Cocurrent Membrane Reactors vs. PFRs for Shifting Dehydrogenation Equilibrium

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Membrane reactor performance in reversible reactions like dehydrogenation is often compared to plug-flow reactor performance. Analysis of cocurrent membrane-reactor design equations shows that as the Damköhler–Peclet product varies from 0 to ∞, the membrane reactor approaches a fully diluted or undiluted plug-flow reactor. If its yield is maximized by varying this parameter, the optimum cocurrent membrane reactor is often one of these limiting cases, and a membrane reactor offers no advantage over a plug-flow reactor. When the optimum membrane reactor does not correspond to one of these limiting cases, there still may be a plug-flow reactor system that offers equal or higher yields. Analysis of plug-flow-reactor performance indicates that there is an optimum degree of dilution; while the optimized membrane reactor yield may be greater than either an undiluted or a fully diluted plug-flow reactor; it may not be greater than an optimally diluted plug-flow reactor. When using porous membranes the membrane reactor yield is at most 7% greater than the yield using a plug-flow reactor. The porous membranes enhance the yields in a regime where the reactor would not be likely to operate. Much larger yield advantages are possible, but only when the membrane is highly permselective, as with dense membranes. Highly permselective membranes also enhance the yields in a regime where the membrane reactor process is likely to be operated.

Introduction

A membrane reactor is typically thought of as a single process unit that combines a chemical reactor and a membrane separator. The ability of a membrane reactor to selectively separate products while reaction is taking place offers the potential for altering reaction selectivities and/or yields as compared to the more conventional arrangement where reaction takes place without any product removal (for reviews, see Armor, 1989; Shu et al., 1991; Tsotsis et al., 1993; Saracco et al., 1994; Zaman and Chakma, 1994). The use of membrane reactors for "equilibrium shifting" is one particularly well-studied situation wherein the product yield from a reversible reaction is altered (examples with a variety of reactions include Ito et al., 1984, 1993; Adris et al., 1991; Okubo et al., 1991; Uemiya et al., 1991; Becker et al., 1993; Edlund and Pledger, 1993; Song et al., 1993; Tiscareno-Lechuga et al., 1993; Collins and Way, 1994; and Deng and Wu, 1994). The dehydrogenation of a paraffin [e.g., ethane (Champagnie et al., 1990, 1991, 1992; Gobina and Hughes 1994), propane (Ziaka et al., 1993,a,b), or butane (Gokhale et al., 1993; Ioannides and Gavalas, 1993; Matsuda et al., 1993)] to an olefin (ethylene, propene, or butene, respectively) is a typical example of a reversible reaction where "equilibrium shifting" is desirable. For simple dehydrogenations there is only one dehydrogenated product, while dehydrogenation of larger paraffins may produce a variety of products. In such situations the membrane may be used as a means of altering the product selectivity as well as for equilibrium shifting. In the present work we consider only equilibrium-shifting applications involving the simpler, single-product dehydrogenation reactions that can be represented generically using Eq. 1 wherein P denotes a paraffin and O denotes an olefin:

$$P \rightleftarrows O + H_2. \quad (1)$$

Figure 1 presents an illustration of a cocurrent flow membrane reactor for "equilibrium shifting" using a concentric

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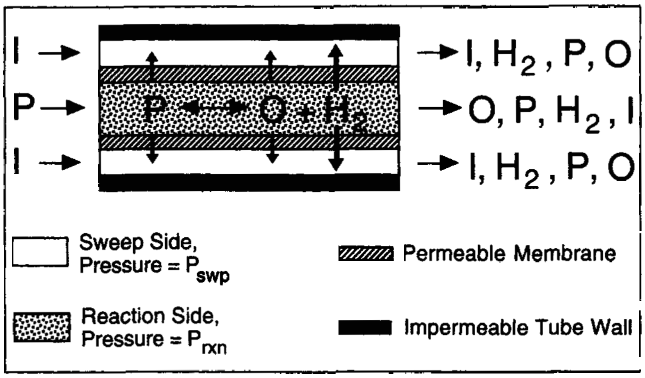

Figure 1. Cocurrent membrane reactor for dehydrogenation of a paraffin, *P*, to an olefin, *O*.

The membrane is typically permselective for H_2, and consequently the sweep-side effluent is richer in inert diluent, *I*, and hydrogen, while the reaction side effluent is richer in hydrocarbons.

tube geometry. As the figure shows, the paraffin reactant is fed on one side of the membrane; the catalyst for reaction 1 is present on this feed side so dehydrogenation can take place. Following most laboratory studies, the diagram shows an inert gas being fed to the "sweep" side of the reactor. For real reactor systems it may prove difficult to identify economically viable sweep gases. The inner tube wall is selectively permeable to H_2, which therefore escapes to the annular space more rapidly than the other components. With porous membranes all species can permeate, whereas with dense membranes (e.g., a Pd alloy) only one species, usually H_2, permeates. In the analysis presented here, both types of membranes are considered, so Figure 1 depicts the general situation wherein all four species are present in both of the effluent streams. Progressing from the inlet along the inner tube of the reactor the conversion of paraffin to olefin increases due to reaction. In a plug-flow reactor (PFR) the conversion increases until thermodynamic equilibrium is attained. At the corresponding conversion in the membrane reactor, the reaction has not reached thermodynamic equilibrium due to the selective removal of the product H_2, and consequently the conversion continues increasing. Thus, the conversion in a membrane reactor becomes greater than that in an undiluted PFR. This is sometimes referred to as "equilibrium shifting" though clearly there is no point within the membrane reactor where equilibrium is surpassed.

Since membrane-reactor technology is not commercially utilized to any significant extent, membrane-reactor performance is often benchmarked against PFR performance. The critical question then becomes "what is the most equitable basis of comparison between membrane reactors and PFRs, given that they are inherently different in design and operation?" A comparison of the membrane-reactor conversion to the equilibrium conversion of an undiluted PFR was a very common performance benchmark in many early membrane-reactor studies. More recently it has become recognized that this is not always an appropriate comparison, as it may give the membrane reactor an advantage (Gokhale et al., 1995). As can be seen in Figure 1, the product streams from the membrane reactor are generally diluted by the inert sweep gas. If the feed to a PFR was equally diluted, it too could attain higher conversions since the equilibrium conversion is favorably affected by dilution. Indeed, it has been demonstrated that in a cocurrent membrane reactor the conversion never exceeds the equilibrium conversion of a comparably diluted PFR (Itoh, 1995).

Comparing the conversion in a cocurrent membranė reactor to the *equilibrium* conversion in a comparably diluted PFR, however, is also inappropriate, as it may give the PFR an advantage (Tsotsis et al., 1993; Itoh, 1995). When the PFR is diluted, the rate of dehydrogenation is lowered. Thus, even though dilution affords a greater ultimate conversion, reaching that greater conversion requires a larger reactor. Therefore use of a membrane reactor can still offer an advantage in terms of residence time or reactor size, and this has been documented for specific cases in the literature (Gokhale, et al., 1995; Itoh, 1995). One might suspect, then, that the best comparison would be between a membrane reactor and a comparably diluted PFR of the same size. It will be argued here that it is not always necessary or desirable to dilute the PFR to the same level as the membrane reactor. It will be shown that for a single PFR at a given duty, there is an optimum dilution ratio that maximizes the yield of olefin. If this optimum dilution ratio is less than the dilution in the membrane reactor, the PFR should only be diluted to this optimum; it should not be diluted fully to the level of the membrane reactor.

As this brief introduction points out, the basis of comparison of membrane reactors to PFRs can bias a performance analysis. This article begins by considering the design equation for a cocurrent membrane reactor used for equilibrium shifting. The nondimensional form of the design equation includes a parameter, *DaPe*, that can be varied so as to maximize the olefin yield from the cocurrent membrane reactor. It is shown that in many cases the value of *DaPe* that maximizes olefin yield results in a cocurrent membrane reactor that behaves just like either PFR or a diluted PFR. Thus the need for comparing the two kinds of reactors is obviated. There are other conditions identified in the present article where the optimum cocurrent membrane reactor is not equivalent to a PFR. At these conditions a comparison is still necessary. While the two reactor types are not the same, and consequently can't be compared on an equal basis, this article attempts to make the comparison as "equitable" as possible. This is done by comparing the olefin yield from an optimized cocurrent membrane reactor to that from an optimized PFR, subject to the following constraints: the two reactors must use the same amount of reactant feed; the two reactors must have the same reaction (or catalyst) volume; the reactors must operate at the same temperature; and the reactors must operate at the same pressure. Furthermore, the PFR is constrained to use no more inert diluent than is used by the cocurrent membrane reactor (though it may use less).

Membrane reactors have been studied in conjunction with a large number of reversible reactions, each with their own unique kinetics, and using a variety of membrane materials, which may offer unique permeation relationships (Tsotsis et al., 1993). The generic analysis presented here is intended to offer a semiquantitative indication of (a) the magnitude of the yield enhancement that can be expected through the use of membrane reactors; (b) the range of conversions where those yield enhancements occur; and (c) the range of membrane-reactor parameters necessary for realizing those yield enhancements. Two sets of membrane parameters are considered, one corresponding to permeation characteristic of porous membrane materials and one corresponding to highly permselective, usually dense, membrane materials. When porous membranes are employed the pressure differential across the membrane cannot be too large or else all the reactant is "blown through"the membrane. Hence, in the present article the focus is limited to situations where a negligible pressure differential is applied across the membrane, and as a consequence, most of the conclusions will be more applicable to porous membranes than to dense membranes. The analysis here assumes that the separation effected by the membrane reactor does not significantly lessen downstream process separation demands. In this case, the membrane reactor must be justified solely on the basis of increased yield.

Reactor Models and Analysis Procedure

Plug-flow reactor

Before comparing cocurrent membrane reactors to PFRs, it is instructive to consider the optimization of each reactor type's performance. Here the reactors' performance will be evaluated using simple, well-established reactor and kinetic models. The rate of simple dehydrogenation reactions like those considered here can be adequately described using a rate expression of the form of Eq. 2.

$$-r_P = kP_P\left(1-\frac{P_O P_{H_2}}{KP_p}\right). \tag{2}$$

For example, Eq. 2 has been used to describe the dehydrogenation of ethane (Champagnie et al., 1992) and cyclohexane (Shinji et al., 1982; Ito et al., 1985; Sun and Khang, 1988; Raich and Foley, 1995) (though many other expressions have also been used for these reactions, e.g., Itoh et al., 1988; Okubo et al., 1991; Gokhale et al., 1993; Raich, and Foley 1995). If this expression is substituted into the material balance for an isothermal PFR and the resulting equation is made nondimensional, Eq. 3 results:

$$\frac{dF_O}{dZ} = Da\frac{1-F_O}{1+Y_I+F_O}\left[1-\frac{F_O^2}{\kappa(1+Y_I+F_O)(1-F_O)}\right] \tag{3}$$

In the present analysis it is assumed that the PFR operates isothermally and with negligible pressure drop along its length, so Eq. 3 is the only equation needed to model the reactor. Here it is also assumed that neither olefin nor hydrogen is fed to the reactor, so Eq. 3 is solved using the initial condition that $F_O = 0$ at $Z = 0$. The (nondimensional) outlet flow rate of olefin is then found by integrating Eq. 3 from $Z = 0$ to $Z = 1$. The PFR material balance was solved analytically, yielding an implicit equation for F_O that was then solved numerically by a globally convergent Newton method (Press et al., 1992). Brent's method in one dimension was used for optimizing reactor parameters (Press et al., 1992).

In the analyses that follow, olefin yield will be determined as a function of the Damköhler number, *Da*, appearing in Eq. 3. A large Damköhler number can be taken to represent a large reactor, a large residence time, or a small duty (amount of paraffin processed). Comparisons will then be made between PFRs and membrane reactors of equal *Da*. The reactors will also be required to operate at equal pressures, so the dimensionless equilibrium constant, κ, for the PFR will equal that for the membrane reactor. The only parameter remaining in Eq. 3 is the dilution, Y_I (the ratio of inert diluent to paraffin in the feed). Figure 2 shows how the yield of olefin, ψ, from a PFR varies as a function of *Da* for several different dilutions (all using $\kappa = 0.1$). Dilution has two opposing effects: it lowers the rate of reaction near the front of the reactor (far from equilibrium), but it increases the ultimate yield. The figure shows that at small values of *Da* (i.e., at small residence times where the reaction is far from equilibrium and the reverse reaction has a negligible effect) an undiluted PFR ($Y_I = 0$) gives the greatest olefin yield. As *Da* increases to ~1.5 (i.e., as the residence time increases and the reverse reaction begins to become significant), the PFR with $Y_I = 1$ gives the greatest olefin yield. This happens because the increase in thermodynamic driving force for the reaction caused by dilution near the end of the reactor more than offsets the decrease in kinetics at the front of the reactor. At higher still *Da*, $Y_I = 3$ gives the greatest yield, and so on. Thus at any particular value of *Da*, there is an optimum value of dilution, Y_{opt} which maximizes the olefin yield. Dilutions greater than Y_{opt} decrease the forward rate of reaction at the front end of the reactor by too much, whereas with dilutions less than Y_{opt} the reverse rate becomes too high near the end of the reactor. For a given *Da*, the dilution that just touches the optimal yield curve (the heavy dashed line in Figure 2) represents Y_{opt} for that value of *Da*. Figure 3a shows the optimal yield curve for several values of κ, and Figure 3b presents the corresponding values of the optimum dilution, Y_{opt}.

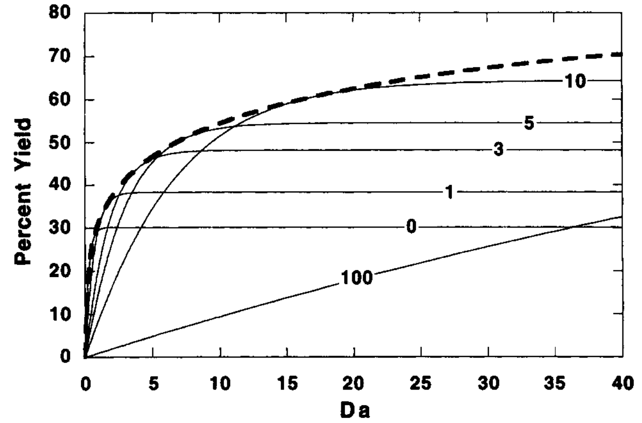

Figure 2. Olefin yield from a PFR as a function of Damköhler number for different levels of inert dilution.

All for a dimensionless equilibrium constant, $\kappa = 0.1$. The heavy dashed curve represents the maximum yield that can be attained at each Damköhler number.

Cocurrent membrane reactor

Dehydrogenation in a cocurrent membrane reactor can be accurately modeled assuming plug flow on both sides of the

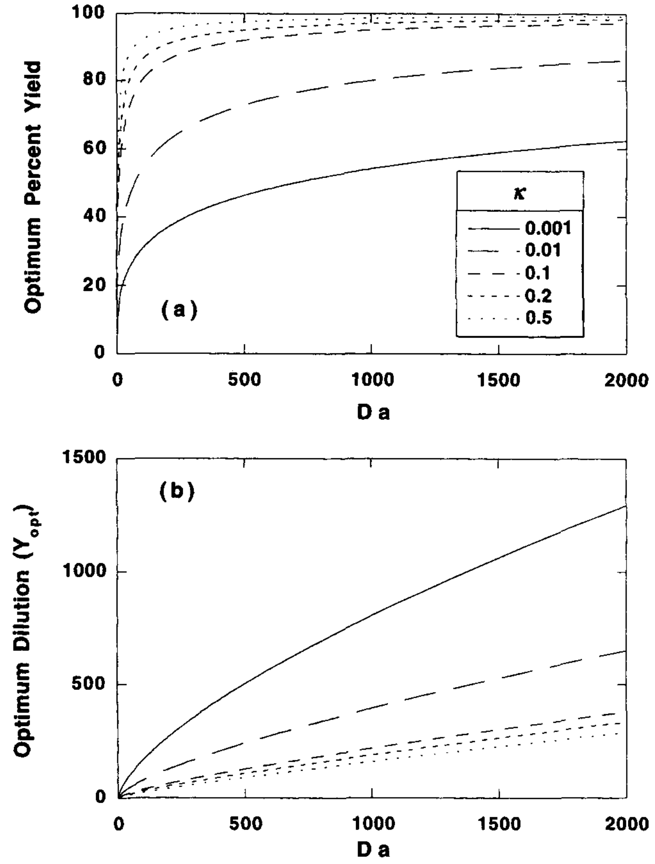

Figure 3. (a) Maximum yield of olefin as a function of Damköhler number for different dimensionless equilibrium constants; (b) corresponding dilutions for the maximum yield at each Damköhler number.

membrane with negligible gradients between the bulk fluid and the membrane surface. Assuming that permeation through the membrane can be described using Fick's law with an effective diffusivity for each species, and using the same rate Eq. 2, a (nondimensional) material balance on species i on the reaction side of the membrane is given by Eq. 4, and a material balance on species i on the sweep side of the membrane is given by Eq. 5:

$$\frac{d(F_i)_{rxn}}{dZ} = Da\left[\nu_i \frac{(F_P)_{rxn}}{(F_{\text{total}})_{rxn}}\left(1 - \frac{(F_O)_{rxn}(F_{H_2})_{rxn}}{\kappa (F_P)_{rxn}(F_{\text{total}})_{rxn}}\right) - \frac{S_i}{DaPe}\left(\frac{(F_i)_{rxn}}{(F_{\text{total}})_{rxn}} - \frac{1}{\Phi}\frac{(F_i)_{swp}}{(F_{\text{total}})_{swp}}\right)\right] \qquad (4)$$

$$\frac{d(F_i)_{swp}}{dZ} = \frac{DaS_i}{DaPe}\left(\frac{(F_i)_{rxn}}{(F_{\text{total}})_{rxn}} - \frac{1}{\Phi}\frac{(F_i)_{swp}}{(F_{\text{total}})_{swp}}\right). \qquad (5)$$

As for the PFR, the temperature is assumed to be constant and the pressure drop along the length of each side of the reactor is assumed to be negligible.

It should be noted that these equations have been shown to accurately model the dehydrogenation of cyclohexane to benzene in a membrane reactor using porous glass and a pressure ratio, $\Phi = 1$ (Shinji et al., 1982; Bernstein et al., 1996). Similar equations have been shown to be accurate for modeling other dehydrogenation reactions in membrane reactors (e.g., Champagnie et al., 1990, 1991, 1992; Gokhale et al., 1995). (For dense membranes, other permeation relationships may apply, e.g., Sievert's law.) At higher transmembrane pressure ratios, boundary layer effects and convective flow through the membrane can become important, and the reactor model must be adjusted accordingly; however, in the absence of reaction an equation like Eq. 5 has been used to accurately describe permeation where one side of the membrane is maintained at 2.0 MPa and the other side is apparently evacuated (Bhandarkar et al., 1992; Shelekhin et al., 1992; 1993; 1995). It has already been noted, too, that a variety of kinetic expressions have been used in modeling dehydrogenation, and the exact form of the rate expression can have a significant effect on some aspects of reactor performance (Raich and Foley, 1995). Nonetheless, the models used here are sufficiently accurate to provide a semiquantitative description of reactor performance; for some systems they can be considered quantitative.

The initial conditions used in solving Eqs. 4 and 5 are that $(F_i)_j = (Y_i)_j$ at $Z = 0$ for $i = P$, O, H_2, and I, and j = "*rxn*" and "*swp*." The Damköhler number is defined identically for the PFR and the membrane reactor. In all simulations here it has been assumed that only paraffin is fed to the reaction side of the membrane reactor and that only inert is fed to its sweep side. Thus $(Y_O)_{rxn}$, $(Y_{H_2})_{rxn}$, $(Y_I)_{rxn}$, $(Y_P)_{swp}$, $(Y_O)_{swp}$, and $(Y_{H_2})_{swp}$ are always zero, and so the *swp* subscript for the dilution, $(Y_I)_{swp}$, can be dropped and Y_I used to denote the dilution. For convenience it has also been assumed that all species except H_2 have similar permselectivities so $S_i = 1.0$ for $i = P$, O, and I. The situation where $Y_I = 1.0$, $\kappa = 0.1$ [of the order expected for the dehydrogenation of propane at 820 K and 1 atm (Ziaka et al., 1993)], and $S_{H_2} = 5.0$ (of the order expected if Knudsen diffusion controls permselectivity during propane or butane dehydrogenation) serves as a base case. It is characteristic of a system using a porous membrane material like porous alumina or Vycor glass. In the analysis to follow a second hydrogen permselectivity, $S_{H_2} = 10{,}000$, is used to simulate the performance of a reactor using a dense membrane like Pd. This finite value is expected to simulate a situation where the dense membrane contains a few pinholes or other defects so that it is not infinitely permselective. The material balances for the membrane reactors were solved numerically using a semi-implicit integration method with adaptive step size (Press et al., 1992). Maxima in the yield were again found using Brent's method in one dimension (Press et al., 1992).

It is instructive to examine membrane-reactor performance before making comparisons to PFRs. The parameters in the membrane-reactor material balances can be split into three arbitrary groups: design parameters (*Da* and *DaPe*), operational parameters (Y_I and Φ), and material parameters (κ and S_i). The Damköhler number can be changed, for example, by increasing or decreasing the reactor volume. The Damköhler–Peclet product (defined here as the ratio of the characteristic rate of reaction to the characteristic rate of permeation) can be varied by altering the membrane area per

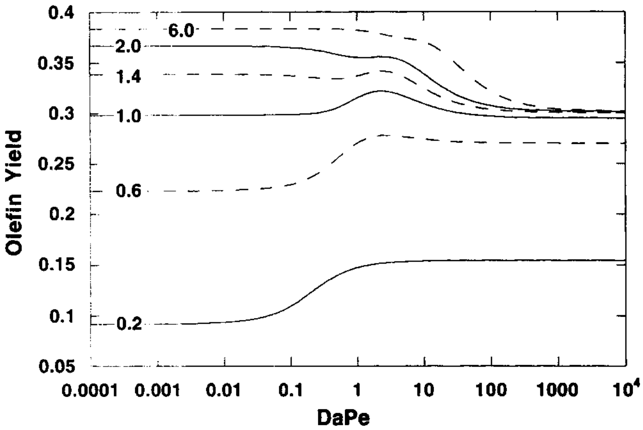

Figure 4. Olefin yield from the base-case membrane reactor with a porous membrane.

($Y_I = 1.0$, $S_{H_2} = 5.0$, $\Phi = 1.0$, and $\kappa = 0.1$) as a function of *DaPe* at several different Damköhler numbers.

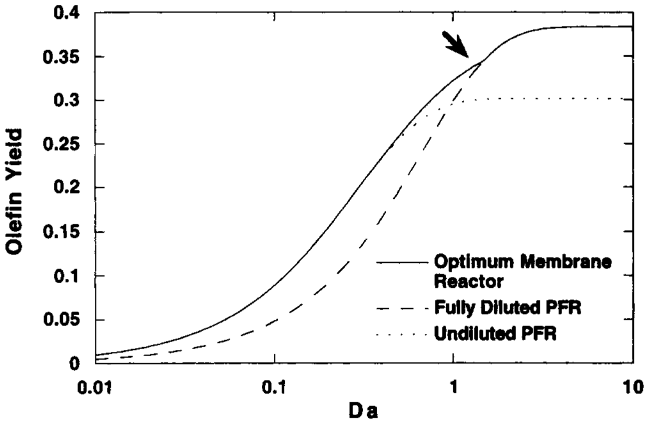

Figure 5. Olefin yield from a membrane reactor using optimum *DaPe* at each Damköhler number.

At low *Da* the optimum *DaPe* is infinite, equivalent to an undiluted PFR, and at high *Da* the optimum *DaPe* is zero, equivalent to a fully diluted PFR. The discontinuity indicated by the arrow corresponds to the point where the optimum abruptly shifts from an intermediate value to zero.

reactor volume (e.g., shell with multiple tubes). The material parameters are dictated by the reaction being run and the membrane being used (though they can be adjusted to some degree through selection of operating temperature and pressure). The approach used here is to select a set of material and operational parameters and hold them fixed. Then, at any given value of *Da*, there will be a value of *DaPe* that maximizes the olefin yield from the reactor.

In the most typical arrangement, the products are recovered from both the reaction side of the reactor and from the sweep side of the reactor. Figure 4 shows how the yield varies with *DaPe* at different values of *Da* when using a porous membrane. When *Da* is small (~ 0.2) the residence time is short, and the reaction is far from equilibrium. Under these circumstances reaction kinetics control performance. Permeation of inert diluent into the reactor reduces the rate and hence the yield. As a consequence the yield is maximized when *DaPe* is very large. In effect, a very large *DaPe* means virtually no permeation, and thus the reactor is just like a PFR. When *Da* is in an intermediate range (~ 0.6 to 1.4 for the base case shown in Figure 4), a maximum appears in the yield curves, and the corresponding *DaPe* is the optimum value. When *DaPe* is at this optimum value, the rate is high at the front of the reactor because dilution is minimal, and toward the end of the reactor the effect of the reverse reaction is mitigated by the diluent, which by then has permeated into the reaction side. Finally, when *Da* is large (> ~ 1.5 for the case shown) the maximum in the yield curve disappears. Here the residence time is sufficient to equilibrate even a fully diluted reactant stream. Under these circumstances the optimum *DaPe* is zero: permeation should be so fast that the two sides are always equal in composition. At this optimum the membrane reactor behaves like a fully diluted PFR.

In summary, when total recovery of products is employed, *DaPe* can be used to optimize membrane-reactor performance at a given Damköhler number. When *DaPe* is very large, the permeation term becomes negligible and the membrane reactor behaves just like a PFR. This is desirable when the Damköhler number places the reactor in a regime dominated by reaction kinetics. When *DaPe* is very small, permeation is so rapid that the composition is always equal on the two sides of the membrane, and the reactor behaves like a diluted PFR. This is desirable when the Damköhler number places the reactor in a regime dominated by thermodynamics. It is only at intermediate values of *DaPe* that selective removal of a product takes place, and this is desirable only when the Damköhler number places the reactor in a regime where both kinetics and thermodynamics affect performance. Figure 5 illustrates this behavior, showing the yield of olefin as a function of Damköhler number for a cocurrent membrane reactor using a porous membrane where *DaPe* has been optimized at each *Da*. The figure shows how the optimum membrane reactor is equal to either an undiluted PFR or a fully diluted PFR in the regimes of kinetic (low *Da*) and thermodynamic (high *Da*) control. For the optimized membrane reactor, the curve shows a discontinuity marked by an arrow. This corresponds to the point where the maximum at intermediate *DaPe* disappears (between $Da = 1.4$ and 2.0 in Figure 4) and the optimum cocurrent membrane reactor becomes a fully diluted PFR. This discontinuity is more pronounced in other examples given later.

It is interesting that this simple optimization of the cocurrent membrane reactor with respect to the Damköhler–Peclet product leads to the result that in many circumstances the best reactor is essentially a PFR (i.e., the optimum *DaPe* is very large, corresponding to an undiluted PFR, or it is very small, corresponding to a fully diluted PFR). However, this does not mean that everywhere else the membrane reactor is better. The membrane reactor can only approximate a fully diluted or an undiluted PFR as *DaPe* is varied. It has already been shown that in some cases the optimum PFR is one with intermediate dilution. For these reasons, it is still appropriate to attempt to define a means by which membrane reactors and PFRs can be equitably compared.

Comparing the Cocurrent Membrane Reactor to the PFR

In regimes where the optimized membrane reactor is not equivalent to a PFR it remains necessary to compare the two reactor types. Perhaps the best means of comparison would be to define a dehydrogenation process using a membrane reactor and then requiring the PFR to "plug into" the process directly. The yield from the process using each reactor type could then be compared. This is not entirely possible because the membrane reactor generates two product streams, whereas a single PFR generates only one. Instead, the following procedure has been used for generating an equitable basis of comparison between membrane reactors and PFRs. First, the cocurrent membrane-reactor process is defined by selecting a set of operational and material parameters (Y_I, Φ, κ, and S_i). Then the yield, as defined in Eq. 6, is calculated a a function of Damköhler number, using the optimum *DaPe* at each Damköhler number:

$$\psi = \frac{(\dot{n}_{\text{olefin}})_{\text{recovered}}}{(\dot{n}_P)^0}. \tag{6}$$

Next, the yield from a PFR process is calculated as a function of Damköhler number, subject to the following constraints: The reactor volume must be the same as the reaction-side volume of the membrane reactor. It must use the same amount of paraffin as the membrane reactor, and at an equal purity. Also the PFR must operate at the same temperature and pressure as the reaction side of the membrane reactor. These three requirements are met in the models by requiring *Da* for the PFR to equal *Da* for the membrane reactor. The PFR should use the optimum amount of inert as defined previously, as long as this amount is less than or equal to the amount used by the membrane reactor. If the optimum amount of inert is more than that used in the membrane reactor, the PFR may only use as much inert as the membrane reactor uses.

The olefin yield for the two optimized processes, calculated as a function of *Da*, can then be used to compare the performance of the two systems. If the olefin yield for the PFR system is greater than or equal to that of the membrane-reactor system, there is no advantage to using the membrane reactor system. Two important distinctions between this basis of comparison and those that have been typically employed in the past are that each of the reactors has been optimized before making the comparison, and that the system inputs (feed rates and reaction volumes) are equal. The yield ratio, defined by Eq. 7, can be used to construct a map of the design parameters (*Da* and *DaPe*) that indicates what combination of these parameters lead to enhanced performance:

$$\eta = \frac{\psi_{\text{membrane system}}}{\psi_{\text{plug-flow system}}}. \tag{7}$$

When the yield ratio equals unity, the reactors offer equivalent performance; values greater than unity represent situations where the membrane reactor performance is superior.

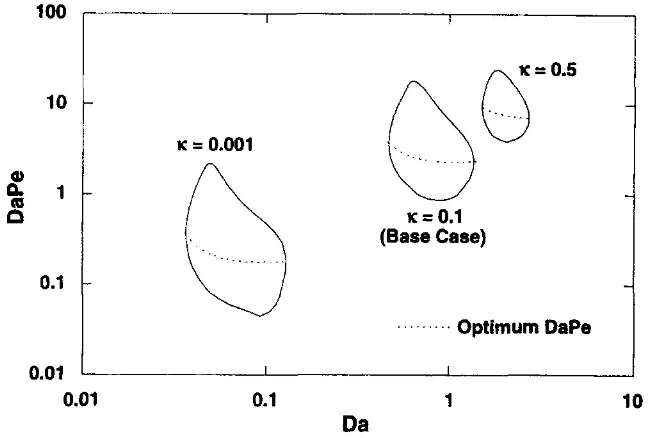

Figure 6. Inside closed curves the yield from the membrane-reactor process is at least 1% greater than that from the PFR.

The three closed curves correspond to the three dimensionless equilibrium constants indicated. The dashed line inside each closed curve identifies the point of maximum olefin yield.

Figures 6 through 8 present maps of design-parameter space that indicate the regimes where the yield ratio is greater than 1.01 (the membrane reactor yield is at least 1% greater than the optimized PFR yield) as the other parameters are varied from the base case. In each of these figures a dashed line indicates the locus of maximum olefin yield within the parameter space where the membrane reactor outperforms an optimized PFR. These dashed lines give the optimum *DaPe* value at each Damköhler number. The enclosed regions represent parameter space where the optimized cocurrent membrane reactor is not equivalent to a PFR, and consequently it is only within these regions that the two reactors need to be compared.

It is most instructive to compare an optimized membrane reactor (one operating on the dashed lines in Figures 6 through 8) to an optimized PFR. By simultaneously plotting yields for the membrane reactor and for the PFR as a function of *Da*, it is easy to see where (at what *Da* values) the membrane reactor outperforms the PFR, what the yields are in this region, and by how much the membrane reactor betters the PFR. Recall that the reactors being compared are

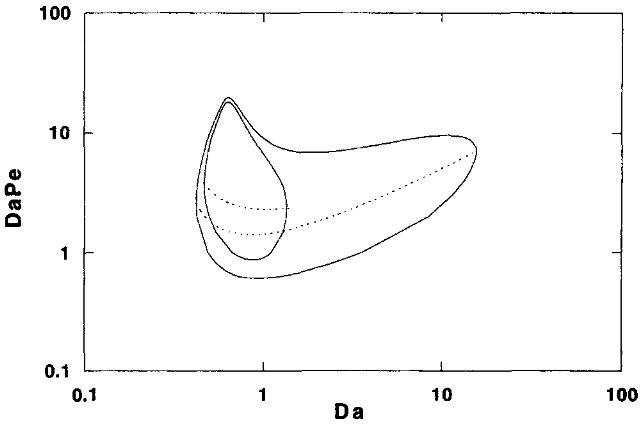

Figure 7. Inner closed curve showing the range of design-parameter space for the base case (with a porous membrane) where the yield ratio is greater than 1.01.

The outer curve shows the effect of increasing the dilution rate (Y_I) from 1 to 100; the dashed lines identify the maximum olefin yields.

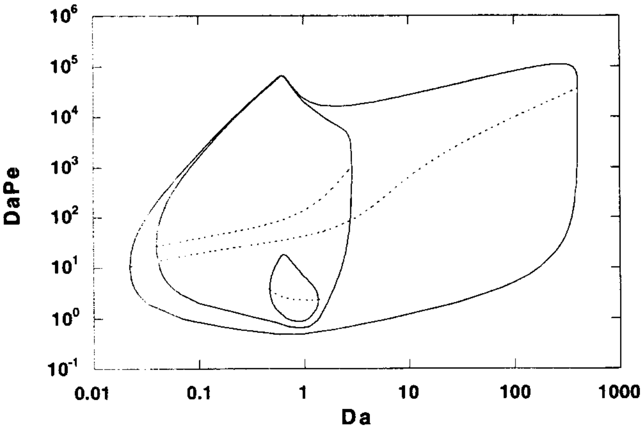

Figure 8. Innermost closed curve showing the range of design-parameter space for the base case (with a porous membrane) where the yield ratio is greater than 1.01.

The intermediate curve shows the effect of increasing the permselectivity of H_2, S_{H_2}, from 5 to 10,000; the outermost closed curve shows the effect of additionally increasing the dilution, Y_I, from 1 to 100.

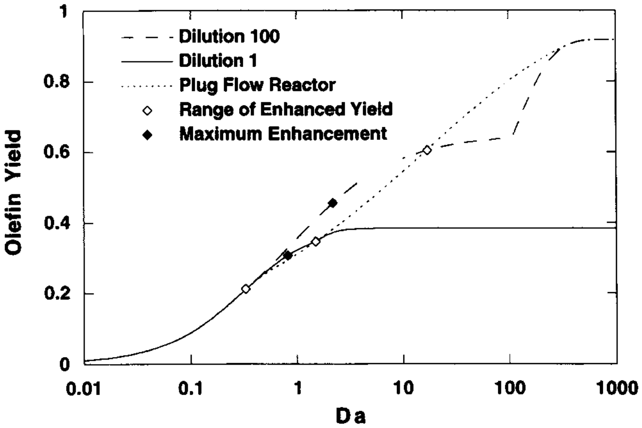

Figure 10. Olefin yields for optimized (porous) membrane and plug-flow reactors as a function of Damköhler number at two different dilutions.

The open diamonds bracket the interval over which the membrane-reactor yield is greater than the PFR yield; the solid diamonds indicate the point of maximum yield enhancement (4.23% @ $Y_I = 1.0$ (base case) and 19.36% @ $Y_I = 100.0$).

each optimized: the PFR uses the optimum dilution for that *Da* (subject to restriction already discussed), and the membrane reactor uses the optimum *DaPe* for that *Da*. Figure 9 presents such a comparison using parameters characteristic of a porous membrane for three different dimensionless equilibrium constants, including the base case of 0.1. As expected from Figures 5 and 6, there is only a small window (bounded by open diamonds in the figure) within which the membrane reactor yield is greater than that of the PFR. This window appears in a region where yield is still increasing sharply with increasing *Da*. The maximum enhancement in yield (indicated by a filled diamond) is at best ~ 7%. Furthermore, it is expected that a commercial process would be designed to operate close to the point where the yield curves plateau, not in the region where the yield is still increasing sharply with increasing *Da*. In short, for a system using a porous membrane, a membrane reactor offers little advantage over a PFR, and the regime where it offers that advantage is not a regime where a process would likely be designed to operate.

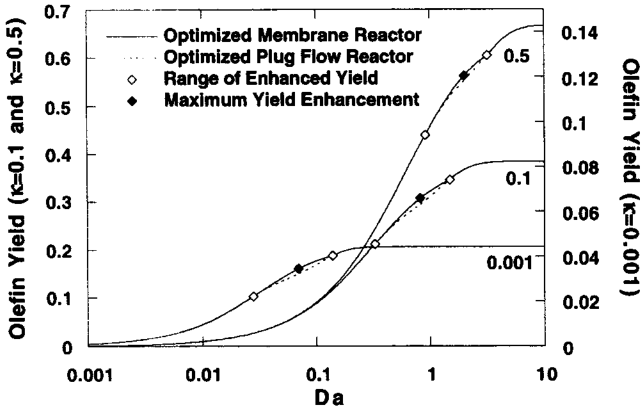

Figure 9. Olefin yields for optimized (porous) membrane and plug-flow reactors as a function of Damköhler number for three different dimensionless equilibrium constants.

The open diamonds bracket the interval over which the membrane-reactor yield is greater than the PFR yield; the solid diamonds indicate the point of maximum yield enhancement (1.84% @ $\kappa = 0.5$; 4.23% @ $\kappa = 0.1$ (base case); and 6.96% @ $\kappa = 0.001$).

It is often thought that increasing the flow rate of the inert improves membrane-reactor performance because it increases the driving force for permeation. Figure 7 shows that increasing the dilution rate does indeed open up a significant amount of parameter space, and the maximum enhancement in yield increases to almost 20%, but Figure 10 reveals that the window of enhanced yields appears at even lower yields compared to the plateau level. Figure 10 also highlights the advantage of using optimal dilution in the PFR as opposed to equal dilution: in the region $\sim 11 < Da < \sim 200$ the PFR yield is *superior* to the membrane reactor. This occurs only if the PFR is optimally diluted, if its dilution is increased to equal that of the membrane reactor, the PFR yield falls below that of the membrane reactor in this region. (The discontinuity in the optimum membrane-reactor yield curve was discussed previously.) Hence, increasing the flow of inert diluent does *not* make a porous membrane reactor any more attractive unless one desires to operate at conversions well below the plateau level.

Figure 11 shows that high permselectivity for hydrogen is critical if a membrane reactor is to be used to enhance yield. In that figure a permselectivity of 10,000 is used; this might correspond to a dense membrane with a few pinholes or other defects (as formulated here the model allows permeation of paraffin, olefin, and inert). When the permselectivity is very high, the optimized membrane reactor reaches the plateau yield at significantly smaller Damköhler numbers than the optimized PFR. In other words, the window of enhanced yield in this case extends into the region where a process would likely be designed to operate. If the sweep-gas flow rate is then increased, the enhancement is even more dramatic as

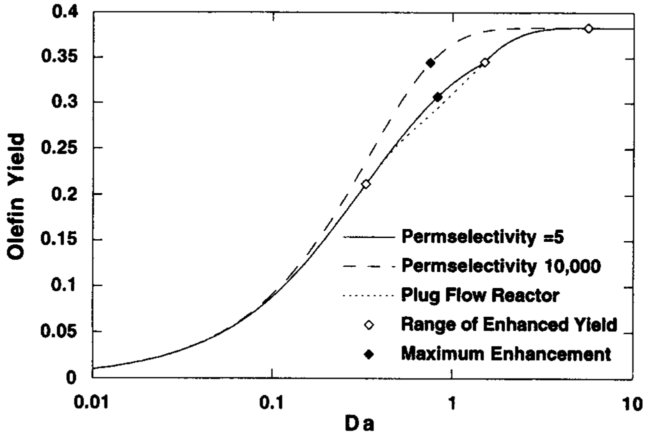

Figure 11. Olefin yields for optimized membrane and plug-flow reactors as a function of Damköhler number for two different hydrogen permselectivities.

The open diamonds bracket the interval over which the membrane-reactor yield is greater than the PFR yield; the solid diamonds indicate the point of maximum yield enhancement (4.23% @ $S_{H_2} = 5.0$ (base case) and 19.91% @ $S_{H_2} = 10{,}000$). (The lower limit of the range of enhanced yield for the high permselectivity case is less than 0.01.)

shown in Figure 12. It can be concluded that for significant yield enhancements the permselectivity for hydrogen must be very large (as is the case with dense membranes); the permselectivity of porous membranes is too small. Indeed, those reports in the literature where membrane reactors are compared to *diluted* PFRs and shown to offer an advantage in terms of reactor size, all involve high permselectivity membranes (Gokhale et al., 1995; Itoh, 1995). The present analysis defines the parameter space within which these advantages can be realized.

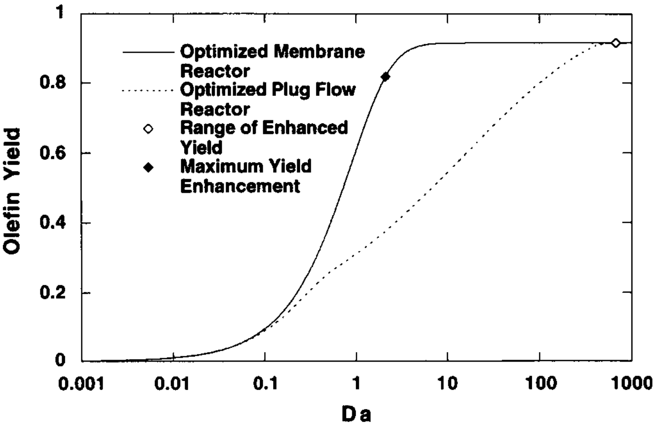

Figure 12. Olefin yields for optimized membrane and plug-flow reactors as a function of Damköhler number for a permselectivity of 10,000 and a dilution of 100.

The open diamonds bracket the interval over which the membrane-reactor yield is greater than the PFR yield; the solid diamonds indicate the point of maximum yield enhancement (116.8%). The lower limit of the range of enhanced yield is less than 0.001.

The present results are quite similar to the case of enhancing intermediate yield in consecutive reactions (Agarwalla and Lund, 1992; Bernstein and Lund, 1993). In that application *DaPe* must be optimized at a given *Da* or else reactant loss is too great (as it is here), and additionally the membrane must be very permselective for the removed product. Once these conditions are satisfied, the yield ratio (membrane reactor to PFR) can be increased substantially by using a high sweep-side dilution. It can be seen in Figure 12 that the latter effect applies in the present example as well. A 100-fold increase in dilution dramatically improves the yield ratio for a highly permselective membrane, but a similar increase does not help if the other parameters (*DaPe* and permselectivity) are not optimal (cf. Figure 10).

General Discussion

The procedure used here to compare membrane reactors and PFRs on an equitable basis should be easily extensible to any specific reaction and reactor geometry. For a specific reaction a more exact analysis can be performed by using experimentally determined permeation and kinetic relations. The form of the kinetic relationship will affect some aspects of membrane reactor performance (Raich and Foley, 1995). It is also possible to operate the membrane reactor with an applied pressure differential across the membrane; this mode of operation has also been evaluated using the procedure developed here (Reo et al., 1997).

In this work, the membrane reactor has been forced to use a single value of *DaPe* that applies throughout the reactor and optimizes process yield. In fact, the membrane reactor could be more highly optimized if *DaPe* were not a global constant, but instead was allowed to vary along the length of the reactor. This would involve altering the membrane area per unit reactor volume or else using membranes where the permeability (but not the permselectivity) varied along the reactor length. The practicality of such an optimization is questionable, but a limited variability might be interesting to consider. For example, if *DaPe* were allowed to assume one of two values, one of which was effectively infinite (like a PFR), an optimization would indicate the best PFR reactor volume and the best *DaPe* for the membrane section of a so-called hybrid reactor (membrane reactor in series with a PFR).

Finally, the approach used here has assumed that *DaPe* is a design parameter that can be adjusted to any desired value. The most straightforward way to vary *DaPe* without simultaneously changing *Da* is to alter the membrane area while holding the reactor volume constant. Going to high values of *DaPe* is relatively easy, it simply requires using a small membrane area. Practically this could be accomplished by putting the catalyst in the annular space and using a single, small-diameter membrane tube. In decreasing *DaPe* (increasing the membrane area per reactor volume) it is possible to use multiple tubes and perhaps even a spiral wound kind of system, but geometric considerations will eventually impose a lower limit on the practical range of *DaPe*. It is important to note (Figures 6 to 8) that the optimum *DaPe* values are all greater than 0.1. A *DaPe* value in this range is practically attainable (Agarwalla and Lund, 1992), but when the approach used here is applied to a particular reaction/membrane system, the practical lower limit on *DaPe* should be estimated and enforced.

Conclusions

The optimization of a membrane reactor with respect to the design parameter *DaPe* reveals conditions where the optimum membrane reactor is either an undiluted (*DaPe* is effectively infinite) or fully diluted (*DaPe* is effectively zero) PFR. At these conditions the membrane reactor offers no advantage over a PFR. At conditions where the optimum *DaPe* is not one of these extremes, a PFR with an intermediate dilution may still outperform the membrane reactor, making it important to compare the two reactors equitably. An optimized membrane reactor and an optimized PFR were so compared for a generic dehydrogenation reaction using membrane reactors with negligible pressure differential across the membrane. This mode of operation is often applied when the membranes are porous because high-pressure differentials lead to excessive reactant loss through the membrane. The analysis shows that for porous membranes very modest gains in yield (or equivalently reactor size) are realized and furthermore, these gains occur in a regime where a commercial process is not likely to operate. In short, it may be concluded that for a membrane-reactor process where the primary function of the membrane is selective removal of a product from the reaction environment, porous membranes simply are not permselective enough. Porous membranes may still be very useful in membrane reactors provided their primary function is not selective product removal. For example, they can be used to distribute reactant along the length of the reactor or to establish a reaction front between the two sides of the reactor.

The present analysis shows that very large increases in yield can be realized via equilibrium shifting of dehydrogenation, but only when highly permselective membranes are employed. In addition the large yield increases for dense membranes occur at conditions where a commercial process could be expected to operate. Of course, for dense membrane systems it is also possible to operate with a significant applied pressure differential. It appears that the biggest obstacle to the use of dense membranes for these reactions lies in the development of materials with adequate permeability, durability, and stability. The kinetic and permeation relationships used for the generic dehydrogenation have been used successfully for modeling real laboratory membrane-reactor systems, so the conclusions based on the generic modeling are expected to apply generally. The formalism used here can be applied using different kinetic and/or permeation relationships pertinent to a particular reaction for a more rigorous evaluation of membrane-reactor efficacy, and it can be extended to systems that use an applied pressure differential

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Notation

Dimensional quantities

D = inside diameter of the reaction side of the reactor
$\mathfrak{D}_i$ = effective diffusivity of species i in the membrane
K = equilibrium constant for reaction 1 in pressure units
k = forward rate coefficient for reaction 1 in units of mol (time)$^{-1}$ (reactor volume)$^{-1}$ (pressure)$^{-1}$
L = total axial length of the reactor
$(\dot{n}_i)_j$ = molar flow rate of species i (P, O, H_2, or I) on side j (*rxn* denoting reaction, or *swp* denoting sweep) of the reactor; a superscript 0 denotes the value at the reactor inlet; subscript i = tot denotes the total molar flow rate; subscript j is not used when describing a PFR
P_j = pressure on side j (*rxn* denoting reaction, or *swp* denoting sweep) of the reactor
R = ideal gas constant
T = absolute temperature
t = membrane thickness
z = axial distance from the reactor inlet

Dimensionless quantities

Da = Damköhler number: $(\pi D^2 L k P_{r\times n})/[4(\dot{n}_p)^0]$
$DaPe$ = Damköhler-Peclet product: $(-kD^2RT)\{\ln[D/(D+2t)]\}/(8\,\mathfrak{D}_p)$
$(F_i)_j$ = dimensionless flow rate of species i on side j of the reactor: $(\dot{n}_i)_j/(\dot{n}_P)^0$
S_i = permselectivity of species i: $\mathfrak{D}_i/\mathfrak{D}_P$
$(Y_i)_j$ = feed ratio of species i (P, O, H_2, or I) on side j (*rxn* denoting reaction, or *swp* denoting sweep) of the reactor $(\dot{n}_i)_{swp}/(\dot{n}_p)^0_{rxn}$
Y_i = feed ratio of inert diluent fed to the process: $(\dot{n}_I)_{swp}/(\dot{n}_P)^0_{rxn}$
Z = dimensionless axial distance from the reactor inlet: z/L
ϕ = pressure ratio: $P_{r\times n}/P_{swp}$
ν_i = stoichiometric coefficient of species i in reaction 1 ($\nu_P = -1$; $\nu_O = 1$; $\nu_{H_2} = 1$; ;$\nu_I = 0$)

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