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THE SIMULATED COUNTERCURRENT MOVING BED CHROMATOGRAPHIC REACTOR

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ABSTRACT

The simulated countercurrent moving bed chromatographic reactor (SCMCR) is a device for carrying out chemical reaction and separation simultaneously in a fixed bed. It mimics the behavior of a countercurrent moving bed, in which a stream of solids flows countercurrent to an inert fluid and past a stationary reactant inlet, by periodically changing feed locations sequentially along a fixed bed. True countercurrent motion is thus replaced by a periodic motion, while overcoming the problems of solids handling and attrition inherent in moving bed operations, as well as avoiding the flow channeling that would be attendant with scaleup to large column diameters. The present investigations seek to determine to what extent the moving bed reactor advantages of high product purity and favorable equilibrium shifts are retained in SCMCR operations. Two configurations of the SCMCR, a single fixed bed having a series of inlets and outlets along its length, and a series of columns with an inlet or outlet between each, are considered. Model calculations predict that both configurations give high purity product streams and nearly unit conversions of the equilibrium limited reaction.

KEYWORDS

Moving-bed reactor; countercurrent reactor; chromatographic reactor; product yield; product purity.

INTRODUCTION

Chromatographic reactors permit reactions to be carried out with separation of individual chemical species. The simultaneous separation of reactants and products in a single reactor-separator can give high purity products, and can shift equilibria to favor the yield of products . Recent research on the continuous countercurrent moving bed chromatographic reactor (CMCR)(Cho *et al.*, 1982; Petroulas *et al.*, 1989) has shown that conditions can be found where product purities in excess of 99%, and nearly unit conversion of equilibrium limited reactions can be achieved.

In the CMCR, granular solids flow slowly past a feedport, against a counterpropagating flow of an inert carrier. Problems associated with solids movement are attrition and the resulting requirement for fines removal, inclusion of a solids handling system for recycling, and the maintenance of a uniform solid flow. The last may become a significant problem in large scale operations using large diameter columns.

The process aspects of a countercurrent moving bed can be simulated by successively switching feed and product take-off streams through a series of inlets located at intervals along a fixed bed. A shift of these positions in the direction of the fluid phase flow simulates movement of solids in the opposite direction. In this way the solids flow problem can be avoided. This kind of process (Sorbex) has been very successfully developed by Universal Oil Products for separation of binary mixtures. However, its use as a chemical reactor for combined reaction-separation operations has not been reported.

In this work we have developed models for two approaches to the simulated countercurrent moving bed chromatographic reactor (SCMCR). One of these employs the Sorbex concept of a single packed tower and turns out to be quite similar to the countercurrent moving bed both in concept and in terms of operation. The other, consisting of packed columns in series is more suited to laboratory scale experimentation, and has different output characteristics. Both configurations predict excellent performance in terms of product purity and improvement of conversion.

SINGLE COLUMN CONFIGURATION

The system is schematically represented in Fig. 1. The fixed bed is divided into two sections. The portion of the reactor located just below the feed point to the take-off point will be identified as section I, while the remainder of the column will be designated section II. Each section is subdivided into several stages, each of which may be used to add feed to the system or remove a product stream. The velocity of the fluid phase in section I is denoted by U_I, which is a factor of $1/\kappa$ times U_{II}, the interstitial fluid velocity in section II. Kappa, κ, is the

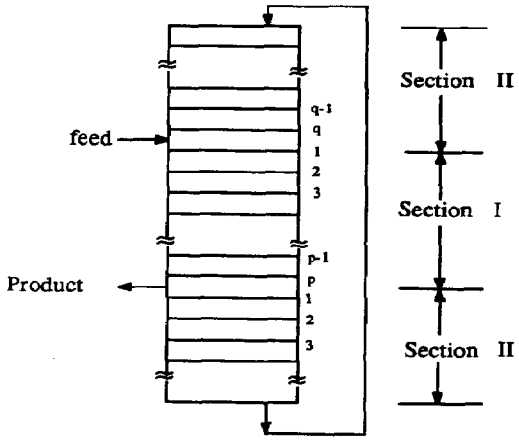

Fig. 1. Discretized simulated countercurrent moving bed reactor.

recycle fraction, where $0 < \kappa < 1$. In order to perform the switching program, the reactor is fitted with a series of inlets that are separated by a constant distance ΔX. The number of segments in sections I and II are p and q, respectively. The corresponding lengths for both sections are L_1 and L_2. Sections I and II remain the same relative to the moving feed and product withdrawal points, but must be redefined with respect to the actual stationary column every time a switch is made.

An equilibrium stage model incorporationg the reaction scheme of equation (1) has been developed, where adsorption is described by a Langmuir isotherm.

$$A(g) \underset{k_{dA}}{\overset{k_{aA}}{\rightleftharpoons}} A_{ads} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B_{ads} \underset{k_{aB}}{\overset{k_{dB}}{\rightleftharpoons}} B(g) \qquad (1)$$

The material balances for the gaseous and solid phases are given by the equations (2).

$$\varepsilon \frac{\partial C^m_{ij}}{\partial t} + \varepsilon u_j \frac{\partial C^m_{ij}}{\partial X} + (1-\varepsilon)\, k_{ai}(N - n^m_{Aj} - n^m_{Bj})\, C^m_{ij} - (1-\varepsilon)\, k_{di}\, n^m_{ij} = 0$$

$$\frac{\partial n^m_{ij}}{\partial t} - k_{ai}(N - n^m_{Aj} - n^m_{Bj})\, C^m_{ij} + k_{di}\, n^m_{ij} + \alpha_i(k_f n^m_{Aj} - k_b n^m_{Bj}) = 0 \qquad (2)$$

where $\alpha_A = -1$, $\alpha_B = 1$.

The two key parameters for simulated systems are the switching time, t_s, which is the time interval between successive switchings, and the switching velocity, ζ, the hypothetical velocity of the solid phase. The switching time is constant and may conveniently be used as a characteristic time for the system. The dimensionless time can thus be defined as $\tau = t/t_s$. The feed and take-off ports are switched when $\tau = 1, 2, 3, \cdots$. The switching velocity can be defined as $\zeta = \Delta X/t_s$ and hence σ, which was found to be the critical parameter for the true countercurrent separator and reactor (Fish et al., 1988), can be defined as

$$\sigma_i = \frac{1-\varepsilon}{\varepsilon} N_{\text{limiting adsorbate}} K_{\text{equil},i} \frac{\zeta}{u_{gas}} \qquad (3)$$

Separation can be accomplished in the reactor by adjusting the carrier gas and pseudo solid velocities, u_g and ζ, such that $\sigma<1$ for one component and $\sigma>1$ for the other. Therefore, by adjusting u_g and ζ we can have one component moving up the column and the other down the column; thus, an observer located at the feed point will observe a countercurrent separation of component A from component B.

The mass balance equations in dimensionless form were discretized to give the equilibrium stage model. The concentration profiles were obtained from the solution of the mass balance equations by a fourth order Runge-Kutta method. Since the period between consecutive switching is constant and equal to 1 (in terms of τ), it is necessary to redefine the stage numbers every time $\tau = 1, 2, 3, \cdots$.

RESULTS

The steady state axial concentration profile of reactant is shown in Fig. 2 for $\tau=6$ (feed plate #7, product take-off plate #15), $\tau = 12$ (13,21) and $\tau = 60$ (1,9). The y-axis scale on the left indicates the stage number and the corresponding numbers on the right indicate values of τ for

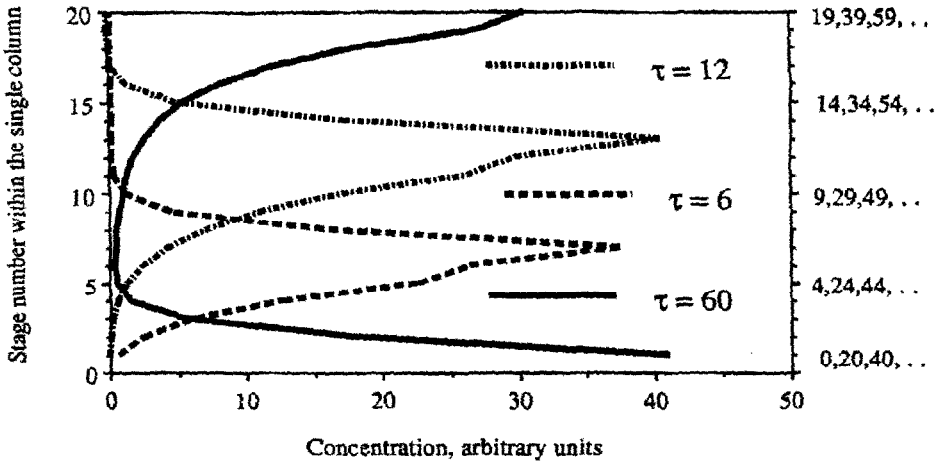

Fig. 2. Concentration profile of A after 6, 12, and 60 feed port switches.

which stages 5, 10, 15 and 20 are the feed plate. Figure 3 shows the steady state concentration profile of both reactant and product along the column for $\tau = 60$. In this figure, the feed enters on plate 1 and product is taken off at plate 9. The parameters used are $L_1 = 160$ cm,

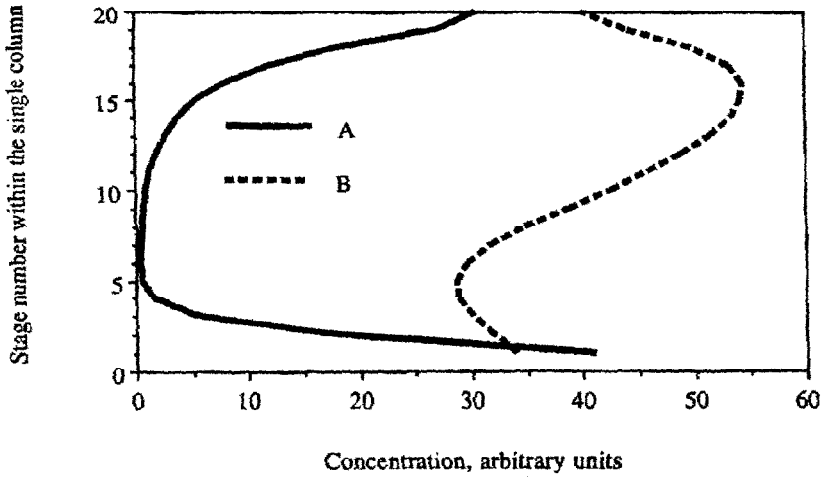

Fig. 3. Concentration profile of A and B.

$L_2 = 240$ cm, $p = 8$, $q = 12$, $\kappa = 0.85$, $t_s = 5$ sec, $\mu_A = 1.5$. The rate constants used are that of Mesitylene hydrogenation reaction at 190°C (Fish et al., 1988). The velocities were set in such a way that $\sigma_A = 1.2$ and $\sigma_B = 0.3$. Under these conditions the conversion was nearly unity and the product purity was 98.5%. The equilibrium conversion at 190°C is 0.62 (Egan and Buss, 1959). All the calculations were done at low feed concentrations, so that the adsorption isotherms are linear. The performance of the simulated countercurrent moving bed reactors for some other values of σ_A, σ_B and $1-\kappa$, the feed rate, are tabulated in Table 1.

Table 1. Performance of simulated reactor

σ_A	σ_B	1-κ	% Purity Product	% Conversion
1.2	0.3	0.15	98.5	99.7
2.0	0.5	0.15	96.3	98.4
1.2	0.3	0.25	95.6	99.1
2.0	0.5	0.25	93.3	98.2

MULTIPLE COLUMN CONFIGURATION

This arrangement consists of a multi-column configuration (see Fig. 4) where the feed port is sequentially moved from one column to the next at specified time intervals. The carrier gas stream enters the system on the column behind the feed column (on the previous feed column) and

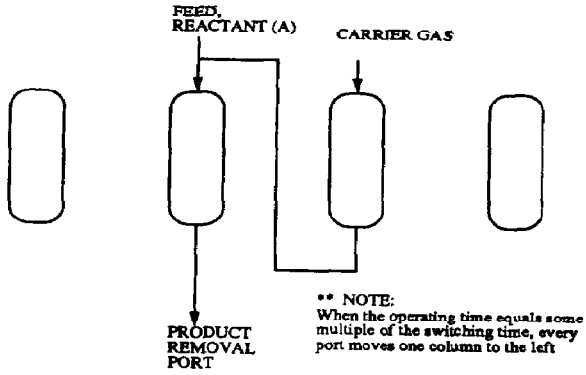

Fig. 4. Simulated countercurrent chromatographic reactor/separator.

and acts to move any remaining material out of this column and add it to the feed. This is analogous to true countercurrent flow of the gas phase past the solid catalyst/adsorbent where the movement of the more strongly adsorbed component (the reactant) is away from the less strongly adsorbed component (the product) relative to the movement of the feed port.

The construction of this alternative model was simple and intuitive. Each column was composed of s theoretical plates. Within each plate the reaction could either completely proceed until the products and reactants had equilibrated or had obtained some fraction thereof. After equilibration (either full or partial) the two components--reactant and product--were then convectively moved down the column a certain number of plates corresponding to their mean velocities. Dispersion was not considered at this point, although it could be included. After the convective movement, the components are now re-equilibrated, new feed is added on the feed column, and the procedure is repeated. This iterative scheme is demonstrated in Fig. 5. After a preset number of iterations (r)--corresponding to a switching time--the feed is moved to the next column and the material remaining in the old column continues to be moved and equilibrated down that column until it is added to the new feed column. This procedure is repeated until a steady-state exiting concentration is observed coming out of successive columns.

One major observation about this model, which is also reflected in experimental results from the simulated countercurrent separator (Fish et al., 1988) and hypothesized to exist for the reactive case as well, is the prediction of dead time in the product concentration. After a column switching there are no products present in the initially clean column, and after some breakthrough time, their elution is observed. This feature is distinctly different from the true countercurrent model where a continuous product stream elutes from the system with a constant concentration. The intuitive realization then can be made for identical overall conversions that the actual product concentrations during the non-dead time period will exceed those for the true countercurrent system. By applying a mass balance on the overall system it becomes apparent that for the case of nearly unit conversion, the sum of the concentration of the continuously fed reactant must equal the sum of the product concentrations during any switching cycle at steady state. Since dead time exists in this system, the concentration of the product after the breakthrough time then must be

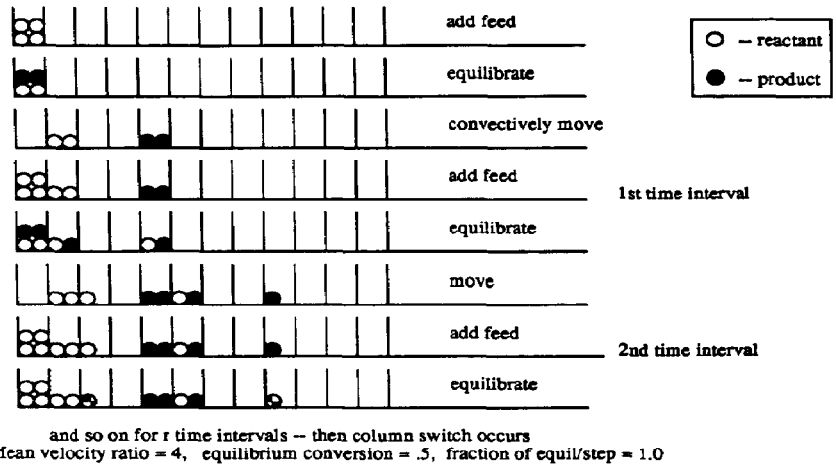

Fig. 5. Example of model construction.

greater than the original feed concentration to satisfy the overall mass balance constraints. In fact, this phenomenon, concentrating of products, has been observed in experimental work on the countercurrent separator and is predicted by this model. The advantage of this result over the traditional countercurrent system could have a major impact on the effectiveness of this system if the reactions are carried out in dilute systems.

Model calculations were carried out to allow comparison with the single column model for the mesitylene hydrogenation reaction. The key model parameters that were used to compare the two cases were the equilibrium conversion (.62) and the ratio of convective velocities of products to reactants (ratio = 4). In this model both the number of plates and the fraction of equilibrium attained at each plate were varied to obtain the best conversions and product purities. A direct correlation between the number of plates used in the single column model and this model could not be made due to the differing definition of the theoretical plate between the two models. The results are presented in Table 2.

Table 2. Parametric variations

Plates/ Column	Fract of Equil/Plate	Conversion	Purity(%)	Normalized Exiting Concentration
4	1	.972	96.81	1.205
4	.1	.985	97.95	1.234
4	.01	.998	99.77	1.248
4	.001	.9992	99.98	1.249
20	.1	.936	90.29	1.194
20	.01	.991	98.43	1.288
20	.001	.999	99.83	1.299
100	.1	.8814	85.57	.979
100	.01	.962	93.17	1.267
100	.001	.9953	99.10	1.323
200	.001	.991	98.25	1.317
400	.001	.983	96.69	1.306

The single column model predicts the reaction to proceed with nearly unit conversion (.997) and produce a high purity product stream (98.5%). Both this degree of conversion and purity could be obtained in this system for a variety of parameters which have been presented in Table 2. For the case of 20 plates, with an equilibrium fraction per plate of .1%, the unsteady concentration profile leading into the steady-state case presented in Fig. 6.

It can be seen that the overall conversion, product purity, and exiting concentration are a function of both the number of plates and the fraction of equilibria that is attained in each plate. Decreasing the equilibrium fraction acts to increase all of the performance criteria. The effect of the number of plates is not as clear. Although the conversion and purity decrease with an increasing number of plates, the exiting concentration appears to undergo a maxima at some intermediate number of plates.

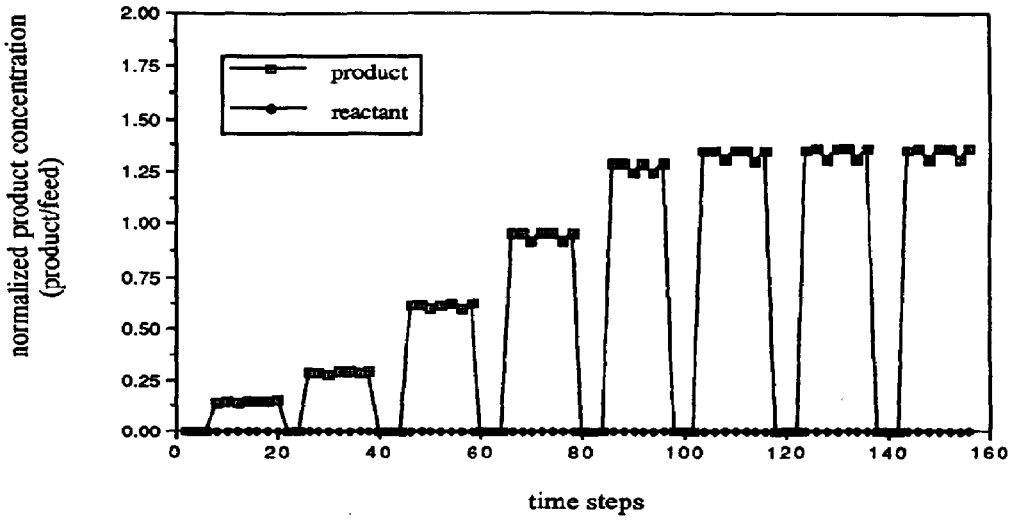

Fig. 6. 20 plates; .1% of equilibrium/plate; --10, 20, 50, 100, 250, 500, 750, 1000 switches; conversion - .999; purity = 99.8%.

Both the single column and multi-column models predict excellent conversions and product purities in the SCMBR for the equilibrium limited Mesitylene hydrogenation. Similar results of nearly unit conversions and purities were obtained experimentally in the true countercurrent reactor (Fish et al., 1989) and predict that equally desirable results can be obtained in the simulated counter-current system.

NOTATION

A	component A, reactant
B	component B, product
C	concentration in the fluid phase
k	rate constant
K	equilibrium constant
L	length
M	number of segments
n	concentration on the solid phase
N	limiting concentration of adsorbates on the solid surfaces
p	number of segments in section I
q	number of segments in section II
t	time
u	velocity
α	stoichiometric coefficients
γ	dimensionless fluid phase concentration
ε	void fraction
κ	fraction recycled
σ	relative carrying capacity
τ	dimensionless time
ζ	switching velocity
r	number of time intervals before column switching
s	number of theoretical plates per column in the multi-column system

SUFFIX

A	component A
a	adsorption
B	component B
b	backward
d	desorption
f	feed, forward
g	gas
i	component i
j	section j
m	mth switching period
r	reaction
s	switching
I	section 1
II	section 2

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