

## Feasibility of Coupling Dehydrogenation of Ethylbenzene with Hydrogenation of Nitrobenzene in an Autothermal Catalytic Membrane Reactor: Modeling Study

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**Abstract:** The coupling of reactions in catalytic membrane reactors provides novel reactor configurations that allow shifting the thermodynamic equilibrium and yields of thermodynamically limited reactions and enhancing significantly the rate of production. An interesting pair to couple is the dehydrogenation of ethylbenzene to styrene and the hydrogenation of nitrobenzene to aniline. Hydrogen produced in the dehydrogenation side diffuses through the membrane and assists in shifting the equilibrium conversion of ethylbenzene and the yield of styrene while the large heat of reaction released from the hydrogenation side is utilized to provide the heat needed on the dehydrogenation side. The feasibility and performance of the co-current integrated catalytic membrane reactor configuration is investigated by means of models based on both homogeneous and heterogeneous fixed bed concepts. The ethylbenzene conversion and styrene yield obtained from the proposed reactor are then compared with those for simple fixed bed reactors without membranes. In the homogeneous modeling, the conversion of ethylbenzene is predicted to be ~39% in the simple fixed bed (without any membrane) compared to ~85% in the proposed catalytic membrane reactor. When intraparticle diffusion resistance is taken into consideration, the integrated reactor is predicted to have an ethylbenzene conversion of ~72% when catalyst pellets are isothermal and ~65% for non-isothermal catalyst pellets. The yields of styrene predicted by the homogeneous modeling are ~35% and ~80% for the simple fixed bed and the catalytic integrated reactor, respectively. The heterogeneous model of the integrated reactor, however, predicts less substantial, though still major gains, than the homogenous model, i.e. a styrene yield of ~70% for the isothermal catalyst pellets compared to ~65% for the non-isothermal catalyst pellets.

**Keywords:** membrane reactor, dehydrogenation, hydrogenation, homogeneous model, heterogeneous model.

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### 1. INTRODUCTION

Styrene is an important monomer for the manufacturing of polystyrene, which is, e.g. used in thermoplastics and synthetic rubber. The catalytic dehydrogenation of ethylbenzene at operating temperatures of 550-650°C and atmospheric or sub-atmospheric pressure in the presence of Fe<sub>2</sub>O<sub>3</sub> catalyst is the main process, producing more than 90% of manufactured styrene. There is an annual growth in worldwide demand of 5 to 6% per year (Stitt, 2004). The reaction is reversible, endothermic and severely limited by the thermodynamic equilibrium, with a maximum ethylbenzene conversion of less than 50% (Abashar, 2004).

The styrene yield cannot be enhanced significantly by catalyst improvement due to the fact that the main bottleneck is related to the thermodynamic equilibrium. Therefore, efforts should be directed to improving the performance through process design modifications (Abashar, 2004). A number of proposals have appeared in the literature in the past decade, involving

various catalytic reactor designs. The common factor in all these proposed reactor configurations is the use of membranes to allow hydrogen to diffuse from the ethylbenzene side to a permeate side where hydrogen is either purged or consumed in another reaction, i.e. combustion or hydrogenation. For instance, Moustafa and Elnashaie (2000) investigated the performance of a catalytic membrane reactor coupling the dehydrogenation of ethylbenzene to styrene with the hydrogenation of benzene to cyclohexane. A hybrid fixed bed reactor was modeled based on a rigorous reactor model, leading to a remarkable enhancement in the prediction of both the conversion of ethylbenzene and the yield of styrene compared to an industrial catalytic reactor operated by the Polymer Corporation in Sarnia, Canada. The ethylbenzene conversion and styrene yield reported were 51% and 45%, respectively. Abashar (2004) investigated a similar configuration and predicted a substantial increase in the conversion of ethylbenzene to nearly 100%. Abdalla and Elnashaie (1993) developed a rigorous reactor model for an industrial reactor to extract intrinsic kinetic data for the dehydrogenation of ethylbenzene. These kinetic data were

used in a later step to evaluate the advantage of the hydrogen permeation membrane to remove hydrogen. The effects of a number of operating and design were investigated. A rigorous heterogeneous model describing the behavior of a membrane reactor in which ethylbenzene was dehydrogenated to styrene, was developed by Abdalla and Elnashaie (1994). This model was used to evaluate the effect of the sweep gas on the performance of the reactor. Significant enhancement was observed in the ethylbenzene conversion, the styrene yield and the selectivity (Abdalla and Elnashaie, 1994). Babiker and Elnashaie (1995), proposed a fluidized bed with and without a selective membrane for catalytic dehydrogenation of ethylbenzene to styrene. Several design and operating parameters like bubble diameter, steam-to-ethylbenzene ratio, feed temperature, and number of fluidized beds in series, were investigated. It was predicted that a careful choice of those parameters could provide a significantly better ethylbenzene conversion and styrene yield compared to industrial fixed bed reactors. Hermann et al. (1997) studied the dehydrogenation of ethylbenzene to styrene in a composite Pd/porous stainless steel membrane fixed bed reactor. A reactor model was presented in which different types of diffusion through membranes were considered. After adjusting the kinetics obtained from the literature to match the conversion and selectivity, the model predicted more than 90% ethylbenzene conversion with increasing reaction pressure, with no observable decrease in styrene selectivity. Abo-Ghander, et al, (2008) introduced a new catalytic membrane reactor coupling the dehydrogenation of ethylbenzene with the hydrogenation of nitrobenzene. Hydrogen-selective membranes were used to transfer hydrogen from the dehydrogenation side to the hydrogenation side, where it reacts with nitrobenzene to produce aniline. It was predicted that transferring hydrogen from the dehydrogenation side and providing the heat of reaction from the hydrogenation side have greatly enhanced the styrene yield compared to that of simple fixed bed reactors.

In our work, an extensive literature review was first conducted to find a pair of industrial reactions which could be coupled in such a way that the hydrogen needed on one side of the membrane could be provided by dehydrogenation on the other side, and, at the same time, heat needed for an endothermic reaction could be supplied by exothermic heat released on the other side. The proposed reactor should also be able to produce another significant product rather than burning or purging the diffused hydrogen. A promising pair was found to be the dehydrogenation of ethylbenzene to styrene, coupled with the hydrogenation of nitrobenzene to aniline.

The aim of the current paper is to investigate the performance of a catalytic membrane reactor coupling the dehydrogenation of ethylbenzene with the hydrogenation of nitrobenzene by considering homogeneous as well as heterogeneous reactor models. The conversion of ethylbenzene, the yield of styrene and the resulting temperature profiles are also compared with those for simple fixed bed reactors without membranes.

## 2. REACTOR CONFIGURATION

The catalytic membrane reactor used to couple the dehydrogenation of ethylbenzene with the hydrogenation of nitrobenzene to aniline is shown schematically in Fig. 1.

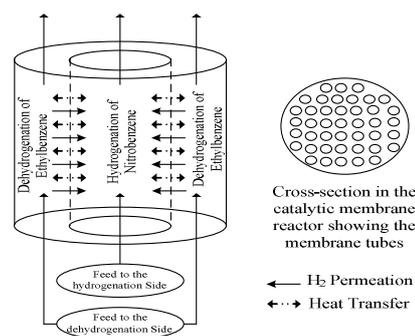
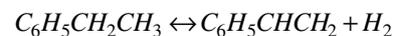


Fig. 1: Scheme of the integrated catalytic membrane reactor.

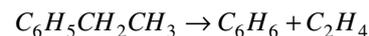
The reactor is composed of two compartments, i.e. shell and tube, each packed completely with catalyst particles. In the shell compartment, ethylbenzene is dehydrogenated to styrene, benzene and toluene. Other light gases, like hydrogen, ethylene, and methane are produced as by-products. The reaction network consists of one main and five side reactions.

Main reaction:

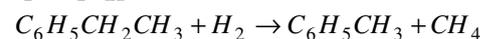


$$r_1 = k_1 \left( p_{EB} - p_{ST} \frac{p_{H_2}}{K_A} \right) \quad (1)$$

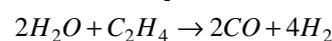
Side reactions:



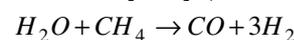
$$r_2 = k_2 p_{EB} \quad (2)$$



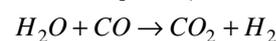
$$r_3 = k_3 p_{EB} p_{H_2} \quad (3)$$



$$r_4 = k_4 p_{H_2O} p_{C_2H_4}^{1/2} \quad (4)$$



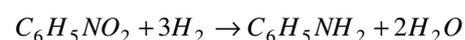
$$r_5 = k_5 p_{H_2O} p_{CH_4} \quad (5)$$



$$r_6 = k_6 \left( \frac{P}{T^3} \right) p_{H_2O} p_{CO} \quad (6)$$

In this reaction network, the main reaction is reversible and endothermic. The forward reaction is favored by high temperature and low pressure. Operating the above network in a simple catalytic fixed bed reactor, results in a limited conversion of ethylbenzene, styrene production, and a drop in temperature along the axial direction due to the endothermicity. In the proposed novel reactor, however, hydrogen produced in the shell compartment due to the dehydrogenation reaction diffuses through the membrane wall of the tube compartment due to the difference in hydrogen partial pressures between the two sides. The diffusion of hydrogen helps to shift the equilibrium conversion and the styrene yield, resulting in a higher conversion of ethylbenzene and a larger production of styrene.

On the tube side, diffused hydrogen reacts with nitrobenzene to produce aniline according to the following stoichiometric equation (Amon et al. 1999):



$$r' = \frac{k'K_{NB}K_{H_2}P'_{NB}\sqrt{P'_{H_2}}}{(1 + K_{NB}P'_{NB} + K_{H_2}\sqrt{P'_{H_2}})^2} \quad (7)$$

This hydrogenation reaction is irreversible and highly exothermic. The heat produced on the tube side as a result of this reaction is transferred through the tube walls to heat the reacting mixture on the shell side. The reaction frequency factors and activation energies of the above reactions are listed in Table 1 (Elnashaie et al. 1993; Amon et al. 1999).

Table 1: Pre-exponential factors and activation energies.

Reaction	$k_{jo}^a$ [kmol/hr/kg cat]	$E_j$ [kJ/kmol]
1 <sup>b</sup>	$8.32 \times 10^3$	$0.909 \times 10^5$
2	$4.23 \times 10^9$	$2.080 \times 10^5$
3	$6.13 \times 10^3$	$0.915 \times 10^5$
4	$3.95 \times 10^3$	$1.040 \times 10^5$
5	$1.42 \times 10^2$	$0.657 \times 10^5$
6	$5.80 \times 10^{12}$	$0.736 \times 10^5$
7 <sup>c</sup>	$1.86 \times 10^{-4}$	$10.0 \times 10^3$

<sup>a</sup>  $k_j = k_{jo} \exp\left(-\frac{E_j}{RT}\right)$ , where  $k_{jo}$  is the pre-exponential factor,

for  $1 \leq i \leq 6$

$k_j = 10^3 k_{jo} \exp\left(-\frac{E_j}{RT}\right)$ , for  $j = 7$ .

<sup>b</sup> The equilibrium constant is given by:

$$K_A = \exp\left(\frac{-\Delta F}{RT}\right),$$

where:  $\Delta F = a + bT + cT^2$ ,

$a = 122725.16 \text{ J/mol}$ ,  $b = -126.27 \text{ J/mol/K}$ ,  $c = -2.194 \times 10^{-3} \text{ J/mol/K}^2$

<sup>c</sup>  $K_{NB} = 1.51 \times 10^{-2} \text{ kPa}$ ,  $K_{H_2} = 0.14 \text{ kPa}^{-0.5}$

### 3. REACTOR MODEL

The model differential equations governing the behavior of mole and energy change along the axial direction of the catalytic membrane reactor were derived by considering a small slice on both sides of the reactor, i.e. tube and shell. Across each slice, there were mole and energy flowing in a co-current fashion in the axial direction. Transfers of moles and energy also occur between the shell side and tube side. Pressure drop along the reactor is calculated based on Ergun's equation. To derive the model for the homogenous case, the following assumptions are adopted.

1. Steady state operation on both sides of the membranes.
2. Ideal gas behavior.
3. Plug flow on both sides.
4. The reacting mixtures have high flowrates that minimize external mass and heat transfer resistances.
5. Catalyst deactivation is negligible.
6. One-dimensional homogenous model.

Based on the above assumptions, the mole balance equations on the *dehydrogenation* side are written as:

$$\frac{dn_i}{dz} = \sum_{j=1}^6 \sigma_{ij} r_j (1-\varepsilon) A_{cs} \rho_s - 2\pi r_3 N a_i J'_i \quad (8)$$

The temperature change on the dehydrogenation side is:

$$\frac{dT}{dz} = \frac{\sum_{j=1}^6 [-\Delta H(T)]_j r_j (1-\varepsilon) A_{cs} \rho_s + NQ}{\sum_{i=1}^{10} n_i C p_i} \quad (9)$$

and the pressure change on the dehydrogenation side equals:

$$\frac{dP}{dz} = -\frac{G}{\rho_g g_c D_p} \left( \frac{1-\varepsilon}{\varepsilon^3} \right) \left[ \frac{150(1-\varepsilon)\mu_g}{D_p} + 1.75G \right] \quad (10)$$

Similarly, the mole and energy change equations for the co-current flow on the *hydrogenation* side are written as:

$$\frac{dn'_i}{dz} = \sigma'_i r' (1-\varepsilon') A'_{cs} \rho'_s + 2\pi r_3 a_i J'_i \quad (11)$$

$$\frac{dT'}{dz} = \frac{(2\pi r_3) \sum_{i=1}^i a_i J'_i \int_T C p_i dT + [-\Delta H'(T')] r' (1-\varepsilon') A'_{cs} \rho'_s - Q}{\sum_{i=1}^4 n'_i C p'_i} \quad (12)$$

and the pressure change on the hydrogenation side is:

$$\frac{dP'}{dz} = -\frac{G'}{\rho'_g g_c D'_p} \left( \frac{1-\varepsilon'}{\varepsilon'^3} \right) \left[ \frac{150(1-\varepsilon')\mu'_g}{D'_p} + 1.75G' \right] \quad (13)$$

For a palladium membrane surface of thickness  $25\mu\text{m}$ , the molar diffusion of hydrogen per unit length of reactor is expressed (Sieverts and Zapf. 1935) as:

$$J'_{H_2} = \frac{Q_o \exp\left(-\frac{E_{H_2,P}}{RT}\right)}{\delta_{H_2}} (\sqrt{P_{H_2}} - \sqrt{P'_{H_2}}) \quad (14)$$

where:

$$Q_o = 7.29 \times 10^{-3} \text{ mol/m/min/atm}^{0.5}$$

$$\delta_{H_2} = 25 \times 10^{-6} \text{ m}, E_{H_2,P} = 20.5 \times 10^3 \text{ J/mol.}$$

The rate of heat transfer between the two compartments per unit length is expressed (Froment and Bischoff. 1990) as:

$$Q = \frac{2\pi r_1 (T' - T)}{\left[ \frac{1}{h'} + \frac{r_1}{k_{ss}} \ln\left(\frac{r_2}{r_1}\right) + \frac{r_1}{k_{pd}} \ln\left(\frac{r_3}{r_2}\right) + \frac{r_1}{r_2 h} \right]} \quad (15)$$

where:

$$k_{ss} = 22.9 \text{ W/m/K}, k_{pd} = 93.3 \text{ W/m/K}$$

$$\frac{hD_t}{k_g} = 0.813 \left( \frac{D_p G}{\mu_g} \right)^{0.9} \exp\left(-\frac{6D_p}{D_t}\right) \quad (16)$$

$$\frac{h'D'_t}{k'_g} = 3.50 \left( \frac{D'_p G'}{\mu'_g} \right)^{0.7} \exp\left(-\frac{4.6D'_p}{D'_t}\right) \quad (17)$$

The boundary conditions at  $z = 0$  are:

- for the dehydrogenation side:

$$n_i = n_{if}, T = T_f, P = P_f \quad (18)$$

- and for the hydrogenation side:

$$n'_i = n'_{if}, T' = T'_f, P' = P'_f \quad (19)$$

Physical properties of the gas mixture, i.e. density, thermal capacity, and viscosity are taken as function of temperature.

To model the catalyst pellets on both sides of the reactor, the following assumptions are adopted:

1. Steady state.
2. Ideal gas behavior.
3. The porous structure inside the catalyst pellet is assumed to be homogenous.
4. The pressure gradient is insignificant, i.e. the effect of viscous diffusion is negligible. Only molecular and Knudsen diffusion are important.
5. To reduce the mathematical complexity, the effective diffusivity is assumed to be independent of temperature and gas composition.
6. Fick's law gives the molar flux inside the catalyst pellet.
7. Symmetrical concentration and temperature profiles at the center of each catalyst pellet.
8. External mass and heat transfer resistances are negligible.

Based on these assumptions, the catalyst model equations can be written as follows. On the *dehydrogenation* side:

- Mole balance:

$$\frac{d^2 C_i}{dy^2} + \frac{2}{y} \frac{dC_i}{dy} = -\frac{1}{D_{ie}} \sum_{j=1}^i \sigma_{ij} r_j \rho \quad (20)$$

- Energy balance:

$$\frac{d^2 T}{dy^2} + \frac{2}{y} \frac{dT}{dy} = \frac{1}{k_e} \sum_{j=1}^i [\Delta H(T)]_j r_j \rho \quad (21)$$

- Boundary conditions:

$$y = 0 \Rightarrow \frac{dC_i}{dy} = 0 \quad \text{and} \quad \frac{dT}{dy} = 0 \quad (22)$$

$$y = R_p \Rightarrow C_i = C_{is} \quad \text{and} \quad T = T_s \quad (23)$$

On the *hydrogenation* side:

- Mole balance:

$$\frac{d^2 C'_i}{dy'^2} + \frac{2}{y'} \frac{dC'_i}{dy'} = -\frac{\sigma'_i r'_i \rho'}{D'_{ie}} \quad (24)$$

- Energy balance:

$$\frac{d^2 T'}{dy'^2} + \frac{2}{y'} \frac{dT'}{dy'} = \frac{[\Delta H(T)]'_i r'_i \rho'}{k'_e} \quad (25)$$

- Boundary conditions:

$$y' = 0 \Rightarrow \frac{dC'_i}{dy'} = 0 \quad \text{and} \quad \frac{dT'}{dy'} = 0 \quad (26)$$

$$y' = R'_p \Rightarrow C'_i = C'_{is} \quad \text{and} \quad T' = T'_s \quad (27)$$

The effective molecular diffusion inside the catalyst particle on the dehydrogenation side is as follows (Bird et. al. 1960):

$$\frac{1}{D_{ie}} = \frac{1}{D_{im}^e} + \frac{1}{D_{ik}^e} \quad (28)$$

where:

$$\frac{1}{D_{im}^e} = \frac{1}{1 - x_i} \sum_{\substack{j=1 \\ j \neq i}}^j \frac{x_j}{D_{ij}} \quad (29)$$

The effective diffusivity is obtained by:

$$D_{im}^e = \frac{\varepsilon}{\tau} D_{im} \quad (30)$$

The catalyst governing equations (20-23) are solved numerically to calculate the reaction rates on the dehydrogenation side, defined as:

$$\eta_j r_j(T_s, C_{is}) = 3 \int_0^{1.0} r_j \omega^2 d\omega \quad (31)$$

Equation (31), which was numerically evaluated in this work using the *trapezoidal technique*, was substituted into (8) as a replacement for the reaction rates evaluated at bulk conditions in homogenous modeling. Similar steps (24-27) were followed on the hydrogenation side.

#### 4. RESULTS AND DISCUSSION

To evaluate the proposed catalytic membrane reactor coupling the dehydrogenation of ethylbenzene with the hydrogenation of nitrobenzene to aniline, a base case was selected in which the dehydrogenation side was run at conditions similar to those of an industrial fixed bed reactor. The feed temperatures on both sides were selected to be below 923 K to ensure the sustainability and the durability of the hydrogen membranes. The operating conditions of the proposed membrane reactor are listed in Table 3.

The membrane reactor was simulated for the co-current configuration for four different cases: simple *homogeneous fixed bed reactor* (without membranes), *homogeneous catalytic membrane reactor* (with membranes), *heterogeneous catalytic membrane reactor* (with membranes and *isothermal catalyst pellets*), and *heterogeneous catalytic membrane reactor* (with membranes and *non-isothermal catalyst pellets*).

Table 2: Operating conditions for the catalytic membrane reactor.

Parameter	Value
<i>Dimensional Variables</i>	
Area-equivalent diameter of dehydrogenation side [m]	1.95
Diameter of hydrogenation tubes [m]	3.5×10 <sup>-2</sup>
Total number of hydrogenation tubes [-]	1500
Length of reactor [m]	4.0
<i>Operating Conditions (Dehydrogenation Side)</i>	
Ethylbenzene [mol/s]	10.242
Steam [mol/s]	125.86
Temperature [K]	880.0
Pressure [bar]	2.5
Catalyst density [kg/m <sup>3</sup> ]	2146.3
Catalyst pore diameter [m]	4800×10 <sup>-10</sup>
Catalyst thermal conductivity [J/m/s/K]	0.03
Catalyst porosity [-]	0.35
Catalyst tortuosity [-]	4.0
<i>Operating Conditions (Hydrogenation Side)</i>	
Nitrobenzene [mol/s]	0.005
Steam [mol/s]	0.008
Temperature [K]	900.0
Pressure [bar]	1.0
Catalyst density [kg/m <sup>3</sup> ]	1400
Catalyst pore diameter [m]	5000×10 <sup>-10</sup>
Catalyst thermal conductivity [J/m/s/K]	0.05
Catalyst porosity [-]	0.40
Catalyst tortuosity [-]	4.0

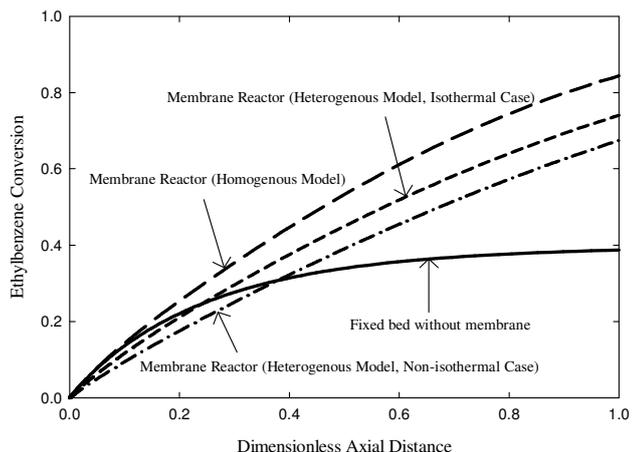


Fig. 2: Ethylbenzene conversion along the fixed bed reactor without membrane, and the dehydrogenation side of the integrated reactor.

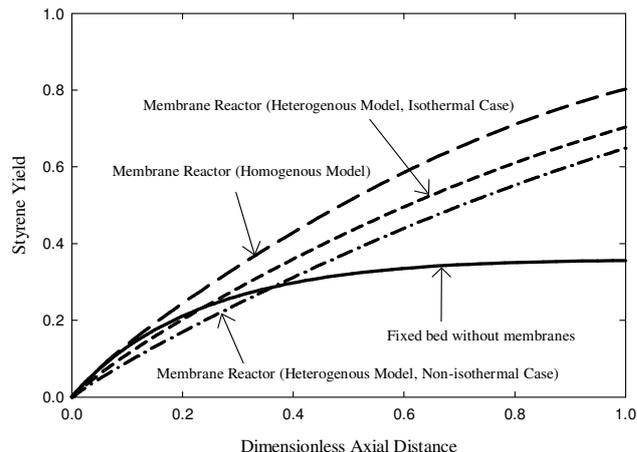


Fig. 4: Styrene yield along the fixed bed reactor without membrane, and the dehydrogenation side of the integrated reactor.

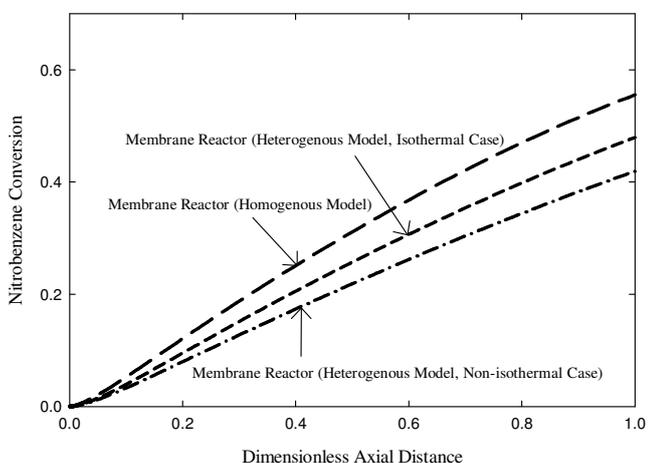


Fig. 3: Nitrobenzene conversion of along the hydrogenation side of the integrated reactor.

#### 4.1 Conversion of ethylbenzene and nitrobenzene

Conversions of ethylbenzene along a simple catalytic fixed bed reactor without membranes and for the proposed integrated reactor are plotted in Fig. 2. The hydrogen permeable membrane in the integrated reactor assists significantly in augmenting the conversion of the ethylbenzene from ~39% for the simple fixed bed to ~85% predicted by the homogeneous modeling for the proposed reactor. When intraparticle diffusion is considered, the model for the integrated reactor predicts ethylbenzene conversions of ~72% and ~65% for the isothermal and non-isothermal catalyst pellets.

The conversion of nitrobenzene on the hydrogenation side of the integrated reactor is plotted as a function of the dimensionless distance along the reactor in Fig. 3. The homogenous model indicates a nitrobenzene conversion of ~55%, while the heterogeneous modeling predicts a nitrobenzene conversion of ~45% for isothermal catalyst pellets, and ~42% for non-isothermal catalyst pellets. Again, the influence of intraparticle diffusion is significant.

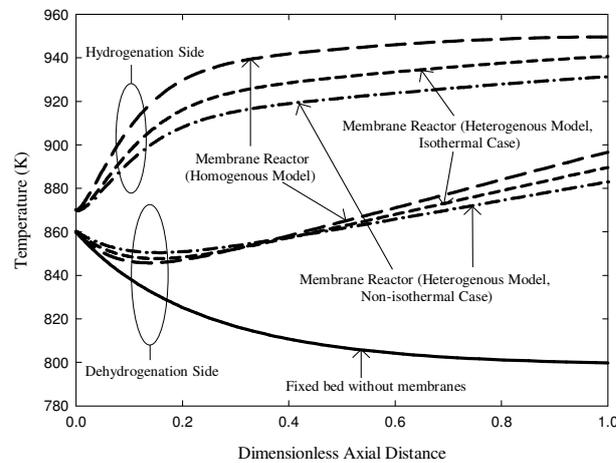


Fig. 5: Temperature profiles along the fixed bed reactor without membrane and the dehydrogenation side of the integrated reactor.

#### 4.2 Yield of Styrene

In Fig. 4, the yield of styrene is plotted versus the dimensionless axial distance for a simple catalytic fixed bed reactor with no membrane, in comparison with the integrated catalytic reactor. Homogenous modeling of a simple fixed bed reactor for the same operating conditions predicts a styrene yield of ~35% and ~80% for the coupled catalytic reactor. Heterogeneous modeling of the integrated reactor, however, results in ~70% conversion for isothermal catalyst pellets and ~65% non-isothermal catalyst pellets. It is clear that the hydrogen membrane greatly assists in promoting the forward reaction and in producing more styrene.

#### 4.3 Temperature profiles

The temperature profiles along the simple fixed bed reactor are plotted in Fig. 5 in comparison with those for both sides of the integrated catalytic reactor. For a simple fixed bed reactor without membranes, the temperature drops along the dehydrogenation reactor due to the endothermality. This drop in temperature can be counteracted in the coupled reactor by the heat supplied by the hydrogenation reaction.

From the above simulation results, coupling the dehydrogenation of ethylbenzene with the hydrogenation of nitrobenzene in this novel catalytic membrane reactor is predicted to be very promising. It greatly assists in enhancing both conversion of ethylbenzene and yield of styrene on the dehydrogenation side, as well as conversion of nitrobenzene on the hydrogenation side by providing enough hydrogen for the transfer through the membrane. Intraparticle diffusion is significant and should be considered when optimizing the reactor.

## 5. CONCLUSION

A reactor model for the proposed catalytic membrane reactor which couples the dehydrogenation of ethylbenzene with the hydrogenation of nitrobenzene is developed in which the effect of intraparticle diffusion is considered. It is shown that coupling this pair of reactions in a catalytic membrane reactor can significantly improve the conversion of ethylbenzene and the styrene yield. The membranes allow the hydrogen produced on the dehydrogenation side to diffuse through to the hydrogenation side, where it reacts with nitrobenzene to produce aniline as a second useful product. Hydrogen diffusion and heat transfer from the hydrogenation side are the two main factors leading to the improvement. This study also shows that intraparticle diffusion resistance is very significant in this type of reactor. Hence, it should not be neglected when the optimizing the design of this novel coupled reactor.

## 6. ACKNOWLEDGMENTS

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## NOTATION

$a_i$	constant, 1 for hydrogen, 0 otherwise, [-].
$A_{cs}, A'_{cs}$	cross-sectional area of shell and tube side, [m <sup>2</sup> ].
$C_i, C'_i$	concentration of component $i$ inside catalyst pellet on shell and tube side, [mole/m <sup>3</sup> ].
$C_{is}, C'_{is}$	concentration of component $i$ at the surface of catalyst pellet on shell and tube side, [mole/m <sup>3</sup> ].
$Cp_i, Cp'_i$	heat capacity of component $i$ on shell and tube side, [J/mol/K].
$D_p, D'_p$	diameter of catalyst particle on shell and tube side, [m].
$D_t$	diameter of tube, [m].
$D_{ie}$	effective diffusivity of component $i$ , [m <sup>2</sup> /s].
$D_{ik}$	Knudsen diffusion coefficient of component $i$ , [m <sup>2</sup> /s].
$D_{im}$	diffusivity of component $i$ into gas mixture, [m <sup>2</sup> /s].
$E_j, E'_j$	activation energy of reaction $j$ on shell and tube side, [J/(mol×K)].
$G, G'$	mass velocity on shell and tube side, [kg/m <sup>2</sup> /s].
$h, h'$	convective heat transfer coefficient on shell and tube side, [J/s/m <sup>2</sup> /K].
$H_i, H'_i$	enthalpy of component $i$ on shell and tube side, [J/mol].

$k_{pds}, k_{ss}$	thermal conductivity of the palladium and stainless steel layer, [J/m/s/K].
$k_e$	effective catalyst thermal conductivity of catalyst pellet on dehydrogenation side, [J/m/s/K].
$k_{j0}$	pre-exponential factor for reaction $j$ , [mol K <sup>m</sup> /kg cat/hr/bar <sup>n</sup> ], (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 $k_6$ , $m=3$ , $n=3$ ).
$L$	total length of reactor, [m].
$N$	number of membrane tubes in hybrid reactor, [-].
$n_i, n'_i$	molar flow rate of component $i$ on shell and tube side, [mol/s].
$J'_i$	molar flux of component $i$ , [mol/(m <sup>2</sup> ×s)].
$p_i, p'_i$	partial pressure of component $i$ on shell and tube side, [bar].
$P, P'$	total pressure on shell and tube side of reactor, [Pa].
$Q$	heat transferred from tube side to shell side, [J/m].
$Q_0$	pre-exponential constant of hydrogen membrane, [mol/(m×s×bar <sup>0.5</sup> )].
$r_j$	rate of reaction $j$ on shell side, [mol/kg cat/s].
$r'$	rate of reaction on tube side, [mol/kg cat/s].
$r_1$	inner radius of hydrogenation tube, [m].
$r_2$	outer radius of hydrogenation tube, [m].
$r_2-r_1$	thickness of palladium membrane, [m].
$R_p$	radius of catalyst pellet on dehydrogenation side [m].
$T, T'$	temperature on shell and tube side of reactor, [K].
$y$	radial coordinate inside catalyst particle, [m].
$z$	axial coordinate inside reactor, [m].
$[\Delta H(T)]_j$	heat of reaction $j$ at temperature $T$ on shell side, [J/mol].
$[\Delta H(T')]_j$	heat of reaction at temperature $T'$ on tube side, [J/mol].
$\rho_s, \rho'_s$	catalyst solid density on shell and tube side, [kg/m <sup>3</sup> ].
$\varepsilon, \varepsilon'$	void fraction on shell and tube side, [-].
$\sigma_{ij}$	stoichiometric number of component $i$ in reaction $j$ , [-].
$\sigma'_i$	stoichiometric number of component $i$ in hydrogenation reaction, [-].
$\delta_{H_2}$	thickness of hydrogen permeation membrane, [m].
$\omega$	dimensionless radial distance inside catalyst pellet, [-].
$\eta_j$	effectiveness factor of reaction $j$ [-].
$\mu_s, \mu'_s$	gas viscosity on shell and tube side, [Pa×s].

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