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Analysis and optimization of cross-flow reactors with distributed reactant feed and product removal

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Abstract

A systematic and general model was proposed for the simulation of cross-flow reactors with product removal and reactant feed policies. Six types of cross-flow reactors were analyzed for reversible series–parallel reaction systems and their optimal feed distributions were determined by maximizing the desired product yield at the outlet of the reactor. The performances of reactors with different types of feed policies were compared at their optimal operating conditions. For irreversible reaction systems with lower order in distributed reactant for the desired reaction than those for undesired reactions, a higher yield and selectivity of the desired product could be achieved with the reactors with staged feed than with conventional co-feed reactors and a sufficiently high residence time was required by staged feed reactors to significantly improve the desired product yields and selectivities over those obtained by a co-feed reactor. However, for reversible reaction systems, the desired product yield always reached a maximum value, and then dropped down as the residence time increased. In addition to the kinetic order and residence time requirements, the rate constants of the reactions involved have to fall within certain ranges for the distributed feed reactor to obtain a higher maximum yield than one-stage co-feed reactors. Optimally distributed feed reactors always give higher maximum product yields than evenly distributed reactors with the same number of feed points. However, the improvement of yields is not as great as that between co-feed reactors and evenly distributed reactors. On the other hand, for reaction systems with higher order with respect to the distributed reactant in the desired reaction than the undesired reactions, co-feed reactors always give higher yield than staged feed reactors.

Keywords: Cross-flow reactor; Membrane reactor; Reactant feed; Optimal reactor design; Reactor analysis

1. Introduction

In most of the commonly used tubular reactors the feed stream is supplied to the reactor system at only one point and the product stream leaves the reactor at the outlet point. However, it is possible to have distributed feed and distributed take-off streams along the reactor length. This type of reactor is called a cross-flow reactor [1] and different flow configurations (and thus axial concentration and temperature distributions) can be obtained by changing the locations of the feed and take-off streams and the flow rate through them. If the desired and undesired reactions differ in their kinetic orders, this will result in either higher or lower yield or selectivity of the desired product according to the circumstances of the kinetics of the reaction system.

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As the number of feed and sink points approach infinity, the cross-flow reactor resembles a membrane reactor. The two most important uses of membrane reactors are: (i) to reach higher conversions of reversible reactions, and (ii) to obtain higher selectivity and yield of parallel–series reactions. In the first case, the membrane is permselective to one or more of the products involved in reversible reactions such as hydrocarbon dehydrogenation and the reaction is shifted by selectively removing the product(s) through the membrane. In the latter case, the membrane is used to supply one of the reactants in a controlled way for a multiple reaction network, where low concentration of the distributed reactant is required in favor of the desired reaction.

Bernstein and Lund [2] studied the enhancement of the intermediate product yield of series–parallel reaction systems by using membrane reactors. Van de Vusse and Voetter [3] determined the optimal concentration gradients in tubular reactors with two feed components by introducing one of the components along the reactor tube. Optimizations were carried out for different reaction rate ratios on an analogue computer and compared with those with one-stage tubular reactors. However, only the continuous feed mode was considered in their study and, furthermore, they took the value of a very important parameter — the overall feed ratio of the two reactants — as unity. Reyes et al. [4] developed a detailed kinetic-transport model including both homogeneous and heterogeneous reactions for methane coupling. They found that staging the introduction of oxygen along the reactor length minimized secondary oxidation reaction by lowering the local oxygen partial pressure and led to a slight increase in product yield. They did not maximize the product yield by adjusting the overall methane to oxygen feed ratio or the oxygen feed distribution. Harold et al. [5] presented a simple model to examine the performance of a supported catalytic membrane with a consecutive–parallel reaction system. Closed-form solution showed that segregation of the two reactants to opposite sides of the membrane is an effective strategy for increasing the yield of desired product. Again, no optimization was done regarding any of the parameters considered in their study.

In this paper a systematic and concise model of cross-flow reactors is proposed. The reactor configuration simulated in this study was a one-dimensional tubular reactor with one of the reactants fed along the reactor length and the other at the inlet. At the same time, any species involved in the reaction may permeate through the reactor wall. The simulation study was focused on the effect of reaction kinetics and reactant feed strategy (rather than the flow pattern, transport properties, etc.) on the performance of the cross-flow reactors. Six types of feed policies were considered and their optimizations were carried out by adjusting the overall feed ratio of the reactants or feed distribution function of the reactant which was fed along the reactor length, so that the yield of the desired product at the outlet of the reactor was maximized.

2. Problem formulation and algorithm

The following parallel–series reaction scheme is considered in this study:

$$A + \nu_1 B \rightarrow \nu_P P + \nu_C C, \quad (1)$$

$$A + \nu_2 B \rightarrow \nu_S S + \nu_D D, \quad (2)$$

$$\nu_P P + (\nu_2 - \nu_1) B \rightarrow \nu_S S + \nu_D D - \nu_C C, \quad (3)$$

$$\nu_P P + \nu_C C \rightarrow A + \nu_1 B, \quad (4)$$

where A and B are the reactants; P is the desired product; and S the undesired product. C and D are called by-products. Suppose that the rate expressions of the four reactions are of the power-law type.

$$r_1 = k_1 C_A^{a_1} C_B^{b_1}, \quad (5)$$

$$r_2 = k_2 C_A^{a_2} C_B^{b_2}, \quad (6)$$

$$r_3 = k_3 C_P^{a_3} C_B^{b_3}, \quad (7)$$

$$r_4 = k_4 C_P^{a_4} C_C^{b_4}. \quad (8)$$

For convenience, the kinetics are said to be favorable, neutral, and unfavorable respectively if b_1 is less than, equal to, or greater than b_2. The development of the reactor model is based on the following assumptions: (a) steady state, isothermal, and isobaric operation; (b) ideal radial mixing and no axial dispersion; (c) only reactant B is fed along the length of the reactor to the reaction side while reactant A fed at the inlet. Six types of feed policies are considered in this study according to the feed policies of the reactant B (Fig. 1); (d) any species may permeate through the reactor wall depending on their permeabilities; and (e) no reaction in the permeation side. The reactor model can be expressed by the following ordinary differential equations:

$$\frac{\mathrm{d}x_1}{\mathrm{d}t} = \frac{\sigma_1 \delta_A^{a_1} \delta_B^{b_1}}{\delta^{a_1+b_1}} - \frac{\sigma_3 \delta_P^{a_3} \delta_B^{b_3}}{\delta^{a_3+b_3}} - \frac{\sigma_4 \delta_P^{a_4}\, \delta_C^{b_4}}{\delta^{a_4+b_4}}, \tag{9}$$

$$\frac{\mathrm{d}x_2}{\mathrm{d}t} = \frac{\sigma_2 \delta_A^{a_2} \delta_B^{b_2}}{\delta^{a_2+b_2}} + \frac{\sigma_3 \delta_P^{a_3} \delta_B^{b_3}}{\delta^{a_3+b_3}}, \tag{10}$$

$$\frac{\mathrm{d}x_i}{\mathrm{d}t} = \lambda_i \left(\frac{\delta_i}{\delta} - \frac{\delta_i'}{\delta'} \right)$$

$$i = A,\ B,\ P,\ S,\ C,\ D,\ I, \tag{11}$$

where t is the dimensionless axial position. x_1 and x_2 are the yields of the desired and the undesired products defined by the fraction of reactant A consumed in the formation of product P and S, respectively. x_i ($i = A,\ B,\ P,\ S,\ C,\ D,\ I$) is the ratio of flow rate of species i in the permeate side to the initial flow rate of reactant A in the reaction side. Expressions for δ_i and δ_i' are listed in Table 1, and

Table 1
Expressions for δ_i and δ_i' used in Eqs. (9)–(13)

Species i	δ_i	δ_i'
A	$1 - x_1 - x_2 - x_A$	x_A
B	$\theta_B - \nu_1 x_1 - \nu_2 x_2 - x_B$	x_B
P	$\nu_P(x_1 - x_P)$	$\nu_P x_P$
S	$\nu_S(x_2 - x_S)$	$\nu_S x_S$
C	$\nu_C(x_1 - x_C)$	$\nu_C x_C$
D	$\nu_D(x_2 - x_D)$	$\nu_D x_D$
I	$\theta_I - x_I$	$\theta_I' + x_I$

$$\delta = 1 + \theta_B + \theta_I + \delta_1 x_1 + \delta_2 x_2 - x_A - x_B - \nu_P \delta_P - \nu_S \delta_S - \nu_C \delta_C - \nu_D \delta_D - x_I, \tag{12}$$

$$\delta' = \theta_I' + x_A + x_B + \nu_P \delta_P + \nu_S \delta_S + \nu_C \delta_C + \nu_D \delta_D + x_I. \tag{13}$$

δ_1 and δ_2 are the net mole number changes in reactions (1) and (2). θ_I and θ_I' are the initial feed ratios of inerts I in the reaction side and

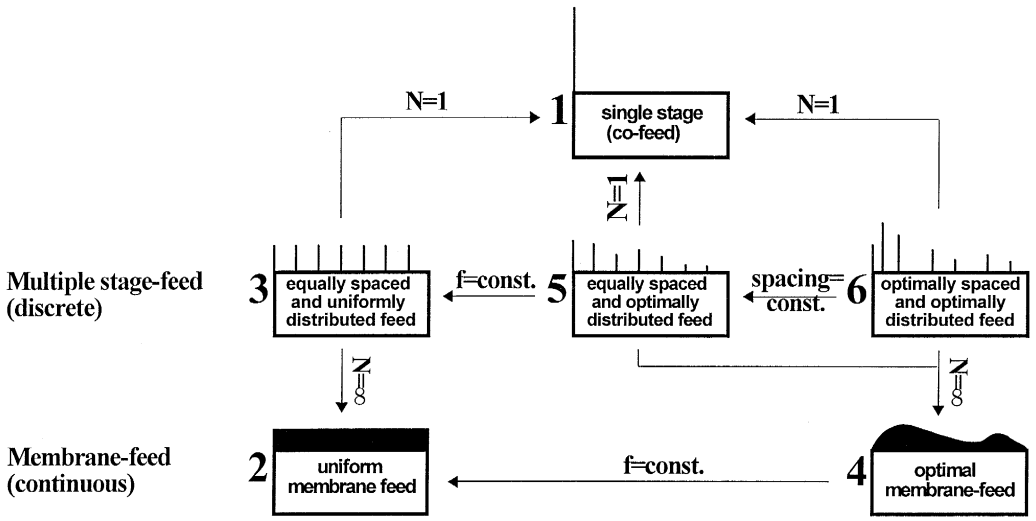

Fig. 1. Six types of feed policies of reactant B and their interrelations. (The numbers labeled next to the rectangles refer to the types of reactors; N is the number of feed points and f is the feed distribution function.)

Table 2
Integral feed ratios of B for different types of feed policies

No	Feed policies	Integral feed ratio (θ_B)	Notes
1	Single-stage	θ_{B0}	$\theta_{B0} = \theta_B\|_{t=1}$ $n = i$, if $\frac{i-1}{N} \le t < \frac{i}{N}$
2	Uniformly distributed, continuous	$\theta_{B0} t$	$n = N$, if $t = 1$
3	Equally spaced and distributed, discrete	$\theta_{B0}(\frac{n}{N})$	$(i = 1, 2, \ldots, N)$ N = number of feed points
4	Arbitrarily distributed, continuous	$\int_0^t \phi(u)\mathrm{d}u$	$n = i$, if $t_i \le t < t_{i+1}$ $n = N$, if $t_N \le t \le 1$
5	Equally spaced and arbitrarily distributed, discrete	$\sum_{i=1}^{n} \phi(\frac{i-1}{N})$	$(i = 1, 2, \ldots, N-1)$ Feed position $t_i = \psi(\frac{i-1}{N})$
6	Arbitrarily spaced and arbitrarily distributed, discrete	$\sum_{i=1}^{n} \phi[\psi(\frac{i-1}{N})]$	ϕ = feed distribution function ψ = feed position function

permeation side to reactant A in the reaction side (F_{A0}). The integral feed ratio θ_B is the ratio of the total mole flow rate of reactant B introduced into the reaction side of the reactor from $t = 0$ to $t = t$ to the initial mole flow rate of reactant A in the reaction side of the reactor. The expressions of integral feed ratios for the six types of feed policies considered are given in Table 2. λ_i is the dimensionless permeability of species i, which is defined by

$$\lambda_i = \frac{\Pi_i \rho_i C_T}{\nu_i \epsilon_i F_{A0}} \qquad i = A, B, P, S, C, D, \text{ or } I,$$

where ρ_i is the permeability, Π_i the area, ϵ_i the thickness of the reactor wall for the permeation of species i. C_T is the total concentration. σ_1, σ_2, σ_3, and σ_4 are dimensionless numbers defined by

$$\sigma_i = k_i \tau_{A0} C_T^{a_i + b_i} \qquad i = 1, 2, 3, 4.$$

The residence time τ_{A0} is the ratio of reactor volume to the initial mole flowrate of reactant A in the reaction side. σ_i will be called the dimensionless residence time (when rate constants are fixed) or dimensionless rate constant (when residence time is fixed) with respect to the ith reaction.

The system equations were integrated by fourth order Runge–Kutta Method with adaptive stepsize control. The Golden Section Search Method was used in the determination of the overall feed ratio θ_{B0} for feed policies of types 1,2, and 3 and optimal residence time. The Hook–Jeeves Method [6] was employed to find the optimal feed distribution functions for feed policies 4, 5, and 6.

3. Results and discussions

Fig. 2 shows the maximum yields of the desired product as functions of the dimensionless residence time for the six types of reactors for the irreversible parallel–series reaction system (consisting of reaction 1, 2 and 3 only) with

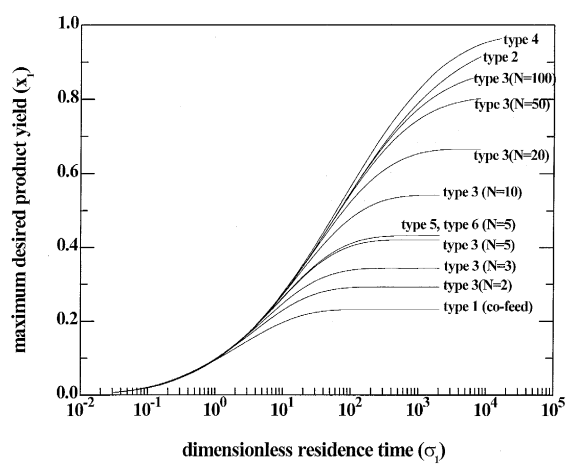

Fig. 2. Dependence of maximum yield of desired product on dimensionless residence time for favorable irreversible parallel–series kinetics.

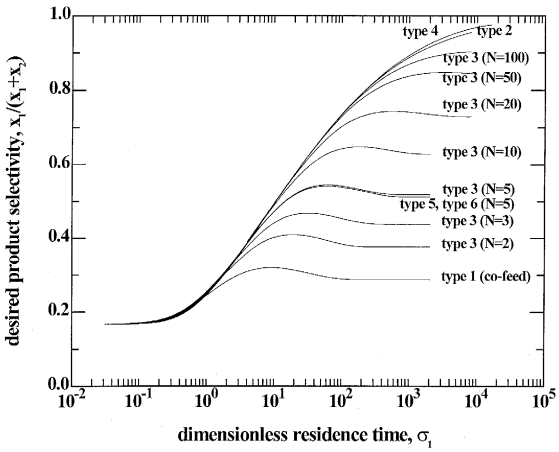

Fig. 3. Selectivity of the desired product at maximum yield as a function of dimensionless residence time for favorable kinetics.

$\nu_i = 1$ $(i = 1,\ 2,\ P,\ S,\ C,\ D)$, $k_1{:}k_2{:}k_3 =$ 1:10:10, and $a_1 = a_2 = a_3 = b_1 = 1$, $b_2 = b_3 = 2$ (favorable kinetics). Fig. 3 shows the selectivities at the same conditions as shown in Fig. 2. It can be seen from these figures that at the optimal feed distribution of reactant B or optimal overall feed ratio of B to A, both selectivity and yield of the desired product increase as the number of feed points and dimensionless residence time increase. In addition, the optimal distributed feed policies always result in a higher maximum product yield than evenly distributed reactors both for discrete (with same number of feed points) and continuous feed modes. In the low σ_1 region, where the residence time is short and the conversion is low, the effect of distributed feed of B has a small effect on the performance of reactors and all the reactors nearly give the same selectivity and yield as the single stage co-feed reactor. This suggests that with favorable kinetics, a sufficiently large σ_1 value is required by the staged feed reactors to realize significantly higher product yields than a co-feed reactor. Therefore, only at higher σ_1 values do staged feed policies show their advantages over co-feed reactors and 100% desired product yield could be realized when both the stage number and residence time approach infinity. However, in the case of unfavorable kinetics, where the desired reaction has a higher kinetic order in reactant B, the distributed feed policy (which lowers the concentration of B) is detrimental to the desired reaction. As a result, the maximum yield achieved by the co-feed reactor is higher than those by distributed feed reactors [7].

A comparison of maximum yields obtained by the co-feed reactor $(N = 1)$ and the membrane-feed reactor $(N = \ )$ for favorable kinetics (with the same kinetic parameters as used in Fig. 2) in terms of dimensionless reaction rate constants (σ_1, σ_2, and σ_3) is demonstrated in Fig. 4. For any reaction system with its dimensionless rate constants (σ_1, σ_2, σ_3) on the

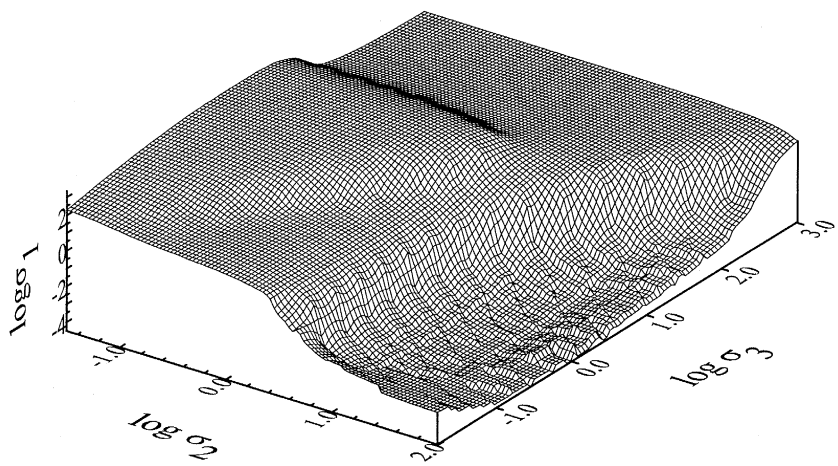

Fig. 4. Comparison of performances between co-feed and membrane-feed reactors with favorable parallel–series kinetics in σ space.

curved surface, the membrane reactor gives the same maximum product yield as the co-feed reactor. Below the surface, the co-feed reactor gives higher maximum product yield; while above the surface, the membrane reactor gives higher maximum product yield. Fig. 4 also tells us that for favorable, irreversible parallel–series reaction system, an increase in either σ_1 or σ_2 will result in the increase of the maximum yield difference between membrane-feed and co-feed reactors (Δy), while an increase in σ_3 causes a decrease of Δy in lower σ_3 region and an increase of Δy in higher σ_3 region.

Fig. 5 shows the dependence of maximum yields of the desired product on the dimensionless residence time for reversible parallel reaction system (reactions 1, 2 and 4) with $\nu_i = 1$ $(i = 1, 2, P, S, C, D)$, $k_1{:}k_2{:}k_4 = 1{:}10{:}1$, and $a_1 = a_2 = a_4 = b_1 = b_4 = 1$, $b_2 = 2$ (favorable kinetics). Again, the membrane feed-reactor offers the highest maximum yield of the desired product and the increasing of the number of feed points results in higher product yield. However, unlike irreversible reaction systems, there exists an optimal residence time for any type of reactor. As the residence time passes this optimal value, the desired product yield begins to drop off due to the continuing of the undesired parallel reaction after the equilibrium

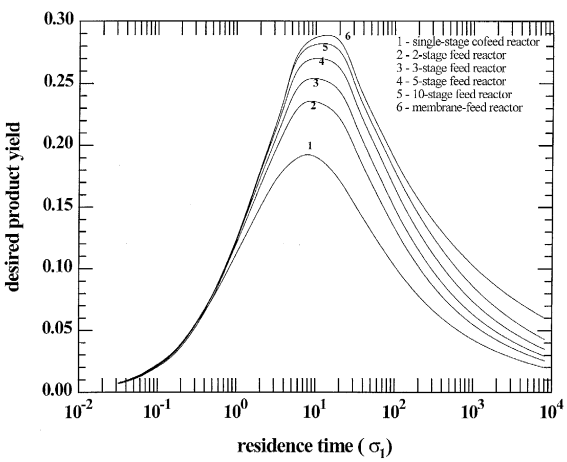

Fig. 5. Desired product yield as a function of dimensionless residence time for favorable reversible parallel kinetics.

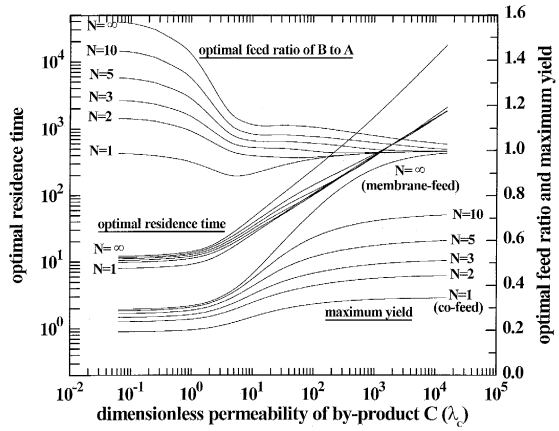

Fig. 6. Maximum yields of cross-flow reactors and their optimal residence times and optimal overall feed ratios of B/A as a function of permeability of removed product for reversible parallel kinetics.

of the reversible reaction has been reached. As in the irreversible system, for unfavorable kinetics the maximum yield achieved by co-feed reactor is the higher than those by distributed feed reactors over the entire σ_1 range (not shown here).

The dependence of maximum yields and their corresponding optimal overall feed ratios and optimal residence times of co-feed, stage-feed, and membrane-feed reactors on the permeability of product C is shown in Fig. 6. Here the kinetic parameters are the same as those used in Fig. 5 and the permeabilities of all the species (except by-product C) are assumed to be zero. It can be seen from Fig. 6 that both residence time and the permeability of the product to be removed have to be high enough for the membrane-feed reactor to realize significant improvement on the desired product yield over the co-feed reactor.

Fig. 7 compares the performances of the co-feed and membrane-feed reactors with favorable kinetics. The dimensionless permeabilities of reactant C used are zero in the bottom graph and 10 in the top one, while the permeabilities of the other species are zero. Since for any reaction system whose $(\sigma_1, \sigma_2, \sigma_4)$ values are located above the curved surface, membrane

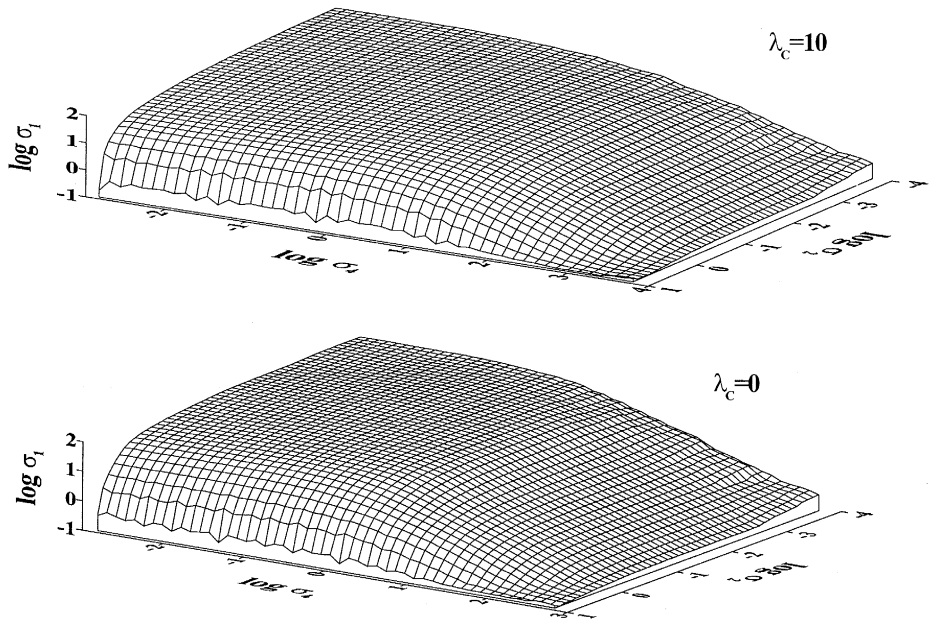

Fig. 7. Comparison of performances between co-feed and membrane-feed reactors with favorable reversible parallel kinetics in σ space.

feed reactor will give higher maximum yield of the desired product, an increase either in desired reaction rate σ_1, parallel reaction rate σ_2, or reversible reaction rate σ_4 will increase the maximum yield of the desired product achieved by membrane-feed reactor more than that by co-feed reactor. Note that the increase in the permeability of the removed product (by-product C) causes the membrane feed reactor-favorable region in the σ-space to become smaller.

4. Conclusions

A systematic model has been presented which describes six types of cross-flow reactors. Optimization of all six types of reactors was carried out by determining the optimal feed distribution of the distributed reactant that has different kinetic orders for desired and undesired reactions so that the desired product yield at the outlet of the reactor was maximized. It must be pointed out that only under their optimal feed ratio will the comparison of performance of different types of reactors be meaningful and reasonable.

Detailed parametric studies showed that the following three requirements have to be satisfied in order that the staged feed reactor can achieve higher maximum yield than the conventional single-stage co-feed reactors. The reaction order of the staged feed reactant for the desired reaction has to be lower than those for the undesired reactions. The residence time and permeability of the product to be removed have to be high enough. The dimensionless rate constants of the reactions involved should be within a certain region. Essentially, Fig. 4 and Fig. 7 can be used to screen reactions as to whether a membrane reactor can provide increased yield of desired product as opposed to conventional plug flow reactors.

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