INTERMEDIATE PRODUCT YIELD ENHANCEMENT WITH A CATALYTIC INORGANIC MEMBRANE—I. ANALYTICAL MODEL FOR THE CASE OF ISOTHERMAL AND DIFFERENTIAL OPERATION

M. P. HAROLD

Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003, U.S.A.

and

V. T. ZASPALIS, K. KEIZER and A. J. BURGGRAAF

Faculty of Chemical Technology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

(First received 20 May 1992; accepted in revised form 18 November 1992)

Abstract—A simple model is developed to examine the performance of a supported catalytic membrane within which occurs the consecutive-parallel reaction system given by $A + B \rightarrow R$, with rate $= k_1 p_A^{\alpha_{A1}} p_B^{\alpha_{B1}}$, and $A + R \rightarrow P$, with rate $= k_2 p_A^{\alpha_{A2}} p_R^{\alpha_{R2}}$. Closed-form solutions reveal that segregation of reactants A and B to opposite sides of the membrane is an effective strategy for increasing the desired product (R) point yield. However, increases in the component R yield come at the expense of the point catalyst utilization, due, in part, to depletion of reacting components B and R. The membrane performance is sensitive to the relative reaction orders with respect to component A for the special case in which the rates are zeroth-order with respect to B and R ($\alpha_B = \alpha_R = 0$). The segregation strategy is shown to be most beneficial if three requirements are met: (i) $\alpha_{A1} < \alpha_{A2}$, (ii) k_1, k_2 sufficiently large and (iii) active layer sufficiently thin compared to support. Under favorable conditions [requirements (i)–(iii) met], component R is selectively produced near the active layer surface, and diffuses out of the membrane before further reaction to undesired product (P). The simulations indicate that the fractional increases in the R yield attained, as the degree of segregation is increased, exceed the fractional decreases in catalyst utilization. A secondary benefit of the membrane design is the confinement of reaction products in the bulk stream on the active layer side, thus reducing the downstream separation needs.

INTRODUCTION

Thin, supported films of inorganic materials have been the focus of considerable research in recent years. The two applications of these inorganic membranes that are of particular interest to chemical engineers are in gas separations and catalysis. The main challenge in the separation applications is to tailor the membrane with a specific permselectivity to effect the high-temperature removal of one component from a gas mixture. There is a great incentive to develop thermally stable, microporous membranes which achieve selectivity greater than the Knudsen selectivities, for example. Recent advances in the preparation of supported ceramic films make this and other goals achievable (e.g. Leenaars *et al.*, 1984; Leenaars and Burggraaf, 1985; Uhlhorn *et al.*, 1987; Gieselman *et al.*, 1988; Keizer *et al.*, 1991; Cini *et al.*, 1991). The main challenges in the catalysis applications are to design supported catalytic films which overcome certain hurdles faced in conventional catalytic reactors. These hurdles include:

- (i) reaction equilibrium limitations,
- (ii) mass transport limitations, which reduce overall activity,
- (iii) intrinsic catalytic activity limitations,

- (iv) strict stoichiometric feed rates of reactants and
- (v) transport limitations which reduce desired-product selectivity.

Applications of inorganic membranes for catalysis have been reviewed by Armor (1989), Hsieh (1989), Zaspalis (1990), and Keizer *et al.* (1991).

Particular attention has been placed on hurdle (i) above. A catalytic membrane can be used to catalyze the equilibrium-limited reaction given by

With a permselective function, the membrane can remove a product (C) selectively and, thus, shift reaction equilibrium to the right. The performance of several different catalytic membrane systems has been tested for dehydrogenation; reactions studied include cyclohexane to cyclohexene (Shinji *et al.*, 1982; Sun and Khang, 1988), ethane to ethylene (Champagne *et al.*, 1990), ethylbenzene to styrene (Gallagher *et al.*, 1990), butane to butene (Zaspalis *et al.*, 1991a, b), and methanol to formaldehyde (Zaspalis *et al.*, 1991a, b). The key operating principle in these studies is to remove hydrogen selectively from the reaction mixture through the membrane. Indeed, this principle is the basis for the much older technology of using dense

Pd films to effect hydrogen separation for improved reactor performance (e.g. Gryaznov, 1986 and references therein; Armor, 1989; Itoh and Govind, 1988).

Catalytic inorganic films can also be used to reduce mass transport limitations in a gas-liquid catalytic reaction system [hurdle (ii) above]. The support membrane serves to segregate the bulk liquid and gas phases (de Vos *et al.*, 1982; Cini and Harold, 1991). This allows the limiting volatile reactant to be supplied directly to the catalytic layer, as long as the gas-liquid interface is properly positioned at the active-layer-bulk-gas interface.

In addressing hurdle (iii) above, dense inorganic films are used as electrochemical pumps of oxygen ions (O^{2-}) and/or protons (H^+) to increase intrinsic catalytic activity (Stoukides, 1988; Vayenas *et al.*, 1990). Solid electrolyte O^{2-} conductors include solutions of oxides such as Y_2O_3/ZrO_2 . An applied current results in the conduction of O^{2-} to the anode (catalyst), where the desired oxidation reaction occurs. Increases in the catalytic activity due to changes in the catalyst work function have been observed during electrochemical pumping (Eng and Stoukides, 1991).

Certain catalytic reactions have strict demands on the feed rates of reactants in order to insure the complete conversion [hurdle (iv) above]. Reactions include the Claus reaction ($2H_2S + SO_2 \rightarrow 3S + 2H_2O$) and NO reduction by ammonia ($NO + NH_3 \rightarrow N_2 + H_2O$). The use of a supported membrane has the advantage of eliminating such feed demands if the catalytic reaction is sufficiently fast. Under such conditions, the molar fluxes of each reactant fed from opposite sides of the membrane are determined by transport parameters (diffusivities, permeability) and the location within the active layer of the reaction plane (i.e. the diffusion length). This concept has been demonstrated successfully (Sloot *et al.*, 1990, 1992; Zaspalis 1990).

Fig. 1. The use of a supported catalytic membrane is proposed to improve desired product yield in a consecutive-parallel reaction system.

Desired product selectivity limitations are often encountered in conventional catalytic reactors due to mass and heat transport limitations [hurdle (v) above]. Thus, an intrinsically selective catalyst (e.g. catalyst powder under differential, isothermal conditions) may not be so under realistic operating conditions (e.g. nonisothermal bed of catalytic pellets with integral conversion). The goal in this application of catalytic inorganic membranes is to improve the overall yield of a desired product in a complex reaction system. Potential strategies include the segregation of the reactants on opposite sides of the membrane, or strategic placement of the active layer within the support. For example, Zaspalis *et al.* (1991b, c) examined different feed strategies for methanol oxidative dehydrogenation on $\gamma-Al_2O_3/\alpha-Al_2O_3$ and $Ag/\gamma-Al_2O_3/\alpha-Al_2O_3$ membranes. Agarwalla and Lund (1992) showed with modeling that the selectivity of the intermediate (B) in a consecutive reaction system ($A \rightarrow B \rightarrow C$) can be improved if the membrane is permselective to B.

REACTANT SEGREGATION TO IMPROVE DESIRED PRODUCT YIELD—RATIONALE

The current modeling study focuses on the use of reactant segregation. More specifically, our objective is to determine the conditions for which such a strategy can improve the yield of the desired intermediate (R) in the reaction system given by

The network is parallel with respect to A and consecutive with respect to B and R. (The convention followed is that the stoichiometric coefficients are all positive. The sign differences between reactants and products are accounted for in the material balances.) Many industrially important catalytic reactions have this structure. Figure 1 gives one example, a hydrocarbon partial oxidation network, where A represents oxygen, B the hydrocarbon (e.g. ethylene), R the desired partial oxidation product (e.g. acetaldehyde), and P the undesired total oxidation product(s) (e.g. carbon dioxide and water).

A major factor affecting the overall yield of the desired product (R) in the consecutive-parallel network is the extent of transport limitations. The transport impact depends not only on the catalytic activity and kinetics, as one would expect, but also on the relative supplies of the reaction components (i.e. which reactant in each reaction is limiting). Under conditions in which component A is the limiting reactant, the reaction system resembles the parallel network given by

The impact of component A transport limitations depends on the reaction orders with respect to A in

each reaction, given by α_{A1} and α_{A2} , respectively. The following rules apply if both reactions are of positive order in A (Froment and Bischoff, 1979):

- If $\alpha_{A1} > \alpha_{A2}$: limitations are detrimental to R yield.
- If $\alpha_{A1} = \alpha_{A2}$: limitations have no effect on the R yield.
- If $\alpha_{A1} < \alpha_{A2}$: limitations are beneficial to R yield.

Independent of the relative magnitudes of α_{A1} and α_{A2} , the transport limitations always have a detrimental impact on the catalyst utilization (or effectiveness). On the other hand, under conditions in which A is in excess, the reaction system resembles the consecutive network given by

For this network, if both reactions are of positive order with respect to B and R, component R transport limitations have a detrimental impact on both the R yield and the catalyst effectiveness.

These limiting-case behaviors of the consecutive-parallel network are the keys to the use of reactant segregation in a supported catalytic membrane as a means of improving catalyst performance. Two basic ideas comprise the membrane design and operational strategy. The first idea is to exploit the beneficial impact of transport limitations on desired product (R) yield for reaction systems which satisfy the kinetic constraint of $\alpha_{A1} < \alpha_{A2}$. As Fig. 1 depicts, reactant A is supplied to the supported active layer from the side of the support and reactant B is supplied from the side of the active layer. With this strategy, the support serves to limit the supply of A to the active layer where it reacts with B. Based on the above arguments, an increase in the R yield over the yield obtained with bulk streams of equal compositions should be the result. This yield increase should come at the expense of active layer utilization, however. The second idea is to use an active layer that is sufficiently thin, to avoid the detrimental component R diffusion limitations anticipated when R is the limiting reactant in the second reaction. A secondary benefit of a sufficiently thick support and thin active layer is that reaction products should exit primarily from the side of the active layer.

This study confronts these ideas by way of modeling. A membrane model is developed that has enough features as to be realistic but enough simplifying assumptions that the results can easily be interpreted. Thus, the consecutive-parallel network with power-law kinetics and isothermal and differential operation is examined. Given this simplified treatment, it is not possible to draw any far-reaching conclusions about the advantages of the membrane reactor over conventional reactors. A more modest goal is to elucidate the reaction-transport interactions within a supported catalytic membrane and how these interactions impact the desired product yield

and catalyst utilization. Simulations using a more sophisticated membrane model which accounts for heat effects and integral operation as well as experimental verification of the model predictions were recently presented (Harold *et al.*, 1992). Details will be reported elsewhere.

MODEL DEVELOPMENT

A schematic of the catalytic membrane is shown in Fig. 2. A porous catalytic layer of thickness δ is supported on a porous, catalytically inert layer of thickness δ_s . Components diffuse within both layers. Given the intended spirit of the study, the following simplifying assumptions are made in constructing the mathematical model:

- The entire system is at a uniform temperature and total pressure. This implies that the reactions are isothermal, nonisobaric intraparticle transport effects are negligible, and no total pressure gradient is applied across the membrane.
- Pore diffusion is described by a simple effective Fickian form. This is a reasonable assumption if a diluent is present in sufficient excess (Cussler, 1984).
- External mass transport limitations are negligible.
- Differential operation is considered. The overall rates of each reaction are computed for a specified set of partial pressures of the reacting components (A, B, R) in the two surrounding bulk phases. Thus, the calculated rates are point values within a reactor.
- The intrinsic kinetics of each reaction are described by the following power-law rate expressions:

$$r_1 = k_1 p_A^{\alpha_{A1}} p_B^{\alpha_{B1}} \quad (1)$$

$$r_2 = k_2 p_A^{\alpha_{A2}} p_R^{\alpha_{R2}} \quad (2)$$

In this study we consider two different combinations of the reaction orders, following the discussion in the Introduction. Case I considers unequal orders with respect to component A (i.e. $\alpha_{A1} = 0$, $\alpha_{A2} = 1$). Case II considers equal orders with respect to component

Fig. 2. Schematic of the membrane to be modeled. The active layer of thickness δ is supported by an inert layer of thickness δ_s . Two bulk streams with specified compositions contact each side of the membrane.

A (i.e. $\alpha_{A1} = 1$, $\alpha_{A2} = 1$). Both cases I and II assume a zeroth-order dependence on components B and R (i.e. $\alpha_B = 0$, $\alpha_R = 0$). The two cases are summarized in equation form as follows:

Case I:

$$r_1 = k_1 H(p_A) H(p_B) \quad (3a)$$

$$r_2 = k_2 p_A H(p_R) \quad (3b)$$

Case II:

$$r_1 = k_1 p_A H(p_B) \quad (4a)$$

$$r_2 = k_2 p_A H(p_R) \quad (4b)$$

Proper handling of the zeroth-order dependences demands the appearance of H (the Heaviside function) in the rate expressions because of possible depletion of reactants A (case I only), B, and R within the active zone. By accounting for depletion, the zeroth-order dependencies are a reasonable approximation of more realistic, positive reaction orders. For example, recall the qualitative resemblance of the effectiveness-Thiele modulus dependence for a unimolecular, zeroth-order catalytic reaction and that of integer-order cases (Froment and Bischoff, 1979). A real advantage of the two cases considered is the ability to get closed-form solutions. This simplifies considerably the analysis and interpretation of the results.

With these assumptions in mind, the mathematical formulation is now described.

In the *active zone* ($0 < z < \delta$) both diffusion and reaction occur. For species A, B and R, we have, respectively,

$$\frac{D_A}{RT} \frac{d^2 p_A}{dz^2} = r_1 + r_2 \quad (5)$$

$$\frac{D_B}{RT} \frac{d^2 p_B}{dz^2} = v_B r_1 \quad (6)$$

$$\frac{D_R}{RT} \frac{d^2 p_R}{dz^2} = -v_{R1} r_1 + v_{R2} r_2 \quad (7)$$

where r_1 and r_2 are given by eqs (3) and (4), respectively, D_I ($I = A, B, R$) is the effective diffusivity of species I in the active zone, R is the gas constant, and T is the temperature.

In the *inert zone* ($-\delta_s < z < 0$) only diffusion occurs:

$$\frac{D_{A0}}{RT} \frac{d^2 p_A}{dz^2} = 0 \quad (8)$$

$$\frac{D_{B0}}{RT} \frac{d^2 p_B}{dz^2} = 0 \quad (9)$$

$$\frac{D_{R0}}{RT} \frac{d^2 p_R}{dz^2} = 0 \quad (10)$$

where D_{I0} ($I = A, B, R$) is the effective diffusivity of species I in the inert zone. D_I and D_{I0} are not equal because of possible morphological differences between the support and active layer.

The *boundary conditions* at both the surface of the support ($z = -\delta_s$) and the surface of the active layer ($z = \delta$) simply convey continuity of partial pressure for each of the reacting species, i.e.

$$z = -\delta_s: p_I = p_{I0} \quad (I = A, B, R) \quad (11)$$

$$z = \delta: p_I = p_{I\delta} \quad (I = A, B, R) \quad (12)$$

where p_{I0} ($p_{I\delta}$) is the bulk partial pressure of component I ($I = A, B, R$) in the support side (active layer side) bulk stream.

Under conditions in which none of the reactants deplete, the catalytic membrane is completely described by eqs (3) or (4), and (5)–(12). There are six dependent variables; i.e. the pressure of each of the three components in the inert and active zones.

As mentioned above, depending upon the catalytic activity (k_1 , k_2) and relative supplies of the reactants (partial pressures in each bulk stream), depletion of one or more of the reactants may occur within the active zone. Figure 3 conveys the added complexity for the case in which there is an adequate supply of species A to prevent its depletion (i.e. in case I), but for which the supplies of B and R are not sufficient to prevent their depletion.

As the catalytic activity is increased from the regime in which no depletion is encountered (first line in Fig. 3), depletion of reaction-1 reactant (B) is encountered within the active zone (second line in Fig. 3). This creates a new zone (labeled 3 in line 2) within which B is depleted and, as a result, only the second reaction occurs. In total, there are four zones to consider. In zone 3 the reacting components satisfy eqs (5)–(7) with $r_1 = 0$. Zones 2 and 4 are described by eqs (5)–(7). In this B-depletion situation there are 14 dependent variables, i.e. partial pressures of the three components in each of the four zones and the two points of component B depletion (z_{B1}^* , z_{B2}^*). In addition to the six boundary conditions at the two external surfaces, continuity of partial pressure and flux apply for the reacting species at $z = 0$, z_{B1}^* , z_{B2}^* . Moreover, the component B partial pressure vanishes at $z = z_{B1}^*$ and z_{B2}^* . The conditions are summarized as

Fig. 3. Schematic of the three situations encountered in the simulations. At low activity, no depletion occurs. At intermediate activity, depletion of B occurs. At high activity, depletion of B and R occurs.

follows:

$z = 0$:

$$p_{I1} = p_{I2} \quad (13a)$$

$$D_{I0} \frac{dp_{I1}}{dz} = D_I \frac{dp_{I2}}{dz} \quad (I = A, B, R) \quad (13b)$$

$z = z_{B2}^*$:

$$p_{I2} = p_{I3} \quad (14a)$$

$$D_{I0} \frac{dp_{I2}}{dz} = D_I \frac{dp_{I3}}{dz} \quad (I = A, B, R) \quad (14b)$$

$$p_{B2} = 0 \quad (14c)$$

$z = z_{B2}^*$:

$$p_{I3} = p_{I4} \quad (15a)$$

$$D_{I0} \frac{dp_{I3}}{dz} = D_I \frac{dp_{I4}}{dz} \quad (I = A, B, R) \quad (15b)$$

$$p_{B4} = 0 \quad (15c)$$

At still higher activity, in reaction 2, reactant R can deplete within the component B depletion zone (third line in Fig. 3). This creates a new zone (labeled 4) within which neither diffusion nor reaction occurs. In this B- and R-depletion situation, there are 22 dependent variables, i.e. partial pressures of the three components in each of the six zones and the two points of depletion for both components B (z_{B1}^* , z_{B2}^*) and R (z_{R1}^* , z_{R2}^*). In addition to the six boundary conditions at the two external surfaces, continuity of partial pressure and flux apply for the reacting species at $z = 0$, z_{B1}^* , z_{R1}^* , z_{B2}^* , and z_{R2}^* , with forms similar to the B-depletion case [eqs (13)–(15)]. Also, depletion conditions apply for components B and R at their respective depletion points.

The models are now *nondimensionalized*. The following dimensionless independent and independent variables are defined:

$$s = \frac{z}{\delta}, \quad \rho_I = \frac{p_I}{p_{I0}} \quad (I = A, B, R)$$

$$s_{IJ}^* = \frac{z_{IJ}^*}{\delta} \quad (I = A, B, R, j = 1, 2). \quad (16)$$

Tables 1–3 provide the complete set of dimensionless model equations describing transport and reaction for the three situations of no B or R depletion, B depletion, and B and R depletion, respectively. Table 4 provides the definitions of the dimensionless parameters which appear in the nondimensionalized models.

Model solutions. Closed-form solutions can be obtained for the two different sets of reaction orders (cases I and II) and for each of the three depletion situations (Tables 1–3). General solutions for the partial pressure profiles of the three components in the

Table 1. Set of governing equations for the situation of no B or R depletion

Differential balances

Zone 1 ($-\sigma < s < 0$):

$$\frac{d^2 \rho_{A1}}{ds^2} = 0 \quad (17)$$

$$\frac{d^2 \rho_{B1}}{ds^2} = 0 \quad (18)$$

$$\frac{d^2 \rho_{R1}}{ds^2} = 0 \quad (19)$$

Zone 2 ($0 < s < 1$):

$$\frac{d^2 \rho_{A2}}{ds^2} = \phi_1^2 (\rho_{A2}^{x_{A1}} + \kappa \rho_{A2}^{x_{A2}}) \quad (20)$$

$$\frac{d^2 \rho_{B2}}{ds^2} = \lambda_B \phi_1^2 \rho_{A2}^{x_{A1}} \quad (21)$$

$$\frac{d^2 \rho_{R2}}{ds^2} = \lambda_R \phi_1^2 (-\rho_{A2}^{x_{A1}} + \nu_R \kappa \rho_{A2}^{x_{A2}}) \quad (22)$$

Boundary conditions

$s = -\sigma$:

$$\rho_{I1} = 1 \quad (I = A, B, R) \quad (23)$$

$s = 0$:

$$\rho_{I1} = \rho_{I2} \quad (I = A, B, R) \quad (24)$$

$$\frac{d\rho_{I1}}{ds} = d_I \frac{d\rho_{I2}}{ds} \quad (I = A, B, R) \quad (25)$$

$s = 1$:

$$\rho_{I1} = \varepsilon_I \quad (I = A, B, R) \quad (26)$$

various zones are readily obtained since the differential equations are linear. The final steps involve solution for the integration constants and depletion points. Solution of the no-depletion situation simply involves application of the six boundary conditions to eliminate the six integration constants. The situations involving depletion are more cumbersome, not only because of the increased number of integration constants, but also because the depletion points are additional unknowns. As in the no-depletion situation, the integration constants appear linearly in the boundary conditions. However, the depletion points appear nonlinearly. For *kinetic case I*, the nonlinearity for the component B depletion points is a quadratic. Consequently, explicit expressions can be derived for s_{B1}^* and s_{B2}^* for both the B-depletion and the B- and R-depletion situations. In the latter situation, the component R depletion points cannot be expressed explicitly and one must solve simultaneously the two implicit equations given by

$$F_{1,j}(s_{R1}^*, s_{R2}^*, \mathbf{p}) = 0 \quad (j = 1, 2) \quad (62)$$

where $\mathbf{p}$ is a vector of model parameters (i.e. see Table 4). For *kinetic case II* the component B depletion points cannot be solved for explicitly in either situation. In the B-depletion situation, one must solve

Table 2. Set of governing equations for the situation of B depletion but no R depletion

Differential balances

Zone 1 ($-\sigma < s < 0$):

Same as eqs (17)–(19) in Table 1.

Zone 2 ($0 < s < s_{B1}^*$):

$$\frac{d^2 \rho_{A2}}{ds^2} = \phi_1^2 (\rho_{A2}^{\alpha_{A1}} + \kappa \rho_{A2}^{\alpha_{A2}}) \quad (27)$$

$$\frac{d^2 \rho_{B2}}{ds^2} = \lambda_B \phi_1^2 \rho_{A2}^{\alpha_{A1}} \quad (28)$$

$$\frac{d^2 \rho_{R2}}{ds^2} = \lambda_R \phi_1^2 (-\rho_{A2}^{\alpha_{A1}} + \nu_R \kappa \rho_{A2}^{\alpha_{A2}}). \quad (29)$$

Zone 3 ($s_{B1}^* < s < s_{B2}^*$):

$$\frac{d^2 \rho_{A3}}{ds^2} = \phi_1^2 \kappa \rho_{A3}^{\alpha_{A2}} \quad (30)$$

$$\frac{d^2 \rho_{B3}}{ds^2} = 0 \quad (31)$$

$$\frac{d^2 \rho_{R3}}{ds^2} = -\lambda_R \phi_1^2 \nu_R \kappa \rho_{A3}^{\alpha_{A2}}. \quad (32)$$

Zone 4 ($s_{B2}^* < s < 1$):

$$\frac{d^2 \rho_{A4}}{ds^2} = \phi_1^2 (\rho_{A4}^{\alpha_{A1}} + \kappa \rho_{A4}^{\alpha_{A2}}) \quad (33)$$

$$\frac{d^2 \rho_{B4}}{ds^2} = \lambda_B \phi_1^2 \rho_{A4}^{\alpha_{A1}} \quad (34)$$

$$\frac{d^2 \rho_{R4}}{ds^2} = \lambda_R \phi_1^2 (-\rho_{A4}^{\alpha_{A1}} + \nu_R \kappa \rho_{A4}^{\alpha_{A2}}). \quad (35)$$

Boundary conditions

 $s = \sigma$:

Same as eqs (20) in Table 1.

 $s = 0$:

Same as eqs (21), (22) in Table 1.

 $s = s_{B1}^*$:

$$\rho_{I2} = \rho_{I3} \quad (I = A, B, R) \quad (36)$$

$$\frac{d\rho_{I2}}{ds} = \frac{d\rho_{I3}}{ds} \quad (I = A, B, R) \quad (37)$$

$$\rho_{B2} = 0. \quad (38)$$

 $s = s_{B2}^*$:

$$\rho_{I3} = \rho_{I4} \quad (I = A, B, R) \quad (39)$$

$$\frac{d\rho_{I3}}{ds} = \frac{d\rho_{I4}}{ds} \quad (I = A, B, R) \quad (40)$$

$$\rho_{B4} = 0. \quad (41)$$

 $s = 1$:

$$\rho_{I4} = \epsilon_I \quad (I = A, B, R). \quad (42)$$

Table 3. (Contd.)

Zone 2 ($0 < s < s_{B1}^*$):

Same as eqs (27)–(29) in Table 2.

Zone 3 ($s_{B1}^* < s < s_{B2}^*$):

Same as eqs (30)–(32) in Table 2.

Zone 4 ($s_{B2}^* < s < s_{R2}^*$):

$$\frac{d^2 \rho_{A3}}{ds^2} = 0 \quad (43)$$

$$\frac{d^2 \rho_{B3}}{ds^2} = 0 \quad (44)$$

$$\frac{d^2 \rho_{R3}}{ds^2} = 0. \quad (45)$$

Zone 5 ($s_{R2}^* < s < s_{B2}^*$):

$$\frac{d^2 \rho_{A5}}{ds^2} = \phi_1^2 \kappa \rho_{A5}^{\alpha_{A2}} \quad (46)$$

$$\frac{d^2 \rho_{B5}}{ds^2} = 0 \quad (47)$$

$$\frac{d^2 \rho_{R5}}{ds^2} = -\lambda_R \phi_1^2 \nu_R \kappa \rho_{A5}^{\alpha_{A2}}. \quad (48)$$

Zone 6 ($s_{B2}^* < s < 1$):

$$\frac{d^2 \rho_{A6}}{ds^2} = \phi_1^2 (\rho_{A6}^{\alpha_{A1}} + \kappa \rho_{A6}^{\alpha_{A2}}) \quad (49)$$

$$\frac{d^2 \rho_{B6}}{ds^2} = \lambda_B \phi_1^2 \rho_{A6}^{\alpha_{A1}} \quad (50)$$

$$\frac{d^2 \rho_{R6}}{ds^2} = \lambda_R \phi_1^2 (-\rho_{A6}^{\alpha_{A1}} + \nu_R \kappa \rho_{A6}^{\alpha_{A2}}). \quad (51)$$

Boundary conditions

 $s = -\sigma$:

Same as eq. (23) in Table 1.

 $s = 0$:

Same as eqs (24), (25) in Table 1.

 $s = s_{B1}^*$:

Same as eqs (36)–(38) in Table 2.

 $s = s_{R1}^*$:

$$\rho_{I3} = \rho_{I4} \quad (I = A, B, R) \quad (52)$$

$$\frac{d\rho_{I3}}{ds} = \frac{d\rho_{I4}}{ds} \quad (I = A, B, R) \quad (53)$$

$$\rho_{R3} = 0. \quad (54)$$

 $s = s_{R2}^*$:

$$\rho_{I4} = \rho_{I5} \quad (I = A, B, R) \quad (55)$$

$$\frac{d\rho_{I4}}{ds} = \frac{d\rho_{I5}}{ds} \quad (I = A, B, R) \quad (56)$$

$$\rho_{R5} = 0. \quad (57)$$

 $s = s_{B2}^*$:

$$\rho_{I5} = \rho_{I6} \quad (I = A, B, R) \quad (58)$$

$$\frac{d\rho_{I5}}{ds} = \frac{d\rho_{I6}}{ds} \quad (I = A, B, R) \quad (59)$$

$$\rho_{B6} = 0. \quad (60)$$

 $s = 1$:

$$\rho_{I6} = \epsilon_I \quad (I = A, B, R). \quad (61)$$

Table 3. Set of governing equations for the situation of B and R depletion

Differential balances

Zone 1 ($-\sigma < s < 0$):

Same as eqs (17)–(19) in Table 1.

Table 4. Definitions of dimensionless parameters appearing in models (refer to Tables 1-3)

$$\sigma = \frac{\delta_2}{\delta}, \quad \phi_1 = \delta \left(\frac{RTk_1 p_{A0}^{\alpha_{A1}-1}}{D_A} \right)^{1/2}, \quad \phi_2 = \delta \left(\frac{RTk_2 p_{A0}^{\alpha_{A2}-1}}{D_A} \right)^{1/2}, \quad \kappa = \frac{k_2 p_{A0}^{\alpha_{A2}-\alpha_{A1}}}{k_1}$$

$$\varepsilon_A = \frac{p_{Aa}}{p_{A0}}, \quad \varepsilon_B = \frac{p_{Ba}}{p_{B0}}, \quad \varepsilon_R = \frac{p_{Ra}}{p_{R0}}, \quad \lambda_B = \frac{v_B D_A p_{A0}}{D_B p_{B0}}, \quad \lambda_R = \frac{v_R D_A p_{A0}}{D_R p_{R0}}$$

$$d_i = \frac{D_i}{D_{A0}} \quad (i = A, B, R).$$

simultaneously the two implicit equations:

$$F_{n,j}(s_{B1}^*, s_{B2}^*, p) = 0 \quad (j = 1, 2). \quad (63)$$

In the B- and R-depletion situation, the following four implicit functions must be solved simultaneously for the B- and R-depletion points:

$$G_{n,j}(s_{B1}^*, s_{B2}^*, s_{R1}^*, s_{R2}^*, p) = 0 \quad (j = 1, 2, 3, 4). \quad (64)$$

The interested reader should refer to Appendices A and B, which provide general solutions and outline the solution approaches for each model.

Analysis strategy. The strategy to be adopted in examining the performance of the catalytic membrane is to compare the model predictions for the membrane exposed to gas streams of varying composition but the same average composition. A conventional catalyst in, say, a fixed-bed-reactor arrangement is obviously exposed to a single bulk stream. On the other hand, the membrane is exposed to two different bulk streams on opposite sides. A key question is whether or not segregation of the two main reactants (A and B) into the two different streams leads to any performance improvements.

To address this question, our analysis strategy is to check the impact of the degree of segregation of reactants A and B on the membrane performance. First we define the *mixed feed* containing components A, B, and R with partial pressures $\hat{p}_A$, $\hat{p}_B$, and $\hat{p}_R$, respectively. These are the feed pressures of each component on both sides of the membrane in the case of no segregation. This situation could represent the conventional case of a single bulk stream passing over a bed of catalyst, for example. Now suppose components A and B are partially segregated on opposite sides of the membrane. We demand that the average partial pressures of A and B are fixed, and the sum of the pressures of A and B on each side are fixed. These demands are translated into the following three independent relations:

$$\frac{1}{2}(p_{A0} + p_{Aa}) = \hat{p}_A \quad (65)$$

$$\frac{1}{2}(p_{B0} + p_{Ba}) = \hat{p}_B \quad (66)$$

$$p_{A0} + p_{B0} = \hat{p}_A + \hat{p}_B. \quad (67)$$

Implementation of these relations are now discussed. In dimensionless form, eqs (65)–(67) are given

by

$$\frac{\hat{p}_A}{p_{A0}} = \frac{1 + \varepsilon_A}{2} \quad (68)$$

$$\frac{\hat{p}_B}{p_{B0}} = \frac{1 + \varepsilon_B}{2} \quad (69)$$

$$\frac{\hat{p}_A}{p_{A0}} \xi + \frac{\hat{p}_B}{p_{B0}} = \xi + 1 \quad (70)$$

where

$$\varepsilon_A = \frac{p_{Aa}}{p_{A0}}, \quad \varepsilon_B = \frac{p_{Ba}}{p_{B0}}, \quad \xi = \frac{p_{A0}}{p_{B0}}. \quad (71)$$

Division of eq. (68) by eq. (69) gives

$$\frac{\hat{p}_A}{\hat{p}_B} = \xi \left(\frac{1 + \varepsilon_A}{1 + \varepsilon_B} \right). \quad (72)$$

Substitution of eqs (68) and (69) into eq. (70) gives

$$\varepsilon_B = \xi(1 - \varepsilon_A) + 1. \quad (73)$$

Various means are possible to define the composition of the two bulk phases using eqs (72) and (73). Our approach is to specify the overall ratio of the species A and B partial pressures, $\hat{p}_A/\hat{p}_B$, and then to vary the ratio of A and B partial pressures in the support side bulk, $\xi = p_{A0}/p_{B0}$, as a parameter. Equations (72) and (73) are then used to calculate ε_A and ε_B . Values of ξ greater than unity correspond to a concentrating of component A (B) on the support (active layer) side. Values of ξ less than unity correspond to concentrating of component A (B) on the active layer (support) side. Extremes in ξ on each side of unity (∞ and 0) correspond to the limiting cases of complete segregation of A on the support side and active layer side, respectively.

Some comments are in order about this approach. By keeping the overall feed ratio of components A and B fixed, a clear assessment of reactant segregation is possible because the mixed-feed case serves as the logical reference. Clearly, the A/B ratio for a mixed-feed situation may be varied in practice in order to improve the R yield for a given catalytic activity. However, one often does not have the unlimited flexibility in this variation. For example, in a partial oxidation system, where A and B represent oxygen and the hydrocarbon, the A/B ratio is confined above a critical level in order to avoid combustion hazards. Moreover, high A/B ratios are an indirect result of the

use of air to supply the oxygen and the heat removal. Thus, it is reasonable to examine if segregation of a feed with a fixed overall composition can result in improved performance.

Some of the other model parameters defined in Table 4 depend on the component A and B partial pressures in the support side bulk stream. It is, therefore, necessary to define modified versions of these parameters which depend, instead, on the average pressure of the component in question. These modified parameters are:

$$\lambda_{Bm} = \lambda_B \left(\frac{1 + \varepsilon_A}{1 + \varepsilon_B} \right), \quad \lambda_{Rm} = \lambda_R \left(\frac{1 + \varepsilon_A}{1 + \varepsilon_B} \right)$$

$$\kappa_m = \kappa \left(\frac{1 + \varepsilon_A}{2} \right)^{\alpha_{A2} - \alpha_{A1}}, \quad \phi_{2m} = \phi_2 \left(\frac{\hat{p}_A}{p_{A0}} \right)^{(\alpha_{A2} - 1)/2} \quad (74)$$

where subscript *m* denotes *mixed-feed* conditions. Thus, λ_B , λ_R , and κ are calculated from eq. (74) given the specified mixed-feed parameter values (λ_{Bm} , λ_{Rm} , κ_m , ϕ_{2m}) and the bulk stream compositions (ε_A , ε_B).

The two key membrane performance indicators to be computed are the utilization of the active layer (*active layer effectiveness*, η) and the *desired product (R) yield* (Y_R). The active layer effectiveness is given by the overall rate of component A consumption normalized by the A consumption rate for a *mixed feed* and in the absence of diffusional gradients. This gives

$$\eta = \frac{1}{\phi_1^2(1 + \kappa)} \left(\frac{d\rho_A}{ds} \Big|_{s=1} - \frac{1}{d_A} \frac{d\rho_A}{ds} \Big|_{s=-\sigma} \right). \quad (75)$$

Thus, the effectiveness is a measure of how efficiently the active material is utilized compared to the case in which there is no reactant segregation or transport limitations. The intermediate component (R) yield is defined as the *net rate* of component R formed, normalized by the rate of consumption of reactant B. With this point-yield definition, Y_R can be positive or negative. A negative value implies a situation in which more R is consumed than produced. This is obviously an undesirable situation and, when encountered, is an effective signal that the membrane performance is poor. Application of this definition gives

$$Y_R = \frac{v_{R1} \lambda_B}{v_B \lambda_R} \left(\frac{\frac{1}{d_R} \frac{d\rho_R}{ds} \Big|_{s=-\sigma} - \frac{d\rho_R}{ds} \Big|_{s=1}}{\frac{d\rho_B}{ds} \Big|_{s=1} - \frac{1}{d_B} \frac{d\rho_B}{ds} \Big|_{s=-\sigma}} \right). \quad (76)$$

The derivatives in eqs (75) and (76) are given by differentiation of the appropriate profile expressions provided in Appendices A and B.

In the simulations which follow, the active layer effectiveness (η) and species R yield (Y_R) are calculated as functions of the catalytic activity for representative combinations of the other model parameters. The ranges of values of the model parameters considered are provided in Table 5. Table 6 lists the three different sets of bulk stream compositions considered. The assigned parameter values are explained below. Parameters that are varied over the indicated ranges have the base case values shown in parentheses. Our particular focus is on checking the impact of the degree of

Table 5. Ranges of model parameter values investigated in simulations

Reaction stoichiometry

$$v_B = 2.0, \quad v_{R1} = 2.0, \quad v_{R2} = 0.4.$$

Catalytic membrane parameters

$$\sigma \left(\equiv \frac{\delta_s}{\delta} \right) = 10^{-4} - 500 \text{ (1)}, \quad \phi_2 \equiv \delta \left(\frac{RTk_2}{D_A} \right)^{1/2} = 10^{-3} - 10^2$$

$$\kappa_m \left(\equiv \frac{k_2}{k_1 (\hat{p}_A)^{\alpha_{A1} - \alpha_{A2}}} \right) = 4.$$

Reaction orders

$$\alpha_{A1} = 0, 1, \quad \alpha_{A2} = 1, \quad \alpha_B = 0, \quad \alpha_R = 0.$$

Effective diffusivities

$$d_i \left(\equiv \frac{D_i}{D_{i0}} \text{ (} i = A, B, R \text{)} \right) = 10^{-2} - 10^{-1} \text{ (} 10^{-1} \text{)}, \quad \frac{D_A}{D_B} = 5.$$

Bulk stream compositions

$$\varepsilon_A \left(\equiv \frac{p_{A0}}{p_{A0}} \right) = 0.2 - 5, \quad \frac{\hat{p}_A}{\hat{p}_B} = 1$$

$$\varepsilon_B \left(\equiv \frac{p_{B0}}{p_{B0}} \right) = 0.2 - 5, \quad \lambda_{Bm} \left(\equiv \frac{v_B D_A \hat{p}_A}{D_B \hat{p}_B} \right) = 10$$

$$\varepsilon_R \left(\equiv \frac{p_{R0}}{p_{R0}} \right) = 1, \quad \lambda_{Rm} \left(\equiv \frac{v_{R1} D_A \hat{p}_A}{D_R \hat{p}_R} \right) = 10.$$

Table 6. Three degrees of reactant segregation considered in the simulations

$\xi = \frac{p_{A0}}{p_{B0}}$	$\varepsilon_A = \frac{p_{A0}}{p_{A0}}$	$\varepsilon_B = \frac{p_{B0}}{p_{B0}}$
0.2	5.0	0.2
1.0	1.0	1.0
5.0	0.2	5.0

segregation (i.e. ξ , ε_A , ε_B) on the η vs ϕ_2 and Y_R vs ϕ_2 dependencies. Note that, since the rate constant ratio (κ_m) is fixed, a variation in ϕ_2 can be interpreted as a variation in the overall catalytic activity. Finally, it is emphasized that the simulations probe the point-performance behavior of the membrane. Thus, the bulk compositions specified correspond to some point in a membrane reactor in which there are gradients in the flow direction, for example.

The choice of parameter values are now assessed (refer to Table 5). The stoichiometry of the two reactions (ν_B , ν_{R1} , ν_{R2}) are selected to represent a typical hydrocarbon partial oxidation reaction system—more specifically, the partial oxidation of ethylene. Component A represents oxygen, B ethylene, R acetaldehyde, and P the total oxidation products. The ratio of the active layer to support layer thickness ($\sigma = \delta_a/\delta$) spans a range from a virtually unsupported active layer ($\sigma = 10^{-4}$) to a very thin layer on a much thicker support ($\sigma = 500$). A catalytic selectivity ratio [$\kappa_m = k_2(\beta_A)^{\alpha_{A2}} - \alpha_{A1}/k_1$] value of 4 means that the catalyst has a rather poor intrinsic selectivity to the desired intermediate R. The catalytic activity (ϕ_{2m} , κ_m fixed) is varied over a wide range to span the reaction-controlling to diffusion-controlling conditions. As mentioned earlier, two different kinetic cases are considered, corresponding to unequal component-A reaction orders ($\alpha_{A1} = 0$, $\alpha_{A2} = 1$) and equal orders ($\alpha_{A1} = \alpha_{A2} = 1$). The ratios of active layer effective diffusivities to the corresponding support layer values are varied to check the impact of morphological differences in the two layers approximately. An equal overall molar ratio of main reactants A and B is supplied to the membrane ($\beta_A/\beta_B = 1$). Referring to Table 6, the degree of segregation of the reactants is examined by varying ξ ($= p_{A0}/p_{B0}$) between 0.2 and 5 to span the cases of concentration of component A on the active layer and support side, respectively. The partial pressure of intermediate R is set equal on each side of the membrane ($\varepsilon_R = 1$).

RESULTS AND DISCUSSION

Mixed-feed results for case I kinetics

The performance of the membrane catalyst when exposed to bulk streams of the same composition needs to be examined before addressing the issue of reactant segregation. Figures 4 and 5 present mixed-feed ($\xi = 1$, $\varepsilon_A = \varepsilon_B = 1$) results for case I kinetics ($\alpha_{A1} = 0$, $\alpha_{A2} = 1$). Figures 4(a) and (b) show the dependence of the overall R yield (Y_R) and active layer effectiveness (η) on the reaction-2-based Thiele

Fig. 4. Case I kinetic results for a membrane exposed to bulk streams of the same composition (mixed feed): (a) the dependence of the R yield (Y_R) on the activity (ϕ_2) for three different support layer thicknesses (σ). Hash marks denote the onset of B depletion; (b) the corresponding dependencies of the effectiveness (η) on activity. All other parameter values assume their base case values provided in Table 5.

modulus (ϕ_2). Three different ratios of the active layer to support layer thickness are considered ($\sigma = 10^{-4}$, 1, 50). The other parameter values are set at their respective base case values provided in Table 5. Figures 5(a)–(d) show the component A, B, and R partial pressure profiles in the active layer ($p_i \equiv p_i/p_{i0}$ vs $s \equiv z/\delta$) at an activity of $\phi_2 = 4$ for four different σ values ($\sigma = 5$ results shown in addition to 10^{-4} , 1, 50).

The dependencies of the R yield (Y_R) and effectiveness (η) on ϕ_2 reveal several noteworthy features for an infinitesimally thin support layer ($\sigma = 10^{-4}$). Y_R exhibits a local maximum at an intermediate ϕ_2 value. To the left of the maximum Y_R is an increasing function of the activity due to the beneficial impact of component A diffusional limitations for this choice of reaction orders (i.e. $\alpha_{A1} < \alpha_{A2}$). Exactly at the yield maximum, component B depletion is initiated within the active layer, as indicated by the hash mark. This creates a zone within which reaction 1 is turned off and, hence, reaction 2 proceeds without competition. To illustrate, Fig. 5(a) shows the component profiles for the $\sigma = 10^{-4}$ case at an activity level of $\phi_2 = 4$. The B depletion zone exists over a wide inner core of the active layer ($s = 0.22$ – 0.78). Subsequent increases in the activity beyond the yield maximum results in an initially sharp decrease in yield. In this ϕ_2 range, the B depletion zone width sharply increases. Y_R approaches an asymptotic value at sufficiently large ϕ_2 .

Fig. 5. Component A, B, and R dimensionless partial pressure profiles for four different support layer thicknesses: (a) $\sigma = 10^{-4}$; (b) $\sigma = 1$; (c) $\sigma = 5$; and (d) $\sigma = 50$. Results apply for a mixed-feed, intermediate activity level ($\phi_2 = 4$), and case I kinetics. All other parameter values assume their base case values provided in Table 5.

The dependence of η on ϕ_2 has the expected monotonically decreasing form over the entire ϕ_2 range [Fig. 4(b)]. This conveys the detrimental impact of diffusional limitations on the utilization of the active layer.

An increase in the thickness of the support layers (σ) has a perceptible but not dramatic effect on the dependencies of η and Y_R on ϕ_2 . For a fixed activity level, an increase in σ reduces η [Fig. 4(b)]. This simply demonstrates that the added transport resistance on one side of the active layer (i.e. the support) reduces the accessibility of the reactants to the active layer. Note that η approaches the same asymptote at high ϕ_2 for the cases $\sigma = 1$ and 50. This shows that the accessibility of the reactants to the active layer from the support side is essentially cut off for a sufficiently thick support.

The impact of σ on the Y_R vs ϕ_2 dependence is more subtle [Fig. 4(a)]. To help interpret this impact, one is referred to Figs 6(a) and (b), which show the dependencies, respectively, of Y_R and η on σ for three different activity levels ($\phi_2 = 1, 5, 20$). Results for both the mixed feed ($\varepsilon_A = 1$) and a segregated feed ($\varepsilon_A = 0.2$) are provided; the latter results are discussed later. For sufficiently low activity (say, $\phi_2 = 1$), Y_R is a monotonically increasing function up to a critical σ value. In this regime the main effect of an increasing σ is an increasing degree of transport limitations of component A. As a result, the R yield increases. At the critical σ value, component B depletion is initiated and Y_R exhibits a maximum (depletion point indicated by hash mark). Subsequent increases in σ reduce Y_R because of an expansion in the B depletion zone within the active layer. Again, in this zone R reacts with A without competition from B. As expected,

Fig. 6(b) shows that η is a monotonically decreasing function of σ over the entire range of σ values. This trend holds true for all activity levels. This result underscores the point made above that the detrimental impact of increased transport limitations reduces the catalyst utilization.

An inspection of Figs 4(a) and 6(a) for higher activity reveals that Y_R exhibits a local minimum at a critical σ value. The minimum is attributed to a complex interaction between the intrinsic kinetics and the support transport resistance. As the support thickness is increased, the component profiles become increasingly asymmetric at an intermediate activity level ($\phi_2 = 4$), as evidenced for $\sigma = 1$ [Fig. 5(b)], 5 [Fig. 5(c)], and 50 [Fig. 5(d)]. Corresponding Y_R values at $\phi_2 = 4$ are $Y_R(\sigma = 10^{-4}) = 0.202$, $Y_R(\sigma = 1) = 0.172$, $Y_R(\sigma = 5) = 0.114$, $Y_R(\sigma = 50) = 0.157$, and $Y_R(\sigma = 500) = 0.172$. The decline in Y_R with increasing σ is primarily a result of a decline in the flux of R out of the catalyst on the support side. For example, a comparison of the R profiles for $\sigma = 10^{-4}$ [Fig. 5(a)] and $\sigma = 1$ [Fig. 5(b)] reveals a more significant change in the slope of the R profile at $s = 1$ compared to $s = 0$ as σ is increased. Since the R profile is linear in the inert zone ($-\sigma < s < 0$), one can conclude that the R flux at $s = -\sigma$ is higher for the $\sigma = 10^{-4}$ case than for the $\sigma = 1$ case. In fact, for a sufficiently thick support layer [e.g. $\sigma = 5$; Fig. 5(c)] there is a shift from R being removed to being supplied at the external surface of the support layer. This is evidence for an increased consumption of R within the active layer and hence an overall lower R yield. If σ is increased in the activity range in which R is supplied from the support side, the results indicate that the support serves as a barrier to the supply of R. Without the

Fig. 6. Impact of the support layer thickness (σ) on the dependence of Y_R on σ at three different activity levels ($\phi_2 = 1, 5, 20$) for the mixed feed ($\varepsilon_A = 1$) and segregated feed ($\varepsilon_A = 0.2$); (b) the corresponding dependencies of the effectiveness (η) on σ . Results apply for case I kinetics. All other parameter values assume their base case values provided in Table 5.

Fig. 7. Impact of reactant segregation on membrane performance for case I kinetics: (a) the dependence of the R yield (Y_R) on catalytic activity (ϕ_2) for three different feeds ($\varepsilon_A = 0.2, 1, 5$) and an intermediate support thickness ($\sigma = 1$); (b) the corresponding dependencies of the effectiveness (η) on activity. All other parameter values assume their base case values provided in Table 5.

supply of R as a reactant, the R yield increases. A contributing factor to the yield increase in this regime is a reduction in the component A concentration within the B depletion zone [compare Figs 5(c) and (d)]. Since the second reaction is first-order in A, its rate declines. Moreover, since the B-depletion-zone thickness is essentially constant in this σ range, the net effect is an increase in the R yield.

Segregated-feed results for case I kinetics

Now the key question of whether reactant segregation can improve yield is addressed. Figures 7(a) and (b) respectively compare the R yield (Y_R) and effectiveness (η) dependencies on the activity (ϕ_2) for the mixed feed ($\xi = 1$: $\varepsilon_A = 1$, $\varepsilon_B = 1$) and two different segregated-feed situations. The two situations correspond to the concentration of reactant A on the support side and reactant B on the active layer side ($\xi = 5$: $\varepsilon_A = 0.2$, $\varepsilon_B = 5$) and *vice versa* ($\xi = 0.2$: $\varepsilon_A = 5$, $\varepsilon_B = 0.2$). Case I kinetics are considered. All other parameters assume their base case values (Table 5). In order to elucidate certain trends, component profiles are provided for the three feed situations at two activity levels ($\phi_2 = 5$ and 20) in Figs 8 and 9.

Fig. 8. Component profiles for three feeds $\varepsilon_A = 0.2$ (a), $\varepsilon_A = 1$ (b), and $\varepsilon_A = 5$ (c) for an intermediate activity ($\phi_2 = \phi = 4$) and case I kinetics. All other parameter values assume their base case values provided in Table 5.

Fig. 9. Component profiles for the three feeds $\varepsilon_A = 0.2$ (a), $\varepsilon_A = 1$ (b), and $\varepsilon_A = 5$ (c) at high activity ($\phi_2 = \phi = 20$) and case I kinetics. All other parameter values assume their base case values provided in Table 5.

Finally, Fig. 10 shows the loci of component B and R depletion points (s_i^* , $i = B, R$) as a function of ϕ_2 for the three feeds.

The comparison simulations reveal improved intermediate product (R) yield [Fig. 7(a)] at the expense of reduced active layer utilization [Fig. 7(b)]. For all catalytic activity levels, the R yield is increased by concentrating reactant A on the support side and B on the active layer side. In the activity regime to the left of the local yield maximum, modest yield improvements are realized. In this regime no depletion of B occurs. Thus, the yield gains result from the aforementioned impact of reactant A diffusional limitations on the relative rates of each reaction. More specifically, there is a more appreciable reduction in the rate of the second reaction compared to the first because of the higher reaction order with respect to A in the second reaction. Note that, since the rates are zeroth-order in nondepleted B and R, there is no diffusional impact with respect to these species. Similar arguments explain the reduced yield and increased effectiveness encountered when A (B) is concentrated on the active layer (support) side. In this case, diffusional limitations with respect to A are

Fig. 10. Loci of the B and R depletion points as a function of catalytic activity (ϕ_2) for three different feeds and case I kinetics: (a) compares the $\varepsilon_A = 0.2$ and $\varepsilon_A = 1$ feeds; (b) compares the $\varepsilon_A = 5$ and $\varepsilon_A = 1$ feeds. All other parameter values assume their base case values provided in Table 5.

reduced. Thus, an opposite effect on Y_R and η is observed.

The results are more interesting once component B depletion is initiated at the critical activity corresponding to the local maximum in R yield. Activity increases beyond this point result in more dramatic departures in the segregated-feed yield and effectiveness from the mixed-feed results. For the intermediate activity regime ($2 < \phi_2 < 6$), Y_R decreases for all three feeds. The decrease in Y_R for each is attributed to an increase in the width of the B depletion zone within the active layer, as encountered for the mixed-feed case above. However, this effect is augmented by another effect because Y_R decreases at different slopes for each feed situation. Indeed, the gaps between both the $\varepsilon_A = 0.2$ and $\varepsilon_A = 1$ cases and the $\varepsilon_A = 5$ and $\varepsilon_A = 1$ cases widen as ϕ_2 increases in this range. This new effect is directly attributed to the asymmetry within the membrane created by the reactant segregation and corresponding diffusion-reaction interactions.

To understand this new effect better, it is revealing to examine the influence of reactant segregation on the component profiles in this intermediate range of activities. Figures 8(a)–(c) show the component profiles over the entire membrane ($-\sigma < s < 1$) for an activity of $\phi_2 = 4$ and feeds corresponding to $\varepsilon_A = 0.2$, 1, and 5, respectively. The component partial pressures are normalized by the support side bulk values (i.e. $p_i(s) \equiv p_i(s)/p_{i0}$, $i = A, B, R$).

The mixed-feed case [$\varepsilon_A = 1$; Fig. 8(b)] clearly shows two local maxima in the component-R profile near the support-active-layer interface ($s \sim 0.04$) and the active layer surface ($s \sim 0.89$). Intermediate R exits the membrane from both sides. Reactant B is depleted in a wide inner core of the active layer ($0.12 < s < 0.78$). Within the zone of B depletion, the R profile exhibits a pronounced minimum. This is a consequence of reaction 2 occurring without competition from reaction 1.

Segregation of reactant A to the support side bulk [$\varepsilon_A = 0.2$; Fig. 8(a)] serves to focus the primary R producing zone on the right side of the active layer (i.e. $s > 0.6$). The asymmetry in the profiles, which is created by segregation, is beneficial to the R yield. Based on an analysis of the R profile slope, the flux of R at the active layer surface ($s = 1$) is clearly higher than the corresponding value for the mixed-feed case. On the other hand, R is now supplied to the membrane rather than removed from the support side. By concentrating B (A) on the active layer (support) side, reaction 1 ($A + B \rightarrow R$) is favored over reaction 2 ($A + R \rightarrow P$) near the active layer surface. The reactant-B depletion zone is shifted away from the active layer surface ($0.06 < s < 0.71$). Thus, ample B is available to react selectively to R with reduced competition from the undesired reaction 2 near the active layer surface. [Recall that reaction 1 (2) is zeroth- (first-) order in A.] The key to this effect is that R can escape to the bulk without reacting further to undesired product P.

An opposite behavior occurs when A is segregated to the active layer side [$\varepsilon_A = 5$; Fig. 8(c)]. In this situation the B depletion zone is shifted towards the active layer surface ($0.21 < s < 0.87$). The limited supply of B from the active layer side results in a poor production of R in the vicinity. The comparatively larger supply of B from the support side means that R is primarily produced near the active-layer-support interface. The R which is produced then has two directions in which to diffuse. The first is through the support layer. The second is through the active layer. The first route is long—an examination of the R profile slope in this region shows that the flux of R out of the support surface is low. The second route is not as long as the first but is sufficiently long that subsequent reaction of R with A occurs to undesired P at this level of activity. Indeed, R is supplied at the active layer surface under these conditions.

At even higher catalytic activity, the ability to focus the desired reaction 1 in a particular part of the active layer by segregating reactants can have dramatic effects on the yield. Figure 7(a) shows that, if A is concentrated on the support side ($\varepsilon_A = 0.2$) for $\phi_2 \approx 4$, the R yield exhibits a local minimum. For ϕ_2 values to the right of this minimum, Y_R is an increasing function of the activity. On the other hand, Y_R becomes a more sharply decreasing function of ϕ_2 if A is concentrated on the active layer side ($\varepsilon_A = 5$).

In order to underscore these trends at high activity, Figs 9(a)–(c) show the component profiles at an activ-

ity level of $\phi_2 = 20$ for the three different feed situations. The combination of reactant segregation and a high activity leads to the depletion of intermediate R within the B depletion zone. On the other hand, R does not deplete in the mixed-feed case [$\varepsilon_A = 1$; Fig. 9(b)]. For the situation of A concentration in the support side bulk [$\varepsilon_A = 0.2$; Fig. 9(a)], the R depletion zone is located near the active-layer-support interface. If A is concentrated in the active layer side bulk [$\varepsilon_A = 5$; Fig. 9(c)], the R depletion zone is located near the active layer surface. The profiles reveal an interesting feature for the segregated cases: component A diffuses from the side of primary supply and is virtually (but not completely) consumed by its reaction with B and R, which diffuse from the opposite direction. It is the fraction of R that is produced which does not react that is key to the membrane performance. This R fraction diffuses away from the R consumption sink. As a rule, the primary R producing zone is located in the zone of highest B and lowest A concentration. For the $\varepsilon_A = 0.2$ feed, R is primarily produced near the support surface, where it can escape before further reaction. For the $\varepsilon_A = 5$ feed, R is produced near the active-layer-support interface, where it cannot easily escape before further reaction to P.

The operating principle of reactant segregation in this parallel-consecutive reaction system is clearly conveyed if one examines the dependence of the depletion point positions (s_i^* , $i = B, R$) on the catalytic activity (ϕ_2). Figure 10 compares the results of the mixed-feed situation with the two segregated-feed situations [i.e. $\varepsilon_A = 1, 0.2$ in Fig. 10(a); $\varepsilon_A = 1, 5$ in Fig. 10(b)]. For $\varepsilon_A = 1$, the B-depletion map has a cusp-like shape. B depletion commences at a point ($\phi_2 \approx 1.6$, $s_B^* \approx 0.4$). As ϕ_2 is increased, the bounds of the depletion zone approach the active layer surface ($s = 1$) and active-layer-support interface ($s = 0$). However, just as the component profiles show in Figs 8(b) and 9(b), R does not deplete for $\varepsilon_A = 1$.

The B-depletion loci exhibit similar trends for the situation of A concentration in the support side bulk [$\varepsilon_A = 0.2$; Fig. 10(a)]. Two differences are worth noting, however. First, B depletion commences at a lower activity ($\phi_2 = 1.55$) and at a position closer to the support-active-layer interface $s_B^* \approx 0.25$. Second, for a fixed ϕ_2 the entire B depletion zone is shifted in the direction of the support (i.e. lower s). These differences simply reflect the shorter supply of B from the support side due to the segregation. The new feature encountered with the $\varepsilon_A = 0.2$ segregation case is the existence of an R depletion which appears at ($\phi_2 \approx 5.2$, $s_R^* \approx 0.20$). The R-depletion map is similarly cusp-shaped. More importantly, its location is clearly confined within the inner half of the active layer (i.e. near support) for all ϕ_2 . Another way of interpreting this result is that R is concentrated in the outer half of the active layer (i.e. near the surface).

Now consider the situation of A concentration in the active layer side [$\varepsilon_A = 5$; Fig. 10(b)]. B depletion commences at a lower activity ($\phi_2 \approx 1.55$) than for the

mixed-feed situation. A similar result was observed for $\varepsilon_A = 0.2$. However, the B depletion location commences at $s_B^* \approx 0.66$, a value which is much higher than that obtained for the $\varepsilon_A = 1$ case ($s_B^* = 0.4$) and the $\varepsilon_A = 0.2$ case ($s_B^* = 0.25$). As ϕ_2 is increased beyond this point, a cusp-shaped R-depletion map emerges at $\phi_2 \approx 5$, $s_R^* \approx 0.71$. Comparison of the $\varepsilon_A = 5$ results with the $\varepsilon_A = 0.2$ results in Fig. 10(a) (using $\varepsilon_A = 1$ as a reference) reveals that both the B- and R-depletion loci are shifted towards the active layer surface. The location of the R depletion zone near the active layer surface, in particular, underscores the detrimental effect of concentrating A (B) in the active layer side (support side) bulk. Now the major R producing zone is located well within the active layer.

A point worth mentioning in the current set of simulations concerns the behavior of the membrane with regards to reaction product removal. The model catalytic membrane does not have a permselective function which aids in the performance improvements described up to this point. Despite this lack of permselectivity, a secondary benefit of the membrane is its ability to confine reaction products on one side. To illustrate, Fig. 11 compares the dimensionless surface fluxes of intermediate R for the mixed-feed [$\varepsilon_A = 1$; Fig. 11(a)] and segregated-feed [$\varepsilon_A = 0.2$; Fig. 11(b)] situations. The fluxes are defined by

$$n_R(s = -\sigma) = -\frac{1}{d_R} \left(\frac{d\rho_R}{ds} \right)_{s=-\sigma} \quad (77)$$

Fig. 11. Dependence of the component-R surface fluxes [see eqs (77) and (78)] on the activity (ϕ_2) for (a) the mixed feed ($\varepsilon_A = 1$), and (b) a segregated feed ($\varepsilon_A = 0.2$). Case I kinetics apply. All other parameter values assume their base case values provided in Table 5.

$$n_R(s = 1) = -\left(\frac{d\rho_R}{ds} \right)_{s=1} \quad (78)$$

The results show that even without reactant segregation ($\varepsilon_A = 1$) there is a preferential removal of R from the active layer surface [Fig. 11(a)]. This is due to the asymmetric nature of the membrane and the mass transfer resistance of the support. However, segregation of A and B magnifies this flux polarization effect [Fig. 11(b)]. That is, most of the additional intermediate R which is produced by the segregation is removed by the bulk stream on the active layer side. This feature is an attractive one since it reduces downstream separation requirements. It can be shown that these effects are even more significant if the support layer thickness (σ) is increased.

The beneficial and detrimental effects of reactant segregation are magnified as the support layer thickness (σ) is increased. Figures 12(a) and (b) show the dependencies of Y_R and η on ϕ_2 for $\sigma = 50$. All other parameters are fixed at base case values. Two points are revealed if one compares the thick-support ($\sigma = 50$) results in Figs 12(a) and (b) with the thin support ($\sigma = 1$) results in Figs 7(a) and (b). First, the qualitative trends in the Y_R and η plots resemble those from the case of a thinner support layer. These trends include the existence of a local yield maximum for all three feeds and also the local minimum for the $\varepsilon_A = 0.2$ case. The reason for the similarities is that the

Fig. 12. Impact of reactant segregation on membrane performance for case I kinetics: (a) the dependence of the R yield (Y_R) on catalytic activity (ϕ_2) for three different feeds ($\varepsilon_A = 0.2, 1, 5$) and a thick support layer ($\sigma = 50$); (b) the corresponding dependencies of the effectiveness (η) on activity. All other parameter values assume their base case values provided in Table 5.

same reaction-transport interactions apply. Second, and more importantly, for the thicker support, there is a more significant difference for all activity levels between the mixed feed ($\varepsilon_A = 1$) and segregated feeds ($\varepsilon_A = 0.2$, $\varepsilon_A = 5$). Thus, at the expense of additional reductions in the catalyst utilization, the intermediate R yield can be increased by increasing the thickness of the support layer. Another difference worth noting with regards to the $\varepsilon_A = 0.2$ feed is that component-R depletion is not encountered with the thicker support ($\sigma = 50$), while it is with the thinner support [$\sigma = 1$; see Fig. 7(b)]. The thicker support reduces the overall supply of component A to the active layer. The result is a reduced consumption of R by the second reaction.

Figure 12(a) also includes the results for a mixed feed which has a composition equal to that of the active layer bulk in the $\varepsilon_A = 0.2$ case. A comparison between the two cases underscores the point that the thick support serves effectively as a mass transfer barrier if the catalytic activity is high. The main evidence for this is the virtual coincidence of the two cases for high ϕ_2 values. In this regime, the composition of the bulk stream on the support side is of little consequence, as the supplies of A and B from that side are severely hindered by the long diffusion path. The A and B fluxes at the support-active-layer interface are vanishingly small.

It is instructive to return to Figs 6(a) and (b) which show the respective dependencies of Y_R and η on the support layer thickness (σ) for the mixed feed ($\varepsilon_A = 1$) and a segregated feed ($\varepsilon_A = 0.2$). Hash marks on a curve identify the onset of depletion of B or R. First the $\varepsilon_A = 0.2$ results are compared for the three activity levels. For very thin support layers ($\sigma < 0.1$), Y_R is a nonmonotonic function of ϕ_2 . This simply reflects the existence of a yield maximum upon the onset of B depletion at a critical activity level. On the other hand, both the yield and effectiveness vary monotonically with σ at a fixed activity (ϕ_2) for the segregated-feed situation. Y_R (η) increases (decreases) as σ is increased. This primarily reflects the effect of focusing the R production zone near the active layer surface becoming the dominant one [refer to Fig. 7(a)]. For very thick support layers ($\sigma > 100$) the yield approaches the same asymptotic value for the three activities. Interestingly, at the lowest activity ($\phi_2 = 1$) component B does not deplete over the entire range of σ . However, component-B depletion is encountered for all σ at the intermediate activity ($\phi_2 = 5$). For the highest activity ($\phi_2 = 20$), both B and R depletion is encountered for all σ up to a critical value ($\sigma \approx 6.6$), as denoted by the hash mark. For σ exceeding this critical value, R depletion is eliminated. This underscores the point made in the above comparison between a thick ($\sigma = 50$) and thin ($\sigma = 1$) support layer.

A comparison of the $\varepsilon_A = 1$ and $\varepsilon_A = 0.2$ feeds in Fig. 6(a) clearly reveals the yield improvement realized by concentrating A (B) in the support (active layer) bulk. At the lowest activity ($\phi_2 = 1$), segregation is beneficial over the entire range of σ . The main effect in this activity regime is the increase in compo-

ent-A transport limitations. A similar comparison applies at the highest activity ($\phi_2 = 20$) but for a different reason. In this activity regime, the main effect is the focusing of the primary R production zone near the active layer surface by concentrating reactant B in the active layer bulk. At the intermediate activity ($\phi_2 = 5$), segregation gives higher yields above a critical support thickness ($\sigma \sim 0.5$). Finally, as has been shown in previous results, yield gains come at the expense of active layer effectiveness losses. Figure 6(b) shows that over the entire range of σ and for the three activities considered, η decreases as ε_A is decreased from 1 to 0.2.

One final set of simulations for the case I kinetics indirectly examines the impact of the support layer morphology on the membrane performance. Figures 13(a) and (b) show the dependencies of Y_R and η on ϕ_2 if the effective diffusivity ratios, d_i (D_i/D_{10} ; $i = A, B, R$), are decreased by a factor of 10 from the base case values of 0.1. One way of interpreting this change is that the effective diffusivities within the support layer increase by a factor of 10. Such an increase may be attained by an increase in the support porosity and decrease in the diffusion path (i.e. reduction in tortuosity). One should compare Figs 13(a) and (b) with the corresponding $\varepsilon_A = 0.2$ and 1 results ($d_i = 0.1$) in Figs 7(a) and (b) to assess the impact of d_i .

The main effect of the reduction in d_i is an increased, beneficial impact of reactant segregation on the component-R yield. This is especially true for low to intermediate activities ($\phi_2 < 10$). To illustrate, Table 7 compares, for four different activities

Fig. 13. Performance of the membrane at a lower diffusivity ratio ($d_i = 10^{-2}$) for the mixed feed ($\varepsilon_A = 1$) and segregated feed ($\varepsilon_A = 0.2$): (a) the (Y_R) vs activity (ϕ_2) dependence; (b) the effectiveness (η) vs activity (ϕ_2) dependence. Results apply for case I kinetics. All other parameter values assume their base case values provided in Table 5.

Table 7. Impact of diffusivity ratio (d_i , $i = A, B, R$) on the reactant segregation effect

ϕ_2	$\Lambda_Y = \frac{Y_R(\varepsilon_A = 0.2)}{Y_R(\varepsilon_A = 1)}$		$\Lambda_\eta = \frac{\eta(\varepsilon_A = 0.2)}{\eta(\varepsilon_A = 1)}$	
	$d_i = 0.1$	$d_i = 0.01$	$d_i = 0.1$	$d_i = 0.01$
0.1	1.240	1.876	0.951	0.823
1	1.159	1.474	0.948	0.813
5	1.682	5.159	0.873	0.671
50	6.254	5.165	0.562	0.513

($\phi_2 = 0.1, 1, 5, 50$), the fractional changes in Y_R and η due to segregation for the $d_r = 0.1$ and 0.01 cases. The following yield improvement factor is defined:

$$\Lambda_Y = \frac{Y_R(\varepsilon_A = 0.2)}{Y_R(\varepsilon_A = 1)} \quad (79)$$

The effectiveness reduction factor is defined as

$$\Lambda_\eta = \frac{\eta(\varepsilon_A = 0.2)}{\eta(\varepsilon_A = 1)} \quad (80)$$

For $\phi_2 \leq 5$, a decrease in d_r increases the beneficial segregation effect on Y_R (i.e. Λ_Y increases). There is a corresponding fractional decrease in the effectiveness (i.e. Λ_η decreases). However, the key point is that the fractional improvement in Y_R exceeds the fractional decline in η (i.e. $\Lambda_Y \cdot \Lambda_\eta > 1$).

Results for case II kinetics

In the introduction and model development sections, it was argued that the relative reaction orders with respect to component A (α_{A1}, α_{A2}) should have an important impact on the reactant segregation effect. More specifically, under condition of excess B and R, the best results should be obtained if $\alpha_{A1} < \alpha_{A2}$. Moreover, no effect on the yield should be observed if $\alpha_{A1} = \alpha_{A2}$, as long as B and R are in sufficiently large excess so that depletion does not occur. However, the effect of segregation is less certain if B and/or R deplete within the active layer. To address these issues, some simulations are carried out in this section for case II kinetics ($\alpha_{A1} = \alpha_{A2} = 1$). Figures 14(a) and (b) show the dependencies of Y_R and η on ϕ_2 for three different feeds ($\varepsilon_A = 0.2, 1, 5$) and a support layer thickness of $\sigma = 1$. Figures 15(a)–(c) show component profiles for each feed at an activity level of $\phi_2 = 20$. All other parameters assume their base case values (Table 4). The results in Figs 14 and 15 can be compared with those in Figs 7, 9, and 11 in order to assess the impact of the different component-A reaction orders. Unfortunately, numerical limitations (the result of overflow problems) prevented a solution for $\phi_2 > 40$ in the simulations presented below.

Figure 14(a) shows that at sufficiently low activity, no depletion of B (and hence R) is encountered for the mixed feed ($\varepsilon_A = 1$) and the segregated feeds ($\varepsilon_A = 0.2, 5$). Under these conditions, the yield is equal to its intrinsic value of 0.2 [Fig. 14(a)]. However, the

Fig. 14. Catalytic membrane performance for case II kinetics and a support of intermediate thickness ($\sigma = 1$): (a) the dependence of the R yield (Y_R) on activity (ϕ_2) for three different feeds ($\varepsilon_A = 0.2, 1, 5$); (b) the corresponding dependencies of effectiveness (η) on ϕ_2 . All other parameter values assume their base case values provided in Table 5.

active layer effectiveness decreases (at a fixed activity) as A is increasingly concentrated in the support side bulk [Fig. 14(b)]. These trends confirm the anticipated behavior for equal component A reaction orders under conditions of excess B and R. That is, component-A diffusional limitations have no effect on the yield but reduce effectiveness under these conditions.

At higher activity, qualitative similarities are noted in the shapes of the R yield (Y_R) vs activity (ϕ_2) curves between case I and II kinetics. At a sufficiently high activity, component B depletion is initiated in the active layer. As obtained for case I kinetics, B depletion commences at a lower activity if the reactants are segregated (either $\varepsilon_A < 1$ or $\varepsilon_A > 1$). As ϕ_2 is increased beyond this critical activity ($\phi_2 \approx 2.1$), the R yield for the mixed-feed case ($\varepsilon_A = 1$) decreases monotonically until $\phi_2 \approx 16$, at which point it exhibits a very shallow, local minimum. Component R does not deplete over this range of ϕ_2 . These mixed-feed features are similar to those obtained for case I kinetics [Fig. 7(a)]. Qualitative similarities are also encountered for the $\varepsilon_A = 0.2$ and 5 feeds. For example, as ϕ_2 is increased from the point of B depletion, the R yield for the $\varepsilon_A = 0.2$ feed proceeds to decrease and then increase. The local minimum is encountered near the point of R depletion. On the other hand, the yield for the $\varepsilon_A = 5$ feed is a monotonically decreasing function of ϕ_2 beyond the B depletion point.

Despite the qualitative similarities between the individual R yield dependencies on activity for case I and II kinetics, there are significant differences in the impact of segregation on the relative yields. The first

Fig. 15. Component profiles for the three feeds $\epsilon_A = 0.2$ (a), $\epsilon_A = 1$ (b), and $\epsilon_A = 5$ (c) at a high activity ($\phi_2 = \hat{\phi} = 20$). Case II kinetics apply. All other parameter values assume their base case values provided in Table 5.

difference is that the mixed-feed R yield exceeds the R yields obtained for the segregated feeds over the entire range of activities considered. (Unfortunately, numerical limitations prevented us from checking if the $\epsilon_A = 0.2$ yield exceeds the $\epsilon_A = 1$ yield at high ϕ_2 .) The second difference is that, for an intermediate range of ϕ_2 , the yield for the $\epsilon_A = 5$ feed exceeds that for the $\epsilon_A = 0.2$ feed. Indeed, even for the $\epsilon_A = 0.2$ feed there is a net consumption of R for $\phi_2 > 2$ (i.e. $Y_R < 0$). This compares with case I kinetics for which R is produced well above the intrinsic level for the same conditions. These differences indicate that there is no apparent benefit of segregating the reactants, at least for this case of a support of moderate thickness ($\sigma = 1$). An examination of the component profiles at $\phi_2 = 20$ for the three feeds [Figs 15(a)–(c)] helps to determine the reason. The concentrating of reactant B (A) on the active layer (support) side does not result in a zone of high R yield near the active layer surface. Since both reactions are first-order in A, both reactions are affected equally by the A shortage in this region. The net effect is that the selective focusing of reaction 1 near the active layer surface that can be

Fig. 16. Dependence of the R yield (Y_R) (a) and effectiveness (η) in (b) on the activity (ϕ_2) for three different feeds and for a thick support layer ($\sigma = 50$). Results apply for case II kinetics. All other parameter values assume their base case values provided in Table 5.

achieved with case I kinetics is not achieved with case II kinetics.

If the support layer thickness is increased, segregation of A to the support side can have a beneficial effect for case II kinetics. Figures 16(a) and (b) show the dependencies of Y_R and η on ϕ_2 for $\sigma = 50$. However, the benefit is solely a result of avoiding B depletion for the $\epsilon_A = 0.2$ feed. Y_R is maintained at the intrinsic value (0.2) for the entire ϕ_2 range. However, a reduction in Y_R below 0.2 is encountered for the $\epsilon_A = 1$ and 5 feeds at a sufficiently high ϕ_2 because depletion of B occurs. It is interesting to note that B depletion is encountered with case I kinetics under the same conditions ($\epsilon_A = 0.2$). The difference has to do with component A diffusion limitations, which are more severe with case II kinetics because of the higher reaction order with respect to A in reaction 1. This is confirmed by comparing the η vs ϕ_2 plots for case II [Fig. 15(b)] and case I [Fig. 7(b)] kinetics. The result is a reduced consumption of component B for a fixed amount in the bulk streams. This reduces the likelihood of B depletion and has a clear impact on the R yield.

CONCLUDING REMARKS

A supported catalytic film separating two bulk streams allows for operation strategies that are not possible with conventional catalytic reactors. One such strategy is the segregation of the two reactants to opposite sides of the catalytic film. The main findings

of this study show that reactant segregation can have a significant effect on the catalyst performance, in terms of desired product (R) yield and catalyst utilization, in a consecutive-parallel reaction system described by

The effect is especially beneficial to overall point yield of R if the reaction system satisfies three requirements:

- (i) $\alpha_{A1} < \alpha_{A2}$,
- (ii) k_1, k_2 sufficiently large and
- (iii) active layer sufficiently thin compared to support layer ($\delta \ll \delta_s$).

Kinetic requirement (i) means that component-A diffusional limitations are less detrimental to reaction 1 than to reaction 2. Kinetic requirement (ii) means that the catalyst is sufficiently active so as to magnify the beneficial diffusion-reaction interactions. If requirement (iii) is satisfied, a large fraction of component R which is produced exits the film, before consumption, to undesired component P. With the three conditions satisfied, desired intermediate R is selectively produced near the active layer surface. Most importantly, the calculations indicate that the percentage gain in the R point yield can exceed the percentage loss in the point catalyst utilization. Moreover, even if requirements (i) and (ii) are not satisfied, reactant segregation can be beneficial.

The results presented in this paper apply strictly to the case of a zeroth-order rate dependence on the hydrocarbon species B and R. While this is a simplification, it permitted the use of semi-analytic analysis. Moreover, proper accounting for B and R depletion extended the generality of the results under transport-limiting conditions. Treatment of non-zero order kinetics cases is the subject of ongoing research.

One might argue in favor of an alternative, less complicated method of increasing the point yield of the intermediate product in a consecutive-parallel network. For example, a reduction in the A/B feed ratio to a conventional fixed-bed reactor for a reaction system satisfying points (i) and (ii) above will result in an increase in the R yield at low conversions [refer to Fig. 6(a)]. However, as mentioned earlier, the feed ratio is often confined to a narrow range because of safety and operability factors. Thus, reactant segregation in the membrane reactor offers a means of controlling the supply rates of the reactants while side-stepping the other process constraints. There is a definite need to carry out a more detailed performance and economic analysis of the membrane reactor given that the reactor choice is intimately tied to feed requirements, downstream separations, process reliability, and safety. Future work that is ongoing should address integral operation, heat effects, more realistic intraparticle transport processes and kinetics (Harold *et al.*, 1992).

The model predictions in this study need to be confirmed both experimentally and theoretically. Our experimental efforts confirm the beneficial effects of reactant segregation (Harold *et al.*, 1992). Results with the partial oxidation of ethylene to acetaldehyde on a $V_2O_5/\gamma\text{-Al}_2O_3/\alpha\text{-Al}_2O_3$ membrane are very encouraging. These performance studies are essential for driving future research in membrane reactors.

Acknowledgements—One of the authors (MPH) acknowledges the support of Universiteit Twente and NWO during his sabbatical leave at U. Twente. The support and hospitality of Prof. A. N. Burggraaf and Drs K. Keizer and V. T. Zaspalis are also gratefully acknowledged.

NOTATION

A	reactant (i.e. oxygen in partial oxidation)
B	reactant (i.e. hydrocarbon in partial oxidation)
d_I	effective diffusivity ratio defined in Table 4 ($I = A, B, R$)
D_I	effective diffusivity of species I in active layer ($I = A, B, R$)
D_{IO}	effective diffusivity of species I in support layer ($I = A, B, R$)
$F_{I,j}$	depletion point (of B) function for kinetic case I ($j = 1, 2$)
$F_{R,j}$	depletion point (of R) function for kinetic case II ($j = 1, 2$)
$G_{R,j}$	depletion point (of R) function for kinetic case II ($j = 1, 2, 3, 4$)
H	Heaviside function
k_i	rate constant for reaction i ($i = 1, 2$)
$\mathbf{p}$	vector of model parameters
P	undesired product (i.e. carbon oxides and water)
p_I	partial pressure of species I within pores ($I = A, B, R$)
β_I	average partial pressure of species I ($I = A, B, R$)
p_{IO}	partial pressure of species I in support side bulk ($I = A, B, R$)
p_{Io}	partial pressure of species I in active layer side bulk ($I = A, B, R$)
R	desired intermediate (i.e. partially oxidized hydrocarbon)
R	gas constant (in differential balances)
r_i	rate of reaction i , species A basis ($i = 1, 2$)
s	dimensionless position in membrane ($= z/\delta$)
s_{Bi}^*	dimensionless location of component B depletion point ($i = 1, 2$)
s_{Ri}^*	dimensionless location of component R depletion point ($i = 1, 2$)
T	temperature
Y_R	overall yield of component R, defined by eq. (76)
z	position in membrane
z_{Bi}^*	location of component B depletion point ($i = 1, 2$)

z_{Ri}^* location of component R depletion point
($i = 1, 2$)

Greek letters

α_{Ai} component A reaction order in reaction i ($i = 1, 2$)
 α_B component B reaction order in reaction 1
 α_R component R reaction order
 δ active layer thickness
 δ_s support layer thickness
 θ_I ratio of species I bulk pressure in active layer and support sides ($= p_{Ia}/p_{Io}$, $I = A, B, R$)
 ϕ_i Thiele modulus for reaction i ($i = B, R$), defined in Table 4
 η active layer effectiveness, defined by eq. (75)
 κ rate constant ratio, defined in Table 4
 λ_I species I supply parameter ($I = B, R$), defined in Table 4
 Λ $(1 + \kappa)^{1/2} \phi_1$
 Λ_Y yield enhancement parameter defined by eq. (79)
 Λ_n effectiveness enhancement parameter defined by eq. (80)
 ν_B stoichiometric coefficient of reactant B
 ν_{R1} stoichiometric coefficient of intermediate R in reaction 1
 ν_{R2} stoichiometric coefficient of intermediate R in reaction 2
 ν_P stoichiometric coefficient of product P
 ρ_I dimensionless partial pressure of species I ($= p_i/p_{Io}$, $I = A, B, R$)
 σ ratio of support to active layer thickness (see Table 4)
 ξ p_{AO}/p_{BO}

Subscripts

m mixed feed
 A component A
 B component B
 R component R
 s support layer
 0 support side bulk gas
 δ active layer side bulk

REFERENCES

- Agarwalla, S. and Lund, C. R. F., 1992, Use of a membrane reactor to improve selectivity to intermediate products in consecutive catalytic reactions. *J. Membrane Sci.* **70**, 129–146.
 Armor, J., 1989, Catalysis with permselective membranes. *Appl. Catal.* **49**, 1.
 Champagnie, A. M., Tsotsis, T. T., Minet, R. G. and Webster, I. A., 1990, A high temperature catalytic membrane reactor for ethane dehydrogenation. *Chem. Engng Sci.* **45**, 2423–2429.
 Cini, P. and Harold, M. P., 1991, Experimental study of the tubular multiphase catalyst. *A.I.Ch.E. J.* **37**, 997–1008.
 Cini, P., Blaha, S. R., Harold, M. P. and Venkataraman, K., 1991, Preparation and characterization of modified tubular ceramic membranes for use as catalyst supports. *J. Membrane Sci.* **55**, 199–225.
 Cussler, E. L., 1984, *Diffusion Mass Transfer in Fluid Systems*. Cambridge University Press, Cambridge.
 de Vos, R., Hatziantoniou, V. and Schoon, N.-H., 1982, The cross-flow catalyst reactor. An alternative for liquid phase hydrogenations. *Chem. Engng Sci.* **37**, 1719.
 Eng, D. and Stoukides, M., 1991, Catalytic and electrocatalytic methane oxidation with solid oxide membranes. *Catal. Rev. Sci. Engng* **33**, 375–412.
 Froment, G. F. and Bischoff, K. B., 1979, *Chemical Reactor Analysis and Design*. Wiley, New York.
 Gallagher, G. R., Wu, J. C. S., Pagano, M. P., Gerdes, T. E., Blave, R. R. and Liu, P. K. T., 1990, The stability of a commercial ceramic membrane use as a dehydrogenation reactor, in *Proceedings of the International Congress on Membranes and Membrane Processes*, Chicago.
 Geiselmann, M. F., Anderson, M. A., Moosemiller, M. D. and Hill, C. G., 1988, Physico-chemical properties of supported and unsupported α - Al_2O_3 membranes. *J. Membrane Sci.* **39**, 285.
 Gryaznov, V. M., 1986, Hydrogen permeable palladium membrane catalysts. *Platinum Metals Rev.* **30**, 68–72.
 Harold, M. P., Zaspalis, V. T., Keizer, K. and Burggraaf, A. N., 1992, Improving partial oxidation product yield with a catalytic inorganic membrane. Paper presented at Fifth Annual Meeting of the North American Membrane Society, Lexington, Kentucky.
 Hsieh, H. P., 1989, Inorganic membrane reactors—a review. *A.I.Ch.E. Symp. Ser.* **85**(268), 53–67.
 Itoh, N. and Govind, R., 1989, Development of a novel oxidative palladium membrane reactor. *A.I.Ch.E. Symp. Ser.* **85**(268), 10–17.
 Keizer, K., Zaspalis, V. T. and Burggraaf, A. J., 1991, Passive and catalytically active membranes for affecting chemical reactions. *Materials Science Monographs*, **66D**, 1511–1524.
 Leenaars, A. F. M. and Burggraaf, A. J., 1985, The preparation and characterization of alumina membranes with ultrafine pores. Part 2. The formation of supported membranes. *J. Colloid Interface Sci.* **105**, 27.
 Leenaars, A. F. M., Keizer, K. and Burggraaf, A. J., 1984, The preparation and characterization of alumina membranes with ultrafine pores. *J. Mater. Sci.* **19**, 1077.
 Mohan, K. and Govind, R., 1988, Analysis of equilibrium shift in isothermal reactor with a permselective wall. *A.I.Ch.E. J.* **34**, 1493–1503.
 Shinji, O., Misonou, M. and Oneda, Y., 1982, The dehydrogenation of cyclohexane by the use of a porous-glass reactor. *Bull. Chem. Soc. Japan* **55**, 2760.
 Slood, H. J., Versteeg, G. F. and van Swaaij, W. P. M., 1990, A non-permselective membrane reactor for chemical processes normally requiring strict stoichiometric feed rates of reactants. *Chem. Engng Sci.* **45**, 2415–2422.
 Slood, H. J., Smolders, C. A., van Swaaij, W. P. M. and Versteeg, G. F., 1992, High-temperature membrane reactor for catalytic gas-solid reactions. *A.I.Ch.E. J.* **38**, 887–900.
 Stoukides, M., 1988, Applications of solid electrolytes in heterogeneous catalysis. *Ind. Engng Chem. Res.* **27**, 1745–1750.
 Sun, Y. M. and Khang, S. J., 1988, Catalytic membrane for simultaneous chemical reaction and separation applied to a dehydrogenation reaction. *Ind. Engng Chem. Res.* **27**, 1136–1142.
 Uhlhorn, R. J. R., Huis in't Veld, M. H. B. J., Keizer, K. and Burggraaf, A. J., 1987, New ceramic membrane materials for the use in gas separation applications. *Sci. Ceram.* **14**, 55.
 Vayenas, C. G., Bebelis, S. and Ladas, S., 1990, *Nature* **343**, 625.
 Zaspalis, V. T., 1990, Catalytically active ceramic membranes. Synthesis, properties, and reactor applications. Ph.D. dissertation, University of Twente.
 Zaspalis, V. T., van Pragg, W., Keizer, K., van Ommen, J. G., Ross, J. R. H. and Burggraaf, A. J., 1991a, Reactions of

methanol over catalytically active alumina membranes. *Appl. Catal.* **74**, 205–222.

Zaspalis, V. T., van Pragg, W., Keizer, K., van Ommen, J. G., Ross, J. R. H. and Burggraaf, A. J., 1991b, Reactor studies using alumina separation membrane for the dehydrogenation of methanol and *n*-butane. *Appl. Catal.* **74**, 223–234.

Zaspalis, V. T., van Pragg, W., Keizer, K., van Ommen, J. G., Ross, J. R. H. and Burggraaf, A. J., 1991c, Reactions of methanol over alumina catalytically active membranes modified by silver. *Appl. Catal.* **74**, 235–248.

APPENDIX A: SOLUTIONS FOR KINETIC CASE I

Three sets of general solutions are provided in this section for kinetic case I ($\alpha_{A1} = 0$, $\alpha_{A2} = 1$). The three sets correspond to the situations of (i) no B or R depletion, (ii) B depletion, and (iii) B and R depletion.

(i) No B or R depletion

• Zone 1 ($-\sigma < s < 0$):

$$\rho_{A1}(s) = K_1 s + K_2 \quad (\text{A1})$$

$$\rho_{B1}(s) = K_3 s + K_4 \quad (\text{A2})$$

$$\rho_{R1}(s) = K_5 s + K_6 \quad (\text{A3})$$

• Zone 2 ($0 < s < 1$):

$$\rho_{A2}(s) = K_7 \sinh(\kappa \phi_1 s) + K_8 \sinh(\kappa \phi_1 (1-s)) + \kappa^{-1} \quad (\text{A4})$$

$$\rho_{B2}(s) = \frac{\lambda_B \phi_1^2}{2} s^2 + K_9 s + K_{10} \quad (\text{A5})$$

$$\begin{aligned} \rho_{R2}(s) = & -\frac{\lambda_R \phi_1^2}{2} s^2 + K_{11} s + K_{12} \\ & + v_R \lambda_R \left[K_1 \sinh(\kappa \phi_1 s) \right. \\ & \left. + K_2 \sinh(\kappa \phi_1 (1-s)) - \frac{\phi_1^2 s^2}{2} \right] \quad (\text{A6}) \end{aligned}$$

where $v_R = v_{R1}/v_{R2}$.

The 12 integration constants are eliminated by applying the 12 boundary conditions provided in Table 1 [eqs (23)–(26)].

(ii) B depletion

• Zone 1 ($-\sigma < s < 0$):

$$\rho_{A1}(s), \rho_{B1}(s), \rho_{R1}(s) \text{ given by eqs (A1)–(A3).}$$

• Zone 2 ($0 < s < s_{B1}^*$):

$$\rho_{A2}(s), \rho_{B2}(s), \rho_{R2}(s) \text{ given by eqs (A4)–(A6).}$$

• Zone 3 ($s_{B1}^* < s < s_{B2}^*$):

$$\rho_{A3}(s) = K_{13} \sinh(\kappa \phi_1 s) + K_{14} \sinh(\kappa \phi_1 (1-s)) \quad (\text{A7})$$

$$\rho_{B3}(s) = K_{15} s + K_{16} \quad (\text{A8})$$

$$\begin{aligned} \rho_{R3}(s) = & K_{17} s + K_{18} + v_R \lambda_R [K_{13} \sinh(\kappa \phi_1 s) \\ & + K_{14} \sinh(\kappa \phi_1 (1-s))] \quad (\text{A9}) \end{aligned}$$

• Zone 4 ($s_{B2}^* < s < 1$):

$$\begin{aligned} \rho_{A4}(s) = & K_{19} \sinh(\kappa \phi s) \\ & + K_{20} \sinh(\kappa \phi_1 s) - \kappa^{-1} \quad (\text{A10}) \end{aligned}$$

$$\rho_{B4}(s) = \frac{\lambda_B \phi_1^2}{2} s^2 + K_{21} s + K_{22} \quad (\text{A11})$$

$$\rho_{R5}(s) = -\frac{\lambda_R \phi_1^2}{2} s^2 + K_{23} s + K_{24} \quad (\text{A12})$$

There are 24 integration constants (K_1 – K_{24}) and two points of depletion (s_{B1}^* , s_{B2}^*) to solve for using the 26 bound-

ary conditions. These are provided by eqs (23)–(25), and (36)–(42). One can eliminate K_1 – K_{24} since they appear linearly. s_{B1}^* and s_{B2}^* appear quadratically and can be solved for explicitly and are given by

$$s_{B1}^* = -\sigma d_B + \left[(d_B \sigma)^2 + \frac{2}{\lambda_B \phi_1^2} \right]^{1/2} \quad (\text{A13})$$

$$s_{B2}^* = 1 - \left[\frac{2e_B}{\lambda_B \phi_1^2} \right]^{1/2} \quad (\text{A14})$$

(iii) B and R depletion

• Zone 1 ($-\sigma < s < 0$):

$$\rho_{A1}(s), \rho_{B1}(s), \rho_{R1}(s) \text{ given by eqs (A1)–(A3).}$$

• Zone 2 ($0 < s < s_{B1}^*$):

$$\rho_{A2}(s), \rho_{B2}(s), \rho_{R2}(s) \text{ given by eqs (A4)–(A6).}$$

• Zone 3 ($s_{B1}^* < s < s_{R1}^*$):

$$\rho_{A3}(s), \rho_{B3}(s), \rho_{R3}(s) \text{ given by eqs (A7)–(A9).}$$

• Zone 4 ($s_{R1}^* < s < s_{R2}^*$):

$$\rho_{A4}(s) = K_{19} s + K_{20} \quad (\text{A15})$$

$$\rho_{B4}(s) = K_{21} s + K_{22} \quad (\text{A16})$$

$$\rho_{R4}(s) = K_{23} s + K_{22} \quad (\text{A17})$$

• Zone 5 ($s_{R2}^* < s < s_{B2}^*$):

$$\rho_{A5}(s) = K_{25} \sinh(\kappa \phi_1 s) + K_{26} \sinh(\kappa \phi_1 (1-s)) \quad (\text{A18})$$

$$\rho_{B5}(s) = K_{27} s + K_{28} \quad (\text{A19})$$

$$\begin{aligned} \rho_{R5}(s) = & K_{29} s + K_{30} + v_R \lambda_R [K_{27} \sinh(\kappa \phi_1 s) \\ & + K_{28} \sinh(\kappa \phi_1 (1-s))] \quad (\text{A20}) \end{aligned}$$

• Zone 6 ($s_{B2}^* < s < 1$):

$$\begin{aligned} \rho_{A6}(s) = & K_{31} \sinh(\kappa \phi_1 s) \\ & + K_{32} \sinh(\kappa \phi_1 (1-s)) - \kappa^{-1} \quad (\text{A21}) \end{aligned}$$

$$\rho_{B6}(s) = \frac{\lambda_B \phi_1^2}{2} s^2 + K_{33} s + K_{34} \quad (\text{A22})$$

$$\begin{aligned} \rho_{R6}(s) = & -\frac{\lambda_R \phi_1^2}{2} s^2 + K_{35} s + K_{36} \\ & + v_R \lambda_R [K_{31} \sinh(\kappa \phi_1 s) \\ & + K_{32} \sinh(\kappa \phi_1 (1-s))] \quad (\text{A23}) \end{aligned}$$

There are 36 integration constants (K_1 – K_{36}) and four points of depletion (s_{B1}^* , s_{B2}^* , s_{R1}^* , s_{R2}^*) to solve for using the 40 boundary conditions. These are provided by eqs (23)–(25), (36)–(38), and (52)–(61). The component-B depletion points can be solved for explicitly and are given by eqs (A13) and (A14). The 36 constants can be eliminated, some of which are expressed in terms of the B and R depletion points. It is not possible to solve for s_{R1}^* and s_{R2}^* explicitly. Instead, two implicit equations are determined during the elimination of the integration constants; see eqs (62).

APPENDIX B. SOLUTIONS FOR KINETIC CASE II

Three sets of general solutions are provided in this section for kinetic case II ($\alpha_{A1} = \alpha_{A2} = 1$). The three sets correspond to the situations of (i) no B or R depletion, (ii) B depletion, and (iii) B and R depletion.

(i) No B or R depletion

• Zone 1 ($-\sigma < s < 0$):

$$\rho_{A1}(s) = K_1 s + K_2 \quad (\text{B1})$$

$$\rho_{B1}(s) = K_3 s + K_4 \quad (\text{B2})$$

$$\rho_{R1}(s) = K_5 s + K_6 \quad (\text{B3})$$

• Zone 2 ($0 < s < 1$):

$$\rho_{A2}(s) = K_7 \sinh(\Lambda s) + K_8 \sinh(\Lambda(1-s)) \quad (\text{B4})$$

$$\rho_{B2}(s) = \beta_B [K_7 \sinh(\Lambda s) + K_8 \sinh(\Lambda(1-s))] + K_9 s + K_{10} \quad (\text{B5})$$

$$\rho_{R2}(s) = \beta_R [K_7 \sinh(\Lambda s) + K_8 \sinh(\Lambda(1-s))] + K_{11} s + K_{12} \quad (\text{B6})$$

where

$$\Lambda = \sqrt{1 + \kappa \phi_1}$$

$$\beta_B = \frac{\lambda_B}{1 + \kappa} \quad \beta_R = \frac{\lambda_R(v_R \kappa - 1)}{1 + \kappa} \quad (\text{B7})$$

(ii) B depletion

• Zone 1 ($-\sigma < s < 0$):

$$\rho_{A1}(s), \rho_{B1}(s), \rho_{R1}(s) \text{ given by eqs (B1)–(B3).}$$

• Zone 2 ($0 < s < s_{B1}^*$):

$$\rho_{A2}(s), \rho_{B2}(s), \rho_{R2}(s) \text{ given by eqs (B4)–(B6).}$$

• Zone 3 ($s_{B1}^* < s < s_{B2}^*$):

$$\rho_{A3}(s) = K_{13} \sinh(\kappa \phi_1 s) + K_{14} \sinh(\kappa \phi_1(1-s)) \quad (\text{B8})$$

$$\rho_{B3}(s) = K_{15} s + K_{16} \quad (\text{B9})$$

$$\rho_{R3}(s) = v_R \lambda_R [K_{13} \sinh(\kappa \phi_1 s) + K_{14} \sinh(\kappa \phi_1(1-s))] + K_{17} s + K_{18} \quad (\text{B10})$$

• Zone 4 ($s_{B2}^* < s < 1$):

$$\rho_{A4}(s) = K_{19} \sinh(\Lambda s) + K_{20} \sinh(\Lambda(1-s)) \quad (\text{B11})$$

$$\rho_{B4}(s) = \beta_B [K_{19} \sinh(\Lambda s) + K_{20} \sinh(\Lambda(1-s))] + K_{21} s + K_{22} \quad (\text{B12})$$

$$\rho_{R4}(s) = \beta_R [K_{19} \sinh(\Lambda s) + K_{20} \sinh(\Lambda(1-s))] + K_{23} s + K_{24} \quad (\text{B13})$$

The situation here is similar to case I kinetics with B depletion. For example, there are 24 constants and two depletion points to solve for. Moreover, the identical boundary conditions are applied. However, it is not possible in this

case to solve for the B depletion points explicitly. Rather, two implicit functions [eqs (63)] are derived after elimination of the integration constants, K_1 – K_{24} , which appear linearly.

(iii) B and R depletion

• Zone 1 ($-\sigma < s < 0$):

$$\rho_{A1}(s), \rho_{B1}(s), \rho_{R1}(s) \text{ given by eqs (B1)–(B3).}$$

• Zone 2 ($0 < s < s_{B1}^*$):

$$\rho_{A2}(s), \rho_{B2}(s), \rho_{R2}(s) \text{ given by eqs (B4)–(B6).}$$

• Zone 3 ($s_{B1}^* < s < s_{R1}^*$):

$$\rho_{A3}(s), \rho_{B3}(s), \rho_{R3}(s) \text{ given by eqs (B8)–(B10).}$$

• Zone 4 ($s_{R1}^* < s < s_{R2}^*$):

$$\rho_{A4}(s) = K_{19} s + K_{20} \quad (\text{B14})$$

$$\rho_{B4}(s) = K_{21} s + K_{22} \quad (\text{B15})$$

$$\rho_{R4}(s) = K_{23} s + K_{24} \quad (\text{B16})$$

• Zone 5 ($s_{R2}^* < s < s_{B2}^*$):

$$\rho_{A5}(s) = K_{25} \sinh(\kappa \phi_1 s) + K_{26} \sinh(\kappa \phi_1(1-s)) \quad (\text{B17})$$

$$\rho_{B5}(s) = K_{27} s + K_{28} \quad (\text{B18})$$

$$\rho_{R5}(s) = v_R \lambda_R [K_{25} \sinh(\kappa \phi_1 s) + K_{26} \sinh(\kappa \phi_1(1-s))] + K_{29} s + K_{30} \quad (\text{B19})$$

• Zone 6 ($s_{B2}^* < s < 1$):

$$\rho_{A6}(s) = K_{31} \sinh(\Lambda s) + K_{32} \sinh(\Lambda(1-s)) \quad (\text{B20})$$

$$\rho_{B6}(s) = \beta_B [K_{31} \sinh(\Lambda s) + K_{32} \sinh(\Lambda(1-s))] + K_{33} s + K_{34} \quad (\text{B21})$$

$$\rho_{R6}(s) = \beta_R [K_{31} \sinh(\Lambda s) + K_{32} \sinh(\Lambda(1-s))] + K_{35} s + K_{36} \quad (\text{B22})$$

This situation is similar to that for case I kinetics with B and R depletion. There are 36 constants and four depletion points to solve for using the same 40 boundary conditions specified for the case I situation. Cumbersome algebra gives four coupled, implicit functions of the depletion points during the elimination of the constants. These functions are represented by eq. (64).