Catalytic Dehydrogenation of Ethylbenzene to Styrene in Membrane Reactors

Babiker K. Abdalla
Petroleum Engineering Dept., King Saud University, Riyadh 11421, Saudi Arabia

Said S. E. H. Elnashaie
Chemical Reaction Engineering Group (CREG), Chemical Engineering Dept.,
King Saud University, Riyadh 11421, Saudi Arabia

Accurate simulation of fixed-bed catalytic reactors requires the computation of the effectiveness factors at each point along the length of the reactor. This requires the formulation and solution of rigorous diffusion-reaction models for the porous pellets based on the more rigorous Stefan-Maxwell equation for multicomponent diffusion rather than the approximate Fick's law formulation (Elnashaie and Abashar, 1993). The conversion attainable from some dehydrogenation reactions is sometimes limited by the thermodynamic equilibrium. An attractive technique for breaking this limitation is through the use of selective membranes in order to remove at least one of the products from the reaction mixture (Itoh, 1987; Perrin and Stern, 1985; Itoh et al., 1985, 1988; Wu and Liu, 1992; Ziaka et al., 1993; Wu et al., 1990; Tiscareno-Lechuga et al., 1993; Becker et al., 1993).

In this investigation a reliable rigorous heterogeneous model is used to study the effect of using thin films of selective membranes over porous support materials for the removal of hydrogen on the conversion of ethylbenzene and yields of styrene, benzene and toluene (Itoh and Govind, 1989; Nagamoto and Inoue, 1985; Ziaka et al., 1993). Palladium membranes, which are known to permeate hydrogen gas only, are selected for this purpose (Itoh and Govind, 1989; Nagamoto and Inoue, 1985; Shu, et al., 1993). The investigation covers the effect of sweep gas molar flow rate. Figure 1 shows the reactor with the jacket for the removal of hydrogen used in this investigation. The performance of the heterogeneous reactor with selective membranes using the kinetic parameters obtained from a laboratory reactor using in-house prepared catalyst (Abdalla et al., 1993) was also investigated. The extra revenues gained from the use of these configurations are estimated.

Rate Expressions

The reactions taking place during the dehydrogenation of ethylbenzene to styrene on iron-promoted catalysts are (Sheel and Crowe, 1969; Crowe, 1989):

Main Reaction

$$C_6H_5CH_2CH_3 \leftrightarrow C_6H_5CHCH_2 + H_2 \quad (1)$$

$$r_1 = k_1(P_{EB} - P_{ST}P_{H_2}/K_{EB}) \quad (2)$$

$$K_{EB} = \mathrm{Exp}(-\Delta F^\circ/RT) \quad (3)$$

$$\Delta F^\circ = a + bT + cT^2 \quad (4)$$

Side Reactions

$$C_6H_5CH_2CH_3 \rightarrow C_6H_6 + C_2H_4 \quad (5)$$

$$r_2 = k_2P_{EB} \quad (6)$$

$$C_6H_5CH_2CH_3 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \quad (7)$$

$$r_3 = k_3P_{EB}P_{H_2} \quad (8)$$

$$2H_2O + C_2H_4 \rightarrow 2CO + 4H_2 \quad (9)$$

$$r_4 = k_4P_{H_2O}P_{ETH}^{0.5} \quad (10)$$

$$H_2O + CH_4 \rightarrow CO + 3H_2 \quad (11)$$

$$r_5 = k_5P_{H_2O}P_{MET} \quad (12)$$

$$H_2O + CO \rightarrow CO_2 + H_2 \quad (13)$$

$$r_6 = k_6(P_T/T^3)P_{H_2O}P_{CO} \quad (14)$$

Correspondence concerning this article should be addressed to S. E. H. Elnashaie.

B. K. Abdalla is presently at the School of Chemical Engineering, University of Science Malaysia, Perak, Malaysia.

The intrinsic kinetic parameters for these reactions to be used in a rigorous heterogeneous model are given by Elnashaie et al. (1993) and Abdalla et al. (1993) for the industrial catalyst and the in-house prepared catalysts. The characteristics of the industrial reactor, catalyst properties, and feed conditions are given in Table 1.

Heterogeneous Model Equations

The catalyst packing the reactor is composed of an iron oxide (Fe_2O_3) promoted with potassium carbonate (K_2CO_3) and chromium oxide (Cr_2O_3). The catalyst particles are extrudates of cylindrical shape. Since at steady state the problem of simultaneous diffusion and reaction are independent of particle shape, an equivalent slab geometry was used for the catalyst pellet with a characteristic length giving surface-to-volume ratio of the slab equal to that of the original shape (Aris, 1957).

The intrapellet mass balance equations are expressed as follows:

$$\frac{dN_i}{dz}=\rho_c R_i \tag{15}$$

where R_i is the net rate of production of component i.

The Stefan-Maxwell equations for multicomponent diffusion (Mason et al., 1967) are given by:

$$-\frac{dC_i}{dz}=\frac{N_i}{D_{K_{e_i}}}+\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{y_iN_j-y_jN_i}{D_{e_{i,j}}} \tag{16}$$

where the effective diffusivities are computed as shown by Abdalla (1993).

Boundary conditions are:

$$\text{at } z=0,\ N_i=0 \text{ and at } z=z_p,\ C_i(z_p)=C_{i_s} \tag{17}$$

where the external mass-and heat-transfer resistances for the catalyst pellet are negligible because of the high gas flow rate in the industrial reactor. Froment and Bischoff (1979) stated that in industrial fixed-bed reactors the flow velocity is generally so high that the temperature and concentration drop over the film surrounding the particle is small at least at steady state. They also gave two examples for a TVA ammonia-synthesis converter and a methanol converter and have shown that even for these fast highly exothermic reactions the external mass-and heat-transfer resistances are negligible. In the present case the rate of the reaction is moderate and the reaction is mildly endothermic and therefore the assumption of negligible external mass- and heat-transfer resistances is strongly justified. The thermal conductivity of this metal oxide catalyst is quite high justifying neglecting internal heat-transfer resistances. Sherwood and Nusselt numbers were also computed to confirm the above widely used assumptions.

The effectiveness factors are computed using the following well-known relations:

Reaction Effectiveness Factors:

$$\eta_j=\frac{1}{z_p r_j^s}\int_0^{z_p} r_j\, dz \tag{18a}$$

The component effectiveness factors are similarly given by the following relations:

$$\eta_j=\frac{1}{z_p R_j^s}\int_0^{z_p} R_j\, dz \tag{18b}$$

The global orthogonal collocation technique (Villadsen and Michelsen, 1987; Villadsen and Stewart, 1967) was used for approximating the derivative and the integrals of the above equations (Eqs. 15, 16, and 18a, b).

Six mass balance differential equations for the six reactions in the bulk gas phase of the reactor are formulated, as well as energy balance and pressure drop equations. Mass balance differential equations for the bulk gas phase are given by:

$$dX_i/dl=\eta_i\rho_c A_B r_i/F_{\mathrm{EB}_F} \tag{19}$$

and

$$dX_j/dl=\eta_j\rho_c A_B r_j/F_{\mathrm{H_2O}_F} \tag{20}$$

where i is for reactions 1, 2 and 3, and X_i is the fractional

Table 1. Industrial Reactor Specification, Catalyst Properties and Feed Conditions

	Symbol	Value	Dimension
Reactor Diameter	D_R	1.95	m
Catalyst Bed Depth	L_B	1.70	m
Catalyst Density	ρ_c	2,146.27	kg/m^3
Catalyst Diameter	D_p	4.7	mm
Catalyst Pore Radius	r_p	2,400	A°
Catalyst Porosity	ϵ	0.35	
Catalyst Tortuosity*	τ	4.0	
Inlet Pressure	P_T	2.4	bar
Inlet Temperature	T	922.59**	K
Inlet Gas molar flow rates			
Ethylbenzene	EB	36.87	kmol EB/h
Styrene	ST	0.67	kmol ST/h
Benzene	BZ	0.11	kmol BZ/h
Toluene	TOL	0.88	kmol TOL/h
Steam	H_2O	453.10	kmol H_2O/h
Total molar feed	TMF	491.63	kmol/h
Total mass flow	TMFR	12,238.79	kg/h

*Calculated using the equation of Carniglia (1986).

**Corrected by Crowe (1989).

conversion of ethylbenzene in each of these reactions; while j is for reactions 4, 5 and 6 and X_j is the fractional conversion of the steam in each of these reactions.

The axial dispersion is negligible because of the high depth of the industrial bed compared with the catalyst particle size, and the high gas-flow rate employed. The value of L_B/D_p in this case is 365 which is much greater than the value of 150 suggested by Carberry (1976) and therefore neglecting axial dispersion of mass and heat is strongly justified (Carberry, 1976; Hill, 1977).

The Ergun equation is used for the pressure drop in the packed bed (Bird et al., 1960):

$$dP/dl = -1.\times 10^{-5}\,\frac{(1-\epsilon)G_o}{D_p\epsilon^3\rho_G g_c}\left[\frac{150(1-\epsilon)\mu_G}{D_p}+1.75G_o\right] \qquad (21)$$

The energy balance differential equation is given by:

$$dT/dl = \sum_{j=1}^{6}(-\Delta H_j)\eta_j r_j \rho_c A_B \Big/ \sum_{i=1}^{10} F_i Cp_i \qquad (22)$$

The permeation rate of hydrogen gas through the palladium membrane Q_{H_2} is assumed to obey the half power pressure law (Bohmholdt and Wicke, 1967):

$$dQ_{H_2}/dl = \alpha_{H_2}\left(\sqrt{\frac{p_{H_2}}{p_o}}-\sqrt{\frac{p'_{H_2}}{p_o}}\right) \qquad (23)$$

where α_{H2} is the permeation rate constant of hydrogen given by:

$$\alpha_{H_2} = \frac{2\pi}{\ln(\Gamma_o/\Gamma_i)}\,DC_o \qquad (24)$$

$$D = 8.28\times 10^{-4}\exp(-21{,}700/RT) \qquad (25)$$

$$c_o = 302.97T^{-1.0358} \qquad (26)$$

and D is Fick's diffusion coefficient of hydrogen dissolved in palladium. Thin films of palladium membranes over porous support materials are used in this investigation, however, other membranes can be used in practical applications to avoid the disadvantages of pure palladium tubes (Tsotsis et al., 1989).

Solution of the Model Equations

Subroutine ZSPOW (IMSL Math/PC-Library) (More et al., 1980) for solving nonlinear algebraic equations was used for solving the algebraic equations resulting from applying the method of orthogonal collocations to the two-point boundary value differential equations of the catalyst pellet. The solution of the pellet equations provides the effectiveness factors of the reactions. The reactor model differential equations (Eqs. 19-22) and hydrogen permeation equation (Eq. 23) are integrated using subroutine DGEAR (IMSL Math/PC-Library) (Hindmarsh, 1974).

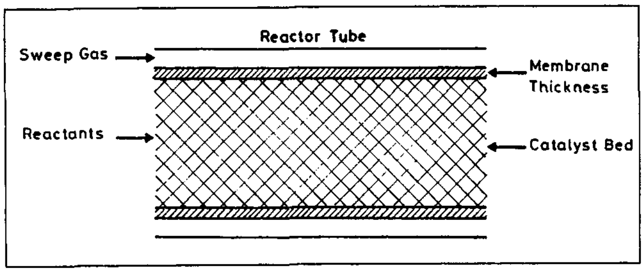

Figure 1. Reactor with the jacket for the removal of hydrogen.

Results and Discussion

The effect of permeable membranes is investigated using the rigorous heterogeneous model with the industrial catalyst and the three in-house prepared catalysts for the configuration shown in Figure 1, where the wall of the catalyst bed is the permeable membrane with 5×10^{-4} mm thickness deposited over a porous support material such as ceramic or vycor glass; and the clearance for the sweep gas flow is equal to 50.0 mm.

In all cases the permeation gas flows co-current to the reacting gas, having the same inlet temperature. Figure 2 shows the effect of sweep gas flow rate on the ethylbenzene conversion (X_{EB}) and the styrene yield (Y_{ST}) for the industrial reactor using the four catalysts. It is clear that considerable increase of X_{EB} and Y_{ST} is achieved for the reactor with selective membrane for the four catalysts used. This improvement in performance increases considerably with the increase in sweep gas flow rate. For high enough flow rate of the sweep gas X_{EB} approaches 52.76, 51.3, 57.2 and 61.8% for the industrial catalyst and catalyst A, B, and C respectively compared with 47.45, 46.6, 52.3 and 51.3% for the reactor without membrane. This represents improvements of 11.19, 10.3, 9.37 and 20.47% in X_{EB} for the industrial catalyst and catalysts A, B and C, respectively. While Y_{ST} approaches 48.2, 39.7, 35.6 and 57.1% for the industrial catalyst and catalysts A, B and C, respectively compared with 40.17, 33.1, 28.4 and 44% for the reactor without membrane. This represents improvements of 19.99, 19.94, 25.0, 35 and 29.78% in Y_{ST} for the industrial catalyst and catalysts A, B and C, respectively. It is also interesting to notice that the difference between X_{EB} and Y_{ST} for the reactor with selective membrane is smaller than that between X_{EB} and Y_{ST} for the reactor without membrane. This means that the selective membrane does not only increase the X_{EB} and Y_{ST} but it also increases selectivity to styrene. This is more profound when the industrial catalyst and catalyst C are used.

The improvements achieved by the use of the palladium membranes are obviously quite considerable. The increase in X_{EB} is clearly due to the suppression of the reversible step in reaction 1, while the improvement in Y_{ST} is mainly due to the suppression of the hydrodealkylation reaction for the production of the toluene (reaction 3, Eq. 7).

Revenues Gain

The use of thin selective membranes improves the yield and selectivity to the styrene produced. These improvements range between 20.0% and 30.0% over the nonmembrane reactor for the cases presented in Figure 2.

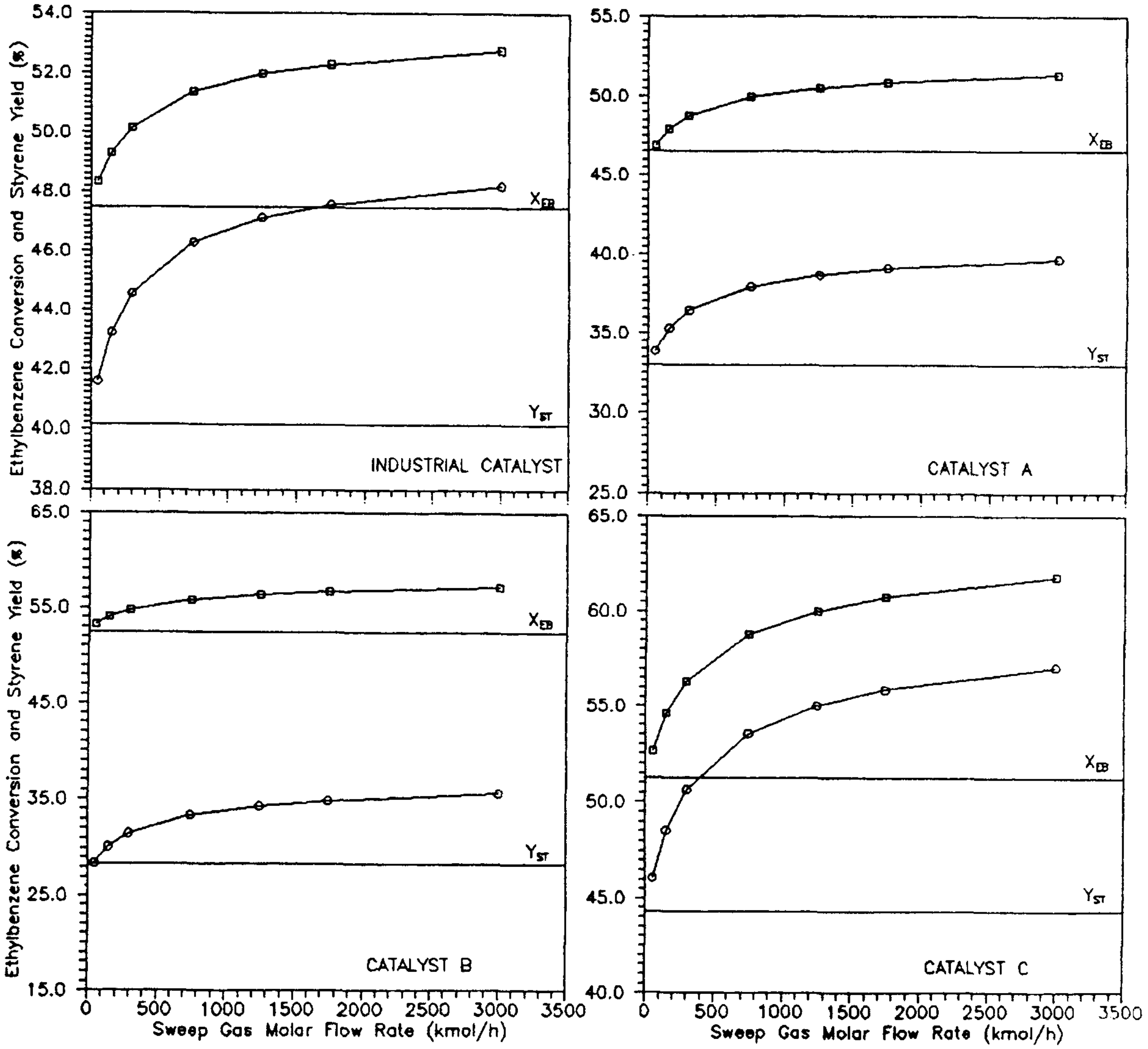

Figure 2. Ethylbenzene conversion and styrene yield at different sweep gas molar flow rates for the industrial catalyst and catalysts A, B, and C.

Membrane side pressure = 1.013 bar, X_{EB}, Y_{ST} = no membrane reactor: conversion of ethylbenzene and yield of styrene respectively.

On the basis of assuming 330 working days a year and the value of $600.00 for a metric ton of styrene (Chemical Marketing Report, 1992), 1% improvement in the styrene production corresponds to a dollar value of about $\$3.762 \times 10^5$ per year for Polymer Corporation, Sarnia, Ontario, Canada (production rate of 190 MTPD) and $\$1.683 \times 10^6$ per year for the Saudi Petrochemical Company (SADAF) of the Saudi Basic Industries Corporation (SABIC), Saudi Arabia (production rate of 850 MTPD). This means that the lowest improvement obtained which is 19.94% will correspond to: 7.5×10^6 \$/year for Polymer Corp., and 33.56×10^6 \$/year for SADAF, SABIC, Saudi Arabia.

Conclusions

The rigorous heterogeneous model developed earlier for the industrial fixed-bed catalytic reactor for the production of styrene from ethylbenzene (Elnashaie et al., 1993) was used to investigate the effect of selective membranes for the removal of hydrogen on the performance of the system.

The magnitude of the increases in ethylbenzene conversion as well as styrene yield and selectivity, which can be achieved using such membrane reactors are quite appreciable.

Notation

A_B = catalyst bed cross-sectional area, m^2

C_o, C_i, C_{i_s} = molar concentrations of H_2 in palladium membrane, of component i and of component i at the catalyst surface (kmol·m^{-3})

C_{p_i} = specific heat capacity of component i, (kJ·kmol^{-1}·K)

D, $D_{e_{i,j}}$, $D_{K_{e_i}}$ = diffusion coefficient of hydrogen through palladium membrane, effective molecular binary diffusivity of components i in j and Knudsen diffusivity of component i, (m^2·h^{-1})

D_p, F_i, G_o = catalyst particle diameter (m), molar flow rate of component i (kmol·h^{-1}) and mass velocity of gas mixture (kg·m^2·h^{-1})

g_c, ΔH_i, K_{EB} = gravitational acceleration (m^2·h^{-1}), reaction enthalpy (kJ·kmol^{-1}), ethylbenzene equilibrium constant (bar)

k_i, L_B, N_i = rate constant of reaction i ($\mathrm{kmol \cdot K^m / kg \cdot h \cdot bar^n}$) (for k_1 and k_2; $m=0$, $n=1$, for k_3 and k_5; $m=0$, $n=2$, for k_4; $m=0$, $n=1.5$, for k_6; $m=3$, $n=3$), catalyst bed length (m), molar flux of component i ($\mathrm{kmol \cdot m^{-2} \cdot h^{-1}}$)

p_i, p_o, p'_{H_2}, P_T = partial pressure of component i, standard pressure of the permeation side, partial pressure of H_2 in the permeation side, total pressure of the reactor, (bar)

Q_{H_2}, r_j, R_i, T = molar rate of H_2 in the membrane tube, ($\mathrm{kmol(H_2) \cdot h^{-1}}$), intrinsic rates of reaction j and of component i ($\mathrm{kmol \cdot kg^{-1} \cdot h^{-1}}$), reactor temperature (K)

X_i, y_i, z_p = conversion of component i, mole fraction of component i, effective radius of the catalyst slab

Greek letters

$\alpha_{H_2}, \epsilon, \eta_j$ = permeation rate constant of hydrogen through the membrane, ($\mathrm{m^2 \cdot h^{-1} \cdot bar}$), catalyst pellet porosity, effectiveness factor of reaction j, dimensionless

Γ_o, Γ_i = outer and inner radii of the permeable tube, m

μ_G, ρ_c, ρ_G = viscosity of the gas mixture ($\mathrm{kgf \cdot h^{-1} \cdot m^{-2}}$), density of the catalyst and of the gas mixture ($\mathrm{kg \cdot m^{-3}}$)

Abbreviations

H_2 = hydrogen

P_{mt} = membrane tube total pressure

X_{EB} = total conversion of ethylbenzene

Y_{ST} = yield of styrene

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