asynchronous switching, complicated control algorithms for the valves are necessary. To overcome these disadvantages, in this contribution a new and simple operation strategy is introduced, where the feed concentration is varied within each switching cycle. To compare it with the mentioned alternative concepts it might be designated as “ModiCon” (periodically modified feed concentration). The concept can be easily applied at existing SMB plants using simple valve circuits or common gradient pumps. To demonstrate the potential of the new approach, a simulation study and experimental results will be used to compare the classical SMB process with constant feed concentrations to an equivalent process with periodically varied feed concentrations. Furthermore, features of the new operating mode will be discussed in the framework of the well-known “Triangle Theory” [7].

2. Modeling

The SMB process is typically quantified by connecting models for the single columns respecting the specific boundary conditions. To describe a single column in this work the *equilibrium dispersive model* [8] is used, where c_i is the concentration of component i in the liquid phase and q_i the corresponding solid-phase concentration. The linear fluid velocity is marked by u , z is the spatial coordinate, t the time and ε the total porosity of the column. The separation of two components is considered.

$$\frac{\partial c_i}{\partial t} + \frac{1 - \varepsilon}{\varepsilon} \cdot \frac{\partial q_i}{\partial t} + u \cdot \frac{\partial c_i}{\partial z} = D_{ap,i} \cdot \frac{\partial^2 c_i}{\partial z^2}$$

$$i = 1, 2 \quad (1)$$

In this model a local equilibrium between the solid and the mobile phases is assumed (i.e., $q_i = q_i(c_1, c_2)$). The contributions to band broadening due to axial dispersion and mass transfer resistances are lumped into the apparent dispersion coefficients $D_{ap,i}$.

The boundary conditions at the inlet (in) and outlet of the connected columns are given by the well known Danckwerts relation.

$$D_{ap,i} \cdot \left. \frac{\partial c_i}{\partial z} \right|_{z=0} - u(c_i|_{z=0} - c_{i,in}) = 0$$

$$D_{ap,i} \cdot \left. \frac{\partial c_i}{\partial z} \right|_{z=L} = 0. \quad (2)$$

The interactions between the different components and the stationary phase are described by the competitive Langmuir isotherm with a_i being the Henry constants and b_i thermodynamical coefficients.

$$q_i(c_1, c_2) = \frac{a_i c_i}{1 + \sum_{j=1}^2 b_j c_j} \quad (3)$$

2.1. Optimization

The determination of suitable operating conditions for the SMB process can be performed, e.g., using common optimization techniques. A different approach will be used in this paper. The flow-rates in the four separation zones will be calculated by applying a control algorithm presented recently [9,10]. This control algorithm uses the theory of nonlinear wave propagation [11]. The components move through the different SMB sections in the form of traveling waves. In the algorithm the concentration fronts are stabilized by the controller by adjusting the four liquid flows in the separation sections in such a way that the desired product purity

at the product outlets is reached. It is shown in Refs. [9,10] that the controller automatically works with minimum solvent consumption and maximum feed throughput. Hence, at the cyclic steady state the controller adjusts the optimum operating conditions without any numerical optimization calculation. Compared to this approach, common numerical optimization procedures are typically more time consuming.

3. Conventional SMB operation

Before introducing the new operating concept a conventional process with constant operating parameters including flow-rates, switching times and inlet concentrations will be designed. As an example a separation of two cycloketones, cyclopentanone (component A) and cycloheptanone (B) using a normal-phase silica gel will be considered. These two components are present in equal parts in the feed mixture. All parameters needed for the simulations were determined at a pilot scale SMB plant used also for the experiments considered in this paper. These parameters are summarized in Table 1.

A set of restrictions has been applied in the process of specifying the SMB operating conditions. It has to be pointed out that these restrictions are valid for every theoretical and experimental inves-

Table 1
Operating parameters for the different operation modes

	(a) Optimized conventional process	(b) Optimized ModiCon process
Number of columns	2/2/2/2	
Total porosity ε	0.83	
Column length	25 cm	
Dispersion coefficients (u = fluid velocity)	$D_{ap,i} = 0.125u \text{ cm}^2/\text{min}$	
Langmuir-parameter	$a_1 = 7.70; b_1 = 0.148\% \text{ (v/v)}^{-1}$ $a_2 = 5.72; b_2 = 0.110\% \text{ (v/v)}^{-1}$	
Switching time T_s	3.0 min	
Liquid flow-rate zone I	59.4 ml/min	
Extract flow	15.2 ml/min	17.8 ml/min
Raffinate flow	8.8 ml/min	8.0 ml/min
Feed flow	8.0 ml/min	8.2 ml/min
Eluent flow	16.0 ml/min	17.6 ml/min
Feed concentration	0.55% (v/v) = const.	0/2.5% (v/v)

tigation in this paper, i.e., for every considered operating mode.

(i) With respect to the maximum acceptable pressure drop the maximum flow-rate in the applied SMB plant (i.e., the flow-rate in zone I) is restricted to 60 ml/min.

(ii) As for the limited precision of pumps at low flow-rates, the flow-rates should not be lower than 8 ml/min.

(iii) A product purity of 95% should be achieved at the extract and raffinate outlets.

(iv) Safety margins of 10% are applied to the flow-rates in zones I and IV in order to guarantee for complete regeneration of the solvent and the stationary phase in these zones.

It was shown (e.g., Refs. [12–14]) that the feed concentration is a main factor in the design of simulated moving bed processes since it has a strong influence on the separation performance. Typically, the productivity increases and the solvent consumption decreases if the feed concentration is increased. The improvements are rather large if the feed concentration is low and smaller if the feed concentration is high. Thus, the slope of the performance versus feed concentration curves decreases. Consequently, low feed concentrations have to be avoided. However, very high feed concentrations will also not be suitable because a further significant increase of the performance cannot be achieved in this concentration range. Very high feed concentrations require the application of low feed flow-rates which might be difficult to control.

With respect to the restriction on the minimum applicable feed flow-rate, a maximum feed concentration of 0.55% (v/v) for each cycloketone in the mixture was fixed in this work for the conventional process (constant feed concentration). In calculations not presented here in detail it was proven that at higher concentrations the desired product purity cannot be achieved without violating the minimum flow-rate requirement of 8 ml/min. Therefore the optimized conventional reference SMB process is operated at a constant feed concentration of 0.55% (v/v) for each component.

By applying the optimization procedure mentioned in Section 2.1 for the given feed concentration the optimum flow-rates can be determined (listed in column (a) of Table 1). As mentioned above, similar

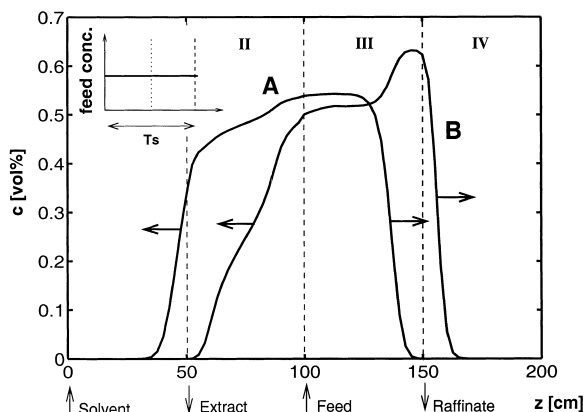


Fig. 2. Steady-state concentration profile in the middle of a switching interval of the conventional SMB process (feed concentrations = 0.55%, v/v).

flow-rates can be achieved by applying a common numerical optimization procedure if the process is optimized with respect to maximum feed throughput and minimum solvent consumption.

The corresponding internal concentration profiles of the conventional process in the middle of a switching interval are shown in Fig. 2. The process is operated at maximum feed throughput and minimum solvent consumption. Cyclopentanone is withdrawn at the extract port, cycloheptanone at the raffinate port. The purity is 95% for each product stream.

4. SMB process with cyclic modulation of the feed concentration

In this section, the new ModiCon operation method for SMB processes will be introduced. Contrary to the conventional operation with constant feed concentrations, these concentrations will now be varied within each switching cycle.

In order to understand the effect of a variation of the feed concentrations, the process has to be analyzed according to the theory of nonlinear wave propagation [11,15,16].

Two kinds of component concentration waves can be distinguished. Constant pattern waves, where each point of the wave has the same velocity, and spreading waves, where each point (corresponding to a certain concentration) has a different velocity. In

particular, for spreading waves the velocity increases with increasing concentration. As a result of the feed position, in the separation sections I and II desorption and in sections III and IV an adsorption of the components at the solid-phase can be observed. For Langmuir type adsorption behavior which is present in the considered example, the adsorption fronts are constant pattern waves (waves in sections III and IV), the desorption fronts in sections I and IV are spreading waves [11]. For fixed flow-rate ratios m^j (the ratios between liquid and solid flow-rates in each separation section j) the velocity of a constant pattern wave depends on the height of the wave, whereas the local velocity of a spreading wave only depends on the local concentration value. Hence, by influencing the height of the constant pattern wave of component A in section III, it is possible to influence the velocity of this wave and therefore the raffinate purity. In contrast, the extract purity is hardly affected.

For increasing raffinate purity, the front of component A in zone III has to be shifted to the left by reducing the corresponding wave velocity. This can be done by reducing the height of the wave through a variation of the feed concentration. Since the front position in zone III is close to the feed at the beginning of the switching period, a reduction of the feed concentration at the beginning of the switching interval immediately reduces the propagation velocity of the shock in zone III. In order to achieve the same feed throughput as for the conventional process, the feed concentration has to be increased

again towards the end of the switching interval. In principal, this accelerates the front in zone III again. However, as the front is far from the feed position at the end of the switching interval, the acceleration is delayed. Therefore, the overall effect of the step change in the feed concentration is a reduction of the mean velocity in the switching interval causing the desired shift of the front in zone III. The front of component B in zone IV is hardly affected because both effects (acceleration and deceleration) extinguish each other.

It is worthwhile mentioning that these considerations can be done in a similar way if the adsorption equilibrium cannot be described by Langmuir isotherms. The position of the different wave types would change and the variations in the feed concentration would have to be adapted accordingly.

To illustrate the new operation mode, for the sake of simplicity the switching period will be divided into two equal parts. In the first half period pure solvent and in the second half period a feed mixture with a high concentration will be fed into the plant. In a first analysis, this concentration is two times higher (i.e., 1.1%, v/v) than the constant feed concentration used in the study of the conventional process (0.55%, v/v). It has to be pointed out, that (in this first study) both SMB processes (conventional and ModiCon) are operated with the same flow-rates and process the same amount of feed.

Fig. 3 (left side) shows the resulting concentration profile of the new operation mode in the middle of a switching interval when the process has reached the

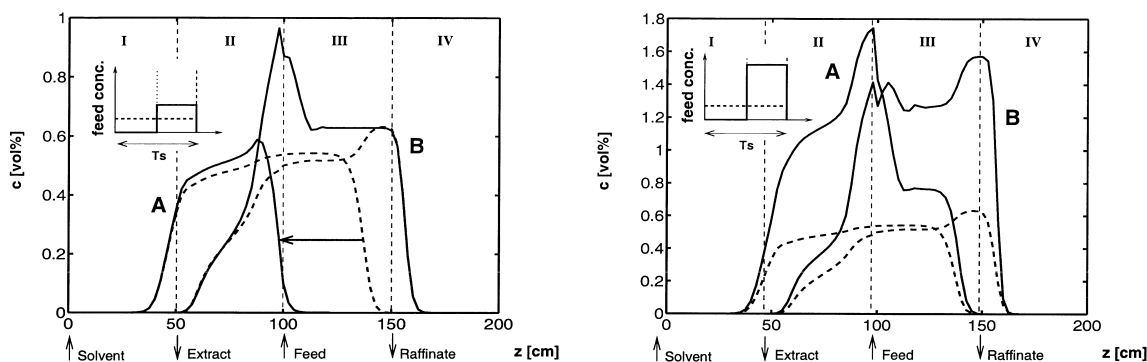


Fig. 3. Concentration profiles in the middle of a switching interval of the SMB process with cyclic modulation of the feed concentration. Dashed lines: profile of the conventional process according to Fig. 2. Left: same flow-rates as for the conventional process. Right: flow-rates and feed concentration are optimized according to Table 1, column (b).

cyclic steady state. Dashed lines mark the equivalent profile for the conventional process according to Fig. 2. In both cases, the same parameters were used for the simulation.

The arrow marks the significant shift of the concentration front of cyclopentanone in section III to the left. As a result, the raffinate purity is increased from 95 to nearly 100%. The feed modulation has only little effect on the spreading waves at the left of the feed node (extract purity 95%).

4.1. Optimization of the new process

The raffinate purity of the SMB process with ModiCon operation mode was increased significantly compared to the conventional operation. Feed throughput and solvent consumption were the same in both cases. Alternatively, the new process with a modulation of the feed concentration can now be optimized regarding to maximum feed throughput and minimum solvent consumption. The restrictions valid also for the conventional operation mode have to be respected in this optimization. In a first step of optimization (Section 2.1), only the flow-rates were adjusted in such a way that the concentration fronts are shifted to their old positions and the desired product purity of 95% was reestablished. A modulation of the feed concentration between 0 in the first half of the switching period and 1.1% (v/v) in the second half was fixed. The shifting of the fronts was performed using an increased feed flow-rate leading to an increased productivity. According to Fig. 4, which will be described in more detail in Section 4.2, the productivity of the new process with a modulation of the feed concentration can be increased by about 50% while the specific solvent consumption simultaneously decreases by about 25% compared to the conventional process with constant feed concentration. Both processes, conventional and new, were operated at an average feed concentration of 0.55% (v/v).

Even though this first optimization step already leads to a huge improvement of the separation performance, the process can be optimized further by including the concentration in the second half of the switching interval into the optimization procedure.

The (in the first step) optimized flow-rates of the new ModiCon process with an average feed con-

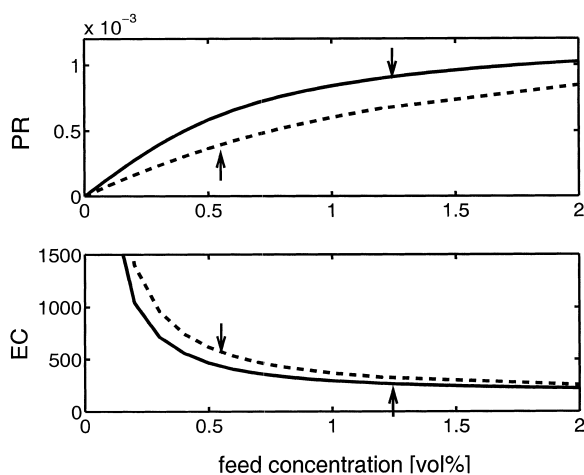


Fig. 4. Productivity PR [$\text{ml}/(\text{min cm}^3)$] and specific solvent consumption EC (ml/ml) versus feed concentration for the considered example (parameters in Table 1). The flow-rates are optimized such that the product purity matches 95%. Dashed lines: conventional process. Solid: ModiCon process with a two-step modulation of the feed concentration according to Section 4 (feed concentration is the average concentration within a switching interval).

centration of 0.55% (v/v) (modulation between 0 and 1.1% (v/v)) are higher than the minimum flow-rate restriction of 8 ml/min. Consequently, the feed concentration in the second half of the switching interval can even be increased further. By optimizing the process respecting the restrictions mentioned in Section 3, the operating parameters in Table 1, column (b) were achieved. The highest possible feed concentration corresponding to the minimum flow-rate of 8.0 ml/min (here: raffinate flow-rate) is 2.5% (v/v). The corresponding concentration profiles in the middle of a switching interval are shown in Fig. 3 (right side). In particular the higher feed concentration leads to increased product concentrations in comparison to the conventional process.

4.2. Comparison of new and conventional SMB process

In order to compare the new optimized process with the conventional process quantitatively, a set of performance parameters has been calculated. These parameters are:

- (i) the average product concentration \bar{c}_i^k which

mark the integral averaged concentration of the desired component i at the respective product port k ;

(ii) The product purity PUR_i^k ;

(iii) The productivity PR_i^k as the produced amount of component i per time and volume of the stationary phase

(iv) The specific solvent consumption EC_i^k which marks the amount of solvent necessary to produce 1 ml of pure product (note that the solvent which is needed in the feed stream was also taken into account).

In Table 2 both processes are compared according to these performance parameters. This comparison can be done because both operating modes are subjected to the same restrictions of a real SMB unit. For the conventional and the ModiCon operation mode, the respective optimum operating parameters were determined. Using a modulation of the feed concentration it was possible to increase the productivity by 127% and simultaneously to decrease the specific solvent consumption by 53%. The product concentrations of extract and raffinate are increased by 93 and 154%, respectively.

In Fig. 4 the influence of the feed concentration on the productivity and specific solvent consumption is shown for the example considered in this paper. The flow-rates were always optimized in a way that the desired product purity of 95% was fulfilled. Solid lines show the new ModiCon process where (in this case) the feed concentration in the first half of the switching interval is zero and in the second half

double of the concentration of the conventional process. Thus, the integral feed concentration for the new process is the mean value. Dashed lines show the performance parameters of the conventional process. Arrows mark the performance values of both processes, conventional and ModiCon for the specific feed concentrations used in the example.

For both processes, the productivity increases and the eluent consumption decreases if the feed concentration is increased. The new process always shows a significantly higher productivity and a lower solvent consumption than the conventional process. Furthermore, the feed flow-rate of the new process (at the same average feed concentrations) is higher and could be therefore controlled easier.

It has to be pointed out, that the used “feed concentration profile” (stepwise change of the concentration in the middle of each switching interval) is not yet optimized. Nevertheless a significant improvement of the process can be already noticed. A further improvement should be possible by optimizing the feed modulation profile itself.

It should be also mentioned, that the remarkable increase of the productivity and the decrease of the solvent consumption was achieved by applying relatively high feed concentrations in the second half of the switching interval. This was possible in the considered example as the solubility of the components in the feed mixture is not restricted. In many other cases, this cannot be assumed. Hence, also the influence of feed concentration variations in the

Table 2

Comparison of the performance parameters of the optimized conventional and the optimized ModiCon mode

		(a) Optimized conventional process, (Table 1, column (a))	(b) Optimized ModiCon process, (Table 1, column (b))
\bar{c}_i^k (%, v/v)	Ex	0.28	0.54 (+93%)
	Ra	0.48	1.22 (154%)
PUR_i^k (%)	Ex		95%
	Ra		
PR_i^k [ml/(min cm ³)]	Ex	4.0×10^{-4}	9.1×10^{-4} (127%)
	Ra		
EC_i^k (ml/ml)	Ex	562	265 (−53%)
	Ra		

The values in brackets represent changes in comparison to the conventional process. Parameters: average product concentrations \bar{c}_i^k , purity PUR_i^k , productivity PR_i^k and specific solvent consumption EC_i^k .

range of lower concentrations was investigated. It was found that even a smaller decrease of the feed concentration at the beginning and a corresponding increase at the end of the switching intervals could improve the separation performance considerably.

4.3. Influence on the size of the separation regions according to triangle theory

For the design of simulated moving bed processes, i.e., the determination of appropriate flow-rates, several simple short cut methods are available. Among them, the “triangle theory” [7] is most popular. The key design parameters of this theory are the net mass flow-rate ratios m^j , defined as the ratio between the liquid and the solid-phase flow-rates in every separation section j . For an SMB unit the m^j values can be calculated according to:

$$m^j = \frac{\varepsilon u_j}{(1-\varepsilon)u_s} - \frac{\varepsilon}{(1-\varepsilon)} \quad j = \text{I, II, III, IV.} \quad (4)$$

The linear velocity of the liquid in separation section j is described by u_j and u_s is the velocity of the solid-phase, which is closely related to the switching time T_s .

Provided the column efficiencies are infinite, the separation is complete (i.e., the product purity is 100%) and the feed concentration is constant, it is possible to obtain explicit criteria on the flow-rate ratios for each section [17]. For that, only knowledge about the adsorption equilibria and the feed concentrations is necessary. The criteria result in triangular-shaped regions in the $m^{\text{II}}-m^{\text{III}}$ plane as shown in Fig. 5 as dotted lines for different feed concentrations. Any operating point within these regions results in a product purity of 100%.

In order to account for deviations from equilibrium theory, variable feed concentrations or a lower product purity, it is possible to obtain the corresponding regions of operating parameters as shown, e.g., in Ref. [12]. By scanning the $m^{\text{II}}-m^{\text{III}}$ plane at fixed grid points, the resulting product purity can be recorded from numerical simulation. Typically, lower purity requirements at constant feed concentrations result in a larger operating region (dashed line, purity 95%, $c_i^{\text{Fe}} = 0.55\%$, v/v) where the vertex of the triangle is situated more remote from the

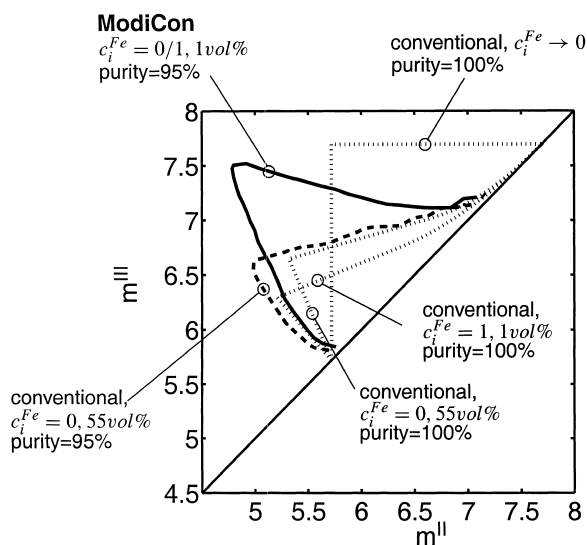


Fig. 5. Separation regions in the $m^{\text{II}}-m^{\text{III}}$ plane according to the triangle theory [7]. The different regions represent conventional and ModiCon mode for different purity requirements and feed concentrations.

diagonal compared to the region of complete separation (dotted line).

The solid line in Fig. 5 marks now the operation region for the new ModiCon process with a two-step modulation of the feed concentration and a purity of 95%. The concentrations were varied between 0 and 1.1% (v/v), i.e., the average feed concentrations were similar for both considered operating modes (conventional and ModiCon, purity 95%). It is evident, that the separation region became significantly larger compared to the conventional case. As the feed flow-rate corresponds to the distance of an operating point from the diagonal, the larger region allows to process a higher feed throughput.

5. Preliminary experimental results

Preliminary experiments were carried out for the separation of two cycloketones, cyclopentanone and cycloheptanone. These two components are liquids at ambient conditions and the feed mixture contains these components in equal parts (1:1 mixture). The separation is performed using silica gel (pore size 120 Å and particle size 12 μm; YMC, Schermbeck,

Germany) as stationary phase and a solvent consisting of *n*-hexane–ethyl acetate (85:15, v/v). A preparative SMB unit (CSEP C912, Knauer, Berlin, Germany) consisting of eight columns was used for the experimental investigations. The feed pump was additionally equipped with a low pressure gradient device (Knauer). During the operation of the plant samples were taken at both product outlets. These samples were analyzed using a commercial HPLC unit (Dionex, Sunnyvale, CA, USA).

In the experiment performed, the SMB unit was operated initially with a modulation of the feed concentration. In the first half of the switching interval, pure solvent, in the second half a feed mixture with a concentration of 2.5% (v/v) for each component was fed into the plant. Because the theoretical considerations were done on the basis of the parameters determined for the real plant, the flow-rates are given in Table 1, column (b). Therefore the plant was operated with optimized operating parameters according to the new ModiCon mode.

After obtaining a cyclic steady state for the product concentrations (180 min), a constant feed concentration of 1.25% (v/v) was introduced to the plant. The unit was operated with the same flow-rates—i.e., there was the same feed throughput for both operating modes.

In Fig. 6 the development of the product purity at the extract and raffinate ports is illustrated. Squares show the experimental results obtained by the HPLC analysis for the extract and crosses for the raffinate outlet. Dotted lines mark the results of an appropriate simulation. The solid line identifies the time were the feed concentration is changed from the modulated to the constant state. By operating the plant with modulated feed concentrations, the purity requirements (dashed line) were fulfilled. Contrary to that, in the conventional operating mode with the same feed throughput, the raffinate purity decreases to nearly 80%. As expected, the extract outlet was only hardly influenced by the change of operation mode.

The observed trend of the product purity agrees with the behavior of the concentrations at the product outlets. The concentration of cyclopentanone at the raffinate outlet, which is responsible for the contamination of this product stream, increases after switching to the conventional mode, whereas the concentration of cycloheptanone (desired product) re-

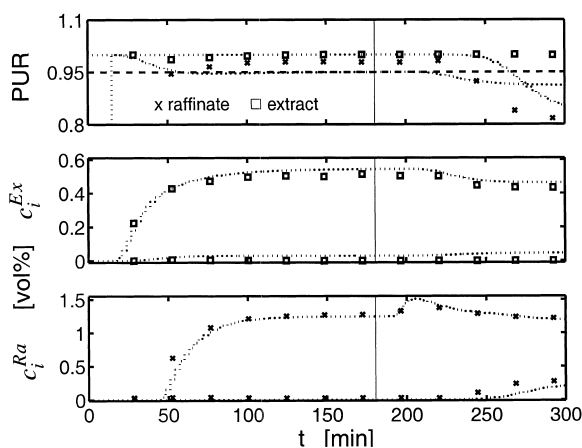


Fig. 6. Experimentally determined product purity and component concentrations at the extract and the raffinate outlet. Dotted lines: simulation. Dashed lines: product specification 95%. Start up of the plant with ModiCon mode, modulation of the feed concentration between 0 and 2.5% (v/v). From time = 180 min: constant feed concentration of 1.25% (v/v). Flow-rates given in Table 1, column (b).

mains constant. At the extract port a decrease of the product concentration can be observed in the conventional operating mode corresponding to a higher dilution of the product stream.

At this stage, the experimental results must be considered as preliminary. The experiment was performed without detailed knowledge of the adsorption isotherm in high concentration regions. Nevertheless it can be stated, that the simulated product concentrations fit very well to the experimental data. Contrary to that, the simulation does not fit exactly to the measured purity. This is because of the fact that a higher product purity is very sensitive to deviations of the concentration values. Nevertheless, it can be stated that the results show the expected behavior—the operation with increased separation performance is possible by a modulation of the feed concentration. A conventional operation with the same performance leads to a strongly decreased product purity.

6. Conclusions

In this paper, a new operating mode for simulated moving bed processes was introduced [18]. By cyclic

modulation of the feed concentration it is possible to improve the separation performance significantly. The productivity and the product concentrations can be increased while simultaneously the specific solvent consumption can be decreased compared to the conventional process with constant feed concentration. The region of accessible operation parameters according to the triangle theory [7] can be significantly extended.

The new concept of modulation of feed concentration is based on an exploitation of nonlinear thermodynamic equilibria. It is therefore not restricted to Langmuir type adsorption behavior used in the example considered in this work. Analyzing the formation of different types of waves in the unit, specific feed concentration variations can be adapted.

The concept described can be applied easily to SMB plants if these are not operated close to the solubility limits of the feed components. For its implementation common gradient pumps or simple valve circuits can be used. An advantage of the new ModiCon concept compared to other concepts based on modulations of flow-rates during the switching interval is that the pumps can be operated with constant load.

A more rigorous and detailed experimental investigation is under way. Further investigations will be done on the optimization of the feed concentration gradient and on combinations of this concept with other concepts (like solvent gradients, VariCol or modulation of flow-rates) to further improve SMB chromatography. Apparently, after the rapid development of discontinuous batch chromatography and the subsequent success of continuous SMB processes a mixed operation mode offers potential for further development.

Acknowledgements

The assistance of Jacqueline Kaufmann in per-

forming the experiments is gratefully acknowledged. Financial support was given by Fonds der Chemischen Industrie.

References

- [1] D.B. Broughton, C.G. Gerhold, US Patent 2 985 589 (1961).
- [2] M.M. Kearney, K.L. Hieb, US Patent 5 102 553 (1992).
- [3] E. Kloppenburg, E.D. Gilles, *Chem. Eng. Technol.* 22 (1999) 813.
- [4] M. Morbidelli, M. Mazzotti, presented at the 15th International Symposium on Preparative/Process Chromatography—Ion Exchange, Adsorption/Desorption Processes and Related Separation Techniques, Washington, DC, 2002, Lecture 201, Book of Abstracts, pp. 53–54.
- [5] O. Ludemann-Hombourger, R.M. Nicoud, M. Bailly, *Sep. Sci. Technol.* 35 (2000) 1829.
- [6] O. Ludemann-Hombourger, G. Pigorini, R.M. Nicoud, D.S. Ross, G. Terfloth, *J. Chromatogr. A* 947 (2002) 59.
- [7] G. Storti, M. Mazzotti, M. Morbidelli, S. Carra, *AIChE J.* 39 (1993) 471.
- [8] G. Guiochon, S.G. Shirazi, A.M. Katti, in: *Fundamentals of Preparative and Nonlinear Chromatography*, Academic Press, Boston, MA, 1994.
- [9] H. Schramm, S. Grüner, A. Kienle, E.D. Gilles, in: *Presented at the European Control Conference ECC '01, Porto, 2001, 2001.*
- [10] H. Schramm, S. Grüner, A. Kienle, *J. Chromatogr. A* 1006 (2003) 3.
- [11] F.G. Helfferich, P.W. Carr, *J. Chromatogr.* 629 (1993) 97.
- [12] M. Kaspereit, P. Jandera, M. Skavrada, A. Seidel-Morgenstern, *J. Chromatogr. A* 944 (2002) 249.
- [13] M. Mazzotti, G. Storti, M. Morbidelli, *J. Chromatogr. A* 769 (1997) 3.
- [14] F. Charton, R.-M. Nicoud, *J. Chromatogr. A* 702 (1995) 97.
- [15] H.K. Rhee, R. Aris, N.R. Amundson, in: *First Order Partial Differential Equations*, Prentice Hall, Englewood Cliffs, NJ, 1989.
- [16] F.G. Helfferich, R.D. Whitley, *J. Chromatogr. A* 734 (1996) 7.
- [17] M. Mazzotti, G. Storti, M. Morbidelli, *AIChE J.* 40 (1994) 1825.
- [18] H. Schramm, A. Kienle, M. Kaspereit, A. Seidel-Morgenstern, Filed as patent DE 102 35 385.9 (2002).