MAXIMUM CONVERSION OF DEHYDROGENATION IN PALLADIUM MEMBRANE REACTORS

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Introduction

Recent experiments with a cocurrent palladium-membrane reactor[1] have shown that this type of reactor equipped with a membrane permeable only to hydrogen can provide very high dehydrogenation performance, even in a single stage. Furthermore, computer simulation[2] has made clear that the countercurrent reactor is superior to the cocurrent one in terms of higher conversion with shorter reactor length. The next important point is to find the limitation of reactor performance for such reactors. Namely, there remains some doubt whether the palladium-membrane reactor really makes it possible to achieve a conversion of dehydrogenation exceeding its thermodynamic limit, which is the most significant feature of the membrane reactor.

The objective of this study is to compare the maximum conversions in two flow models—cocurrent and countercurrent—for the palladium-membrane reactor with that in a conventional catalytic reactor, whose maximum conversion is determined thermodynamically.

1. Maximum Conversion and Hydrogen-Concentration Profiles

Taking dehydrogenation of cyclohexane as a model reaction, the simultaneous ordinary differential equations developed in the previous paper[2] to simulate both conversion and hydrogen-concentration profiles in the two reactor models were numerically solved by the Runge-Kutta-Gill method.

Figure 1 shows the conversion and hydrogen-concentration profiles along the length of the cocurrent reactor when the hydrogen permeation rate

is large enough to attain a state of dynamic equilibrium, where the hydrogen-concentrations on both sides become identical. Two cases are shown: the one where that equilibrium is reached near the outlet of the reactor, and the other, with a larger value of Tu than the former, where equilibrium is reached near the middle. In the case of the cocurrent reactor, it is found from Fig. 1 that such a limiting situation is attained when the concentration (partial pressure) of hydrogen permeated to the separation-side stream is the same as that remaining in the reaction-side stream. However, the final conversions obtained for the two cases are the same although the increasing rate of conversion curve in the case using larger Tu is clearly larger. In short, when such a dynamic equilibrium is attained the net reaction can no longer proceed.
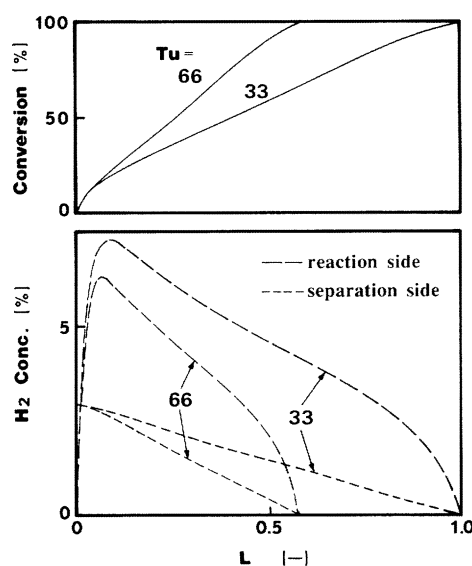

Fig. 1. Conversion and hydrogen-concentration profiles for a cocurrent reactor using sweep gas ($Da = 50$, $U_I^0 = 4$, $V_I^0 = 100$, 473 K)

On the other hand, the countercurrent reactor can achieve perfect conversion without being limited by such a dynamic equilibrium with regard to hydrogen concentration (partial pressure), as seen in **Fig. 2**. This is because complete separation of all the hydrogen produced by dehydrogenation from the reaction-side stream is possible in this reactor.

2. Maximum Conversion

2.1 Cocurrent reactor

In the previous section, it was shown that when $\pi_{Hr} = \pi_{Hs}$, no further reaction can proceed and accordingly the corresponding conversion also reaches a limit. The maximum conversion, X_l, is given by the following relation (**Appendix**).

$$K_P = P_r^m \frac{m^m X_l^{m+1}}{(1 - X_l)(1 + U_I^0 + V_I^0 + m X_l)^m} \quad (1)$$

This equation means that X_l increases as much as the dilution ratio becomes large by V_I^0 compared with the equilibrium conversion when U_I^0 is used as the dilution ratio. In other words, the maximum achievable conversion in a conventional catalytic reactor when the dilution ratio is taken as $U_I^0 + V_I^0$ is identical with that in the cocurrent membrane reactor. From the standpoint of shifting the reaction equilibrium, therefore, the countercurrent reactor should be employed although the cocurrent reactor still has another profitable feature, which is to make the reaction proceed faster by removing the hydrogen, from the reaction field than it would proceed without hydrogen removal.

2.2 Countercurrent reactor

In this case, it is clear that there is no limit to the rise in conversion; that is, 100% conversion is attainable, as seen in Fig. 2. Let us follow the change of hydrogen concentration along the reactor length from the inlet of the reaction side, using the curve with $Tu = 66$ in Fig. 2 as an example. As the dehydrogenation proceeds, part of the hydrogen produced passes to the separation side through the membrane, where the driving force is a concentration (or pressure) difference of hydrogen between the reaction and separation sides. Although the concentrations of hydrogen in both the reaction- and separation-side streams decrease along the reactor length, it is obvious that the former is always larger than the latter. Since this is true even if their concentrations become extremely small, hydrogen permeation will continue as long as hydrogen is present in the reaction-side stream. Thus the complete removal of hydrogen and the resulting 100% conversion become possible if only Da, Tu and V_I^0 are large enough. **Figure 3** shows the minimum conditions necessary for obtaining 100% conversion. This figure
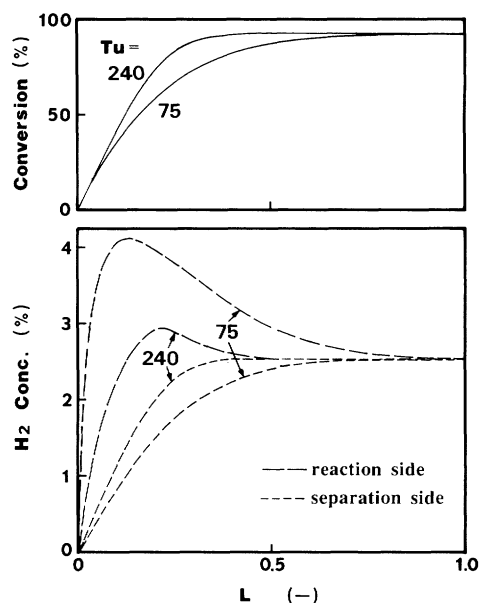

Fig. 2. Conversion and hydrogen-concentration profiles for a countercurrent reactor using sweep gas ($Da = 50$, $U_I^0 = 4$, $V_I^0 = 100$, 473 K)
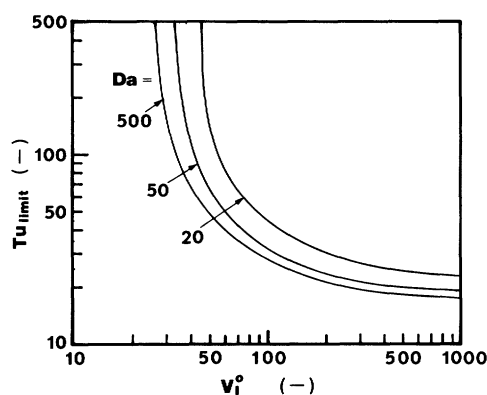

Fig. 3. Conditions for obtaining 100% conversion in a countercurrent reactor ($U_I^0 = 4$, 473 K)

suggests that when $V_I^0 = 60$ and $Da = 50$, for example, Tu must be more than 50 so as to achieve 100% conversion.

Conclusion

Cocurrent and countercurrent models for a palladium-membrane reactor were taken to compare their maximum conversions for dehydrogenation with that in a conventional catalytic reactor, i.e., the thermodynamic equilibrium conversion.

The maximum conversion of the cocurrent reactor was found to be the same as that determined thermodynamically. The countercurrent reactor realized perfect conversion.

Appendix

On the reaction side, since the dehydrogenation reaction is at a state of equilibrium, the following relation holds.

$$K_P = P_r^m \frac{X_t(mX_{Hr})^m}{(1-X_t)(1+U_I^0+mX_{Hr})^m} \qquad \text{(A-1)}$$

where X_t is maximum conversion, and X_{Hr} is a kind of conversion calculated from the amount of hydrogen present in the reaction-side stream. As a matter of course, X_t is related to H_{Hs} and X_{Hr} as follows.

$$X_t = X_{Hr} + X_{Hs} \qquad \text{(A-2)}$$

The relation $\pi_{Hr} = \pi_{Hs}$ can be rewritten as follows.

$$P_r \frac{mX_{Hr}}{1+U_I^0+mX_{Hr}} = P_s \frac{mX_{Hs}}{V_I^0+mX_{Hs}} \qquad \text{(A-3)}$$

X_t will be obtained by solving Eqs. (A-1), (A-2) and (A-3) simultaneously. In the present case, since $P_r = P_s$, X_t is given by

$$K_P = P_r^m \frac{m^m X_t^{m+1}}{(1-X_t)(1+U_I^0+V_I^0+mX_t)^m} \qquad \text{(A-4)}$$

Nomenclature

A	= membrane area	[m^2]
C_0	= concentration of hydrogen dissolved in palladium membrane	[mol·$^{-3}$]
D	= diffusion coefficient of hydrogen through palladium membrane	[m^2·s^{-2}]
Da	= Damkohler number, $k_r v_r^e P_r / u_C^0$	[—]
k_r	= rate constant	[mol·m^{-3}·s^{-1}·Pa^{-1}]
K_P	= equilibrium constant for dehydrogenation	[Pa^3]
L	= dimensionless reactor length	[—]
m	= stoichiometric number	[—]
p_i	= partial pressure of gas i	[Pa]

P_r	= total pressure on reaction side	[Pa]
P_s	= total pressure on separation side	[Pa]
P_0	= reference pressure, 1.01325×10^5	[Pa]
t_m	= thickness of membrane	[m]
Tu	= dimensionless number representing the ratio of hydrogen permeation rate to feed rate, $DC_0A/(t_m u_C^0)$	[—]
u_C^0	= flow rate of reactant at reaction-side inlet	[mol·s^{-1}]
u_I^0	= flow rate of inert gas in reaction-side stream	[mol·s^{-1}]
U_I^0	= dimensionless flow rate of inert gas in reaction-side stream, u_I^0/u_C^0	[—]
v_I^0	= flow rate of inert gas in separation-side stream	[mol·s^{-1}]
V_I^0	= dimensionless flow rate of inert gas in separation-side stream, v_I^0/u_C^0	[—]
v_r^e	= reaction-side volume	[m^3]
X_e	= thermodynamic equilibrium conversion	[—]
X_{Hr}, X_{Hs}	= conversion estimated from hydrogen balance on reaction and separation sides, respectively	[—]
X_t	= maximum conversion	[—]
π_{Hr}, π_{Hs}	= dimensionless pressure, p_{Hr}/P_0, p_{Hs}/P_0	[—]

Literature Cited

1) Itoh, N.: *AIChE J.*, **33**, 1576 (1987).
2) Itoh, N., Y. Shindo and K. Haraya: *J. Chem. Eng. Japan*, **23**, 420 (1990).