

Modeling of Ethylbenzene Dehydrogenation Membrane Reactor to Investigate the Potential Application of a Microporous Hydroxy Sodalite Membrane

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Abstract

In this study the catalytic dehydrogenation of ethylbenzene to styrene was investigated in a simulated tubular sodalite membrane reactor. The high quality microporous sodalite membrane was synthesized by direct hydrothermal method and characterized by single gas permeation measurements. The performance of the prepared membrane showed high potential for application in a dehydrogenation membrane reactor (MR). The performance of the MR was evaluated using a pseudo-homogeneous model of the fixed bed that was developed in this purpose. The obtained results were evaluated in comparison with corresponding predictions for a plug flow reactor (PFR) operated at the same conditions. The modeling results confirmed the high performance of a MR over a conventional PFR. Ethylbenzene conversion and styrene yield increased about 3.45% and 8.99% respectively which is attributed to the effect of hydrogen removal from reaction side. The results demonstrate that the styrene yield in the MR is predicted to be more effective than that of in the conventional PFR.

Keywords: Ethylbenzene dehydrogenation, Membrane reactor, Microporous membrane, Simulation, Sodalite membrane

Introduction

Styrene as one of the most important monomers, is mainly produced via ethylbenzene dehydrogenation at operating temperatures of 823-923 K and atmospheric or sub-atmospheric pressure in the presence of commercial Fe_2O_3 catalyst [1-3]. One of the main problems in the actual ethylbenzene dehydrogenation process is the need for reactant recycle. This problem is due to the thermodynamic limitations and high endothermicity of the reaction resulting in the low conversion per pass [1]. So that, an attractive technique for breaking this limitation is the use of selective membranes in order to remove at least one of the products from the reaction media [4]. In this regard, membrane reactor is a type of multifunctional reactors and is currently being applied to many chemical reactions worldwide [5]. By the use of MR for

dehydrogenation reactions, the reaction can be carried out at lower temperatures [3,6-7]. The lower operating temperature in a MR can be a suitable solution to the above mentioned problems, as hydrogen removal from the reaction side leads to enhancement of conversion and then styrene production [8]. The combination of catalysis and gas separation requires a membrane with high selectivity, adequate permeating rate, mechanical, thermal and chemical stability [4]. Considering the some drawbacks of palladium membrane as early membrane reactors studied for styrene dehydrogenation such as these membranes cost, permeability and stability, recently various studies focused on the enhancement of microporous zeolite membrane performance in dehydrogenation processes [3,9-10].

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Due to the high separation potential of zeolite membranes based on their molecular sieving and selective adsorption, this type of membranes are frequently applied in MR systems [3,6-7,10-14]. Among the zeolites, hydroxysodalite is crystalline aluminosilicate with a three dimensional channel network and pore size of 2.8 Å [15]. Because of the small pore size and high ion exchange capacity, sodalite has attracted considerable attentions [16]. So, this zeolite can be an ideal candidate for the separation of small molecules such as H₂ (2.89 Å) from gas mixtures [17].

As mentioned above, membrane reactor efficiency and its performance are highly associated to its membrane performance and

one of the most important parameters that affects this efficiency is the performance of membrane at reaction conditions. Therefore, in this work, sodalite membrane was synthesized on the outer surface of homemade macroporous tubular ceramic support via hydrothermal method. Then, for the first time the performance of this kind of membrane was investigated at high temperatures. Also the empirical correlations for the permeation of gases through sodalite membrane as a function of temperature have been developed. Then, the simulation results which compare the performance of two types of reactor systems (a MR consisting of a sodalite on α -alumina support and a PFR) were investigated.

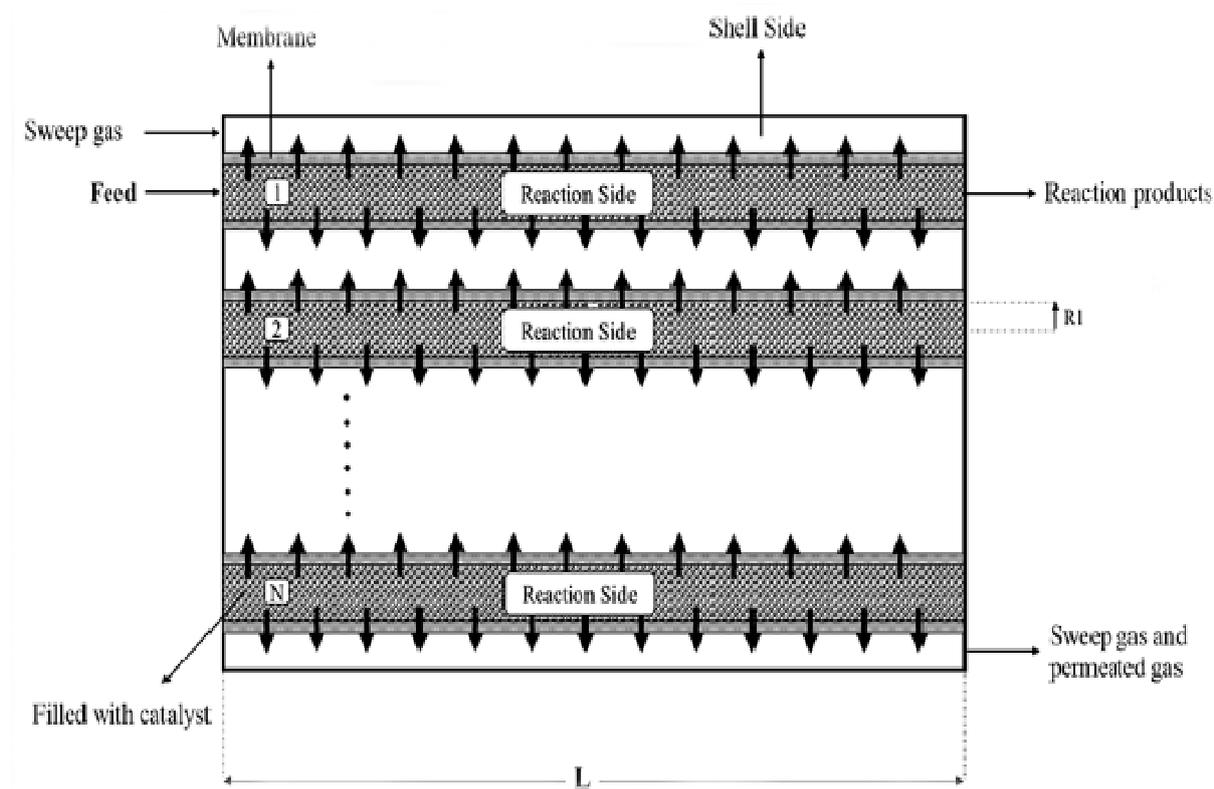


Figure 1: A schematic representation of the membrane reactor

2. Theory

2.1. Model Development

In order to evaluate the potential performance of hydroxysodalite membrane in the MR of ethylbenzene in comparison with a conventional PFR, a mathematical model was developed. The model is based on the governing equations describing a conventional PFR operation, taking into account the experimental permeation measurements correlated by an equation. The schematic representation of the membrane reactor is presented in Figure 1

2.2. Assumption

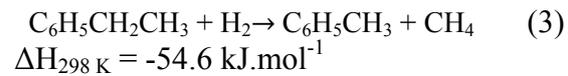
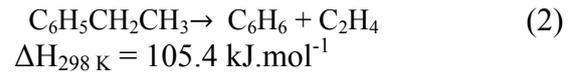
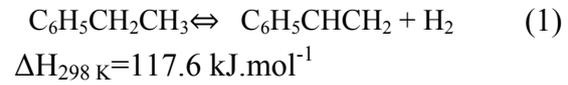
In order to derive the governing equations used to represent the MR operation, the following assumptions are adopted:

- Steady state operation
- Reaction occurs only inside the catalyst bed on the reaction (tube) side and the mixture of EB and nitrogen is fed into the reaction side at gas state
- Nitrogen as sweep gas is introduced to the shell side (permeate side) because using the steam at sodalite membrane reactor is not possible (the membrane would be blocked immediately)
- The sweep gas in shell side and feed in tube side are assumed to flow in co-current mode
- The effectiveness factors of reaction rates are taken to be equal to unity
- Temperatures of tube and shell side are the same
- Plug flow for both shell and tube sides is assumed
- Catalyst deactivation is neglected
- The pressure drop along the catalyst bed (tube side) is calculated based on Ergun's equation

- Pressure drop at permeate side is neglected

2.3. Reaction Kinetics

The reaction network for the dehydrogenation of EB to SM in the absence of steam is [2]:



The corresponding rate equations, expressed as functions of component partial pressure in bars, are [2]:

$$r_1 = k_1 \times \left(P_{\text{EB}} - \frac{P_{\text{SM}} \times P_{\text{H}_2}}{K_P} \right) \quad (4)$$

$$r_2 = k_2 \times P_{\text{EB}} \quad (5)$$

$$r_3 = k_3 \times P_{\text{EB}} \times P_{\text{H}_2} \quad (6)$$

Where rate constants are defined as:

$$k_i = \exp \left(A_i - \frac{E_i}{RT} \right) \quad (7)$$

The numerical values of A_i and E_i are listed in Table 1 [2]. With these constants, the reaction rates are expressed in $\text{kmol.kg cat}^{-1}.\text{h}^{-1}$.

Also Table 2 lists the enthalpy data used for the simulation [18].

Table 1: Arrhenius equation and equilibrium constants for ethylbenzene reactions (Abo-glander et al., 2008)

Reaction No.	Enthalpy of Reaction: $\Delta H_R = a + bT + cT^2$		
	a[J.mol ⁻¹]	b[J.mol ⁻¹ .K ⁻¹]	c[J.mol ⁻¹ .K ⁻²]
1	115000	26.83	-0.01378
2	106700	-2.798	-0.002446
3	-46290	-28.89	0.009625

Table 2: Enthalpy correlation and its constants for ethylbenzene reaction network (Hermann et al., 1997)

Reaction No.	Frequency factor	Activation energy, kJ.mol ⁻¹
1	0.85	90.0
2	14.00	208.1
3	0.56	91.5
Equilibrium constant $K_A = \exp(-\Delta F/RT)$		
$\Delta F = a + bT + cT^2$		
$a = 122725.157 \text{ kJ.kmol}^{-1}$		
$b = -126.2674 \text{ kJ.kmol}^{-1}.\text{K}^{-1}$		
$c = -2.194 \times 10^{-3} \text{ kJ.kmol}^{-1}.\text{K}^{-2}$		

2.4. Governing Equation for Membrane Reactor

To obtain the mole balance equations, a differential element along the axial direction inside the MR was considered. The processes occurring in the tube and shell side of MR are represented by mass balance equations as follows:

$$\frac{dF_{ti}}{dZ} = (1 - \varphi)\pi R_1^2 \rho_{catalyst} \sum_{j=1}^3 (\pm \beta_{ij} r_j) \pm 2\pi R_1 J_i \Delta P \quad (8)$$

$$\frac{dF_{si}}{dZ} = \pm 2\pi N R_3 J_i \Delta P \quad (9)$$

In Eq. (8) " β_{ij} " is stoichiometric coefficient of reactant i in reaction j . In Eq. (9), " N " is the number of membrane tubes. The flux term " J_i " in Eqs. (8) and (9) is only applied to hydrogen; this term disappears for all other components. The hydrogen flux through the membrane is obtained by experimental data.

The energy balance for MR along the axial direction is obtained by:

$$F_T C_p \frac{dT}{dZ} = -\pi R_1^2 \rho_{catalyst} \sum_{j=1}^3 (\pm \Delta H_j r_j) \quad (10)$$

The pressure drop at the tube side is expressed as:

$$\frac{dP_{tT}}{dZ} = -150 \times 10^{-5} \frac{\mu_t u_{tz} (1 - \varphi_b)^2}{(2r_p)^2 \varphi_b^3} - 1.75 \times 10^{-5} \frac{\rho_g u_{tz}^2}{2r_p} \left[\frac{1 - \varphi_b}{\varphi_b^3} \right] \quad (11)$$

The mole fraction and partial pressure for tube and shell side are:

$$P_{ti} = \frac{F_{ti} \times P_{tT}}{\sum_{i=1}^8 F_{ti}} \quad (12)$$

$$P_{si} = \frac{F_{si} \times P_{SM}}{\sum_{i=1}^2 F_{si}} \quad (13)$$

$$y_{si} = \frac{F_{si}}{\sum_{i=1}^2 F_{si}} \quad (14)$$

$$y_{ti} = \frac{F_{ti}}{\sum_{i=1}^8 F_{ti}} \quad (15)$$

2.5. Numerical Solution

The final model consist of a system of 12 ordinary differential equations (ODEs) with the corresponding initial conditions was solved by the fourth order RungeKutta routine method.

2.6. Boundary Condition

For the co-current operation case, the set of equations give an initial value problem. So the boundary conditions are:

$$\text{At } Z = 0$$

$$\text{Tube side: } F_{ti}=F_{ti0} \text{ ,} \quad (16)$$

$$T=T_0 \text{ , } P_t=P_{t0}$$

$$\text{Shell side: } F_{si}=F_{si0} \text{ ,} \quad (17)$$

$$T=T_0 \text{ , } P_s=P_{s0}$$

2.7. Operating Condition

The operating conditions for both sides of the membrane reactor are given in Table 3. At the first step, the MR modeling results for only the main reaction of ethylbenzene dehydrogenation were compared with the confirmed modeling results of Gobina's work [19] and validated. Then the modeling procedure was expanded to the mentioned MR conditions and reactions.

3. Experimental

The tubular hydroxysodalite membrane used in this study was synthesized via direct hydrothermal method. The membrane had a multilayer asymmetric structure consist of an α -alumina tube (12 mm outer diameter, 3 mm inner diameter, 7 cm length, 570 nm

mean pore diameter), and several outside hydroxysodalite layers. The synthesis solution was prepared by mixing the aluminate and silicalite solutions. The aluminate solution was prepared by dissolving sodium hydroxide (>99%, Merck) in deionized water followed by the addition of pure aluminum (>99%, Merck). The silicalite solution was made by mixing sodium hydroxide and deionized water with silica sol (>99%, Merck). The two solutions were mixed for 15 min in order to produce a homogenous solution. Synthesis was carried out at 363 K for 12 h, after which the tube was thoroughly washed with water until the pH of the residue was about neutral. Single gas permeation experiments were used to evaluate the separation performance of the membrane. It should be noted that the procedure of membrane synthesis was explained with more details in our previous work [20].

Table 3: Operating conditions for sodalite membrane reactor dehydrogenation reaction of ethylbenzene to styrene

Parameter	Value and dimensions
Inlet Temperature	853 K
Inner Diameter of Tube	16 mm
Outer Diameter of Tube	22 mm
Effective thickness of Membrane	20 μm
Catalyst Density	1500 kg.m^{-3}
Diameter of Catalyst Particle	2 mm
Void Fraction of Catalyst	0.6
Length of the reactor	1 m
Surface area of membrane	6900 m^2
Feed molar flow rates of Ethylbenzene at tube side	150 mol.s^{-1}
Feed molar flow rates of Nitrogen at tube side	220 mol.s^{-1}
Feed molar flow rates of Nitrogen at shell side	30 mol.s^{-1}

4. Result and Discussion

4.1. Membrane Characterization

Fig. 2 displays a result summary of the gas permeation experiments related to H₂, N₂ and CH₄ at 308 K. As can be seen, permselectivity of H₂ over N₂ and CH₄ is near to Knudsen mechanism. More investigation about the effect of temperature on the performance of the membrane showed that over 373 K the permeance of gases except H₂ is not measurable. So this result shows efficient H₂ separation performance of sodalite membrane for membrane reactor applications. Also, the results of gas permeation measurements of benzene, toluene, ethylbenzene and styrene monomer at temperatures higher than their boiling points show no permeation for them. Considering the kinetic diameters of the investigated gases, it can be claimed that the size of intercrystalline pores in the synthesized membrane cannot be higher than 5Å.

The gas permeation results presented in Fig. 3 clearly indicate the pressure independency of H₂ permeance. So the H₂ permeance at high temperatures can be correlated as function of temperature only:

$$\begin{aligned} \text{Permeance} &= 1.925377061 \\ &\times 10^{22} \\ &\times T^{-12.22428129} \end{aligned} \quad (18)$$

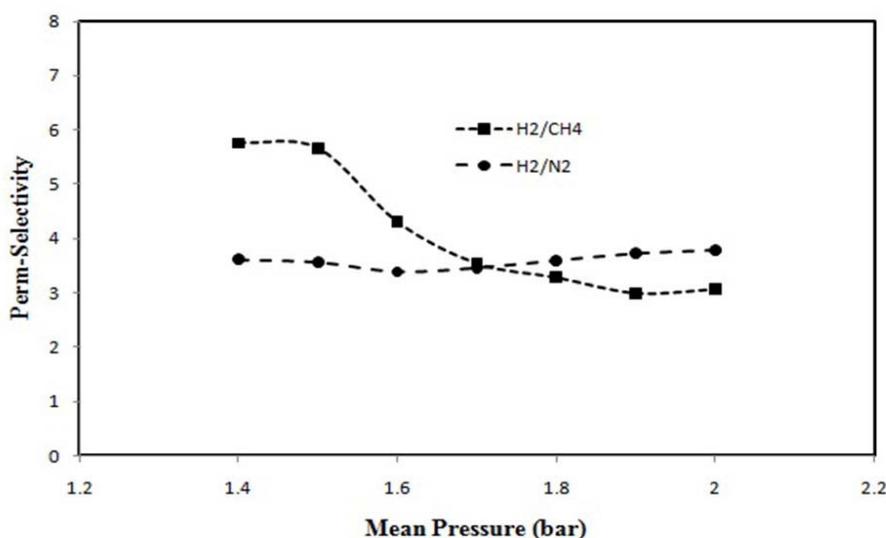


Figure 2: Perm-selectivity of H₂ over N₂ and CH₄ versus average pressure (bar) at 308 K

4.2. Modeling Result

Figs. 4 and 5 show the flow rate profiles of hydrogen and ethylbenzene evolved in a conventional PFR and MR respectively. In the conventional PFR and MR (Fig. 5), ethylbenzene flow rate decreases. But, hydrogen flow rate increases, passes through a maximum and then decreases again due to selective removal through the membrane (tube side) and also consumption in side reactions (Fig. 4). Also, hydrogen permeation rate is much lower than the hydrogen formation rate near the entrance of the reactor and thus the MR operates similar to a conventional PFR because the partial pressure of ethylbenzene and the rate of reaction are high, but the amount of produced hydrogen is low (low driving force for membrane diffusion). It can be concluded that by increasing of hydrogen partial pressure and thus its permeation rate, the MR becomes much more efficient than the PFR. Hydrogen removal from the reaction side (Fig. 4) shifts the equilibrium to the products side and increases the ethylbenzene conversion and decreases the flow rate of ethylbenzene both in PFR and MR.

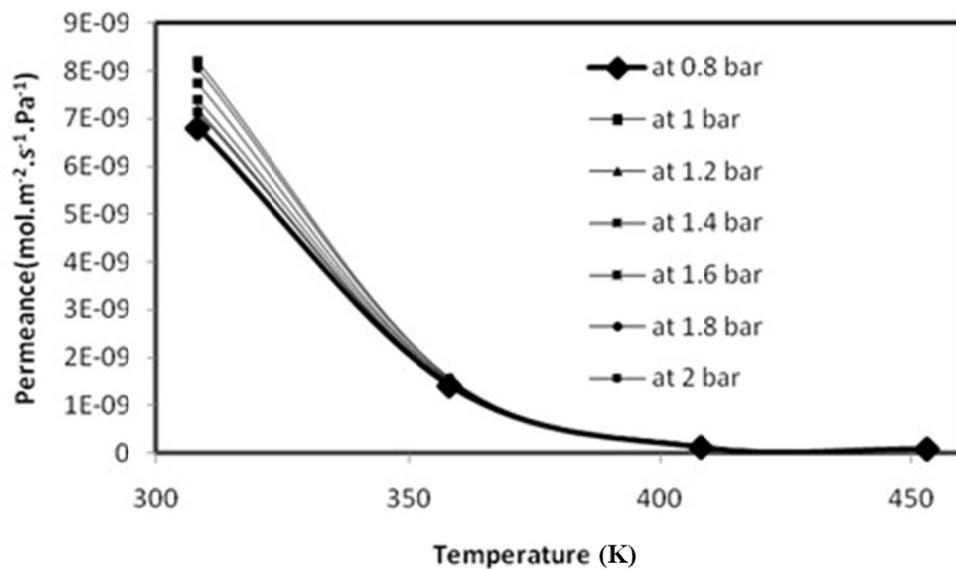


Figure 3: Permeance of H₂ versus temperature at different pressure through the membrane

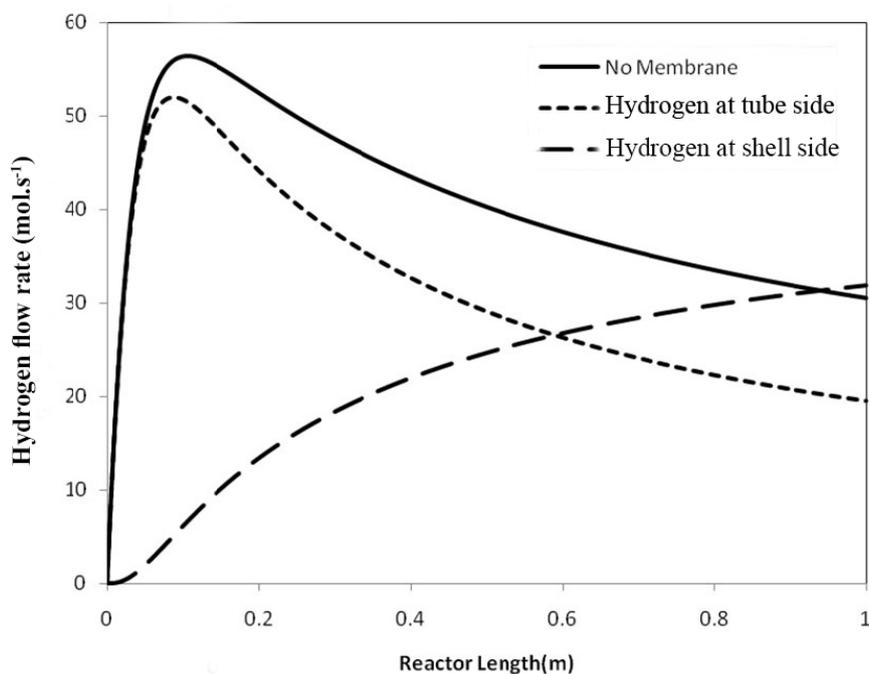


Figure 4: Molar flow of hydrogen on conventional PFR and the sodalite membrane reactor

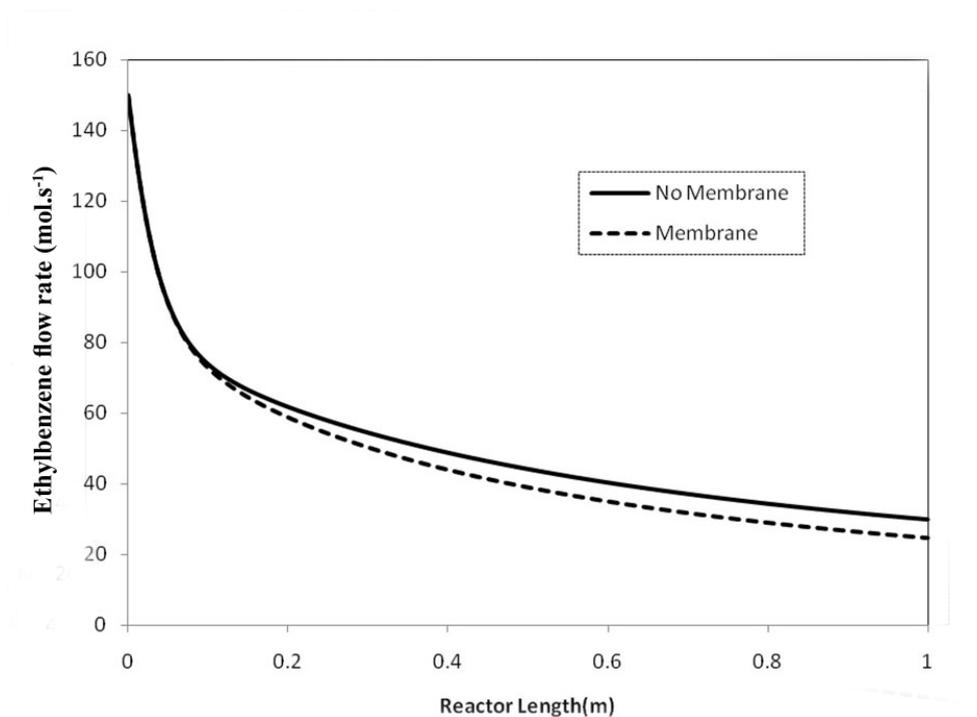


Figure 5: Molar flow of ethylbenzene on conventional PFR and the sodalite membrane reactor

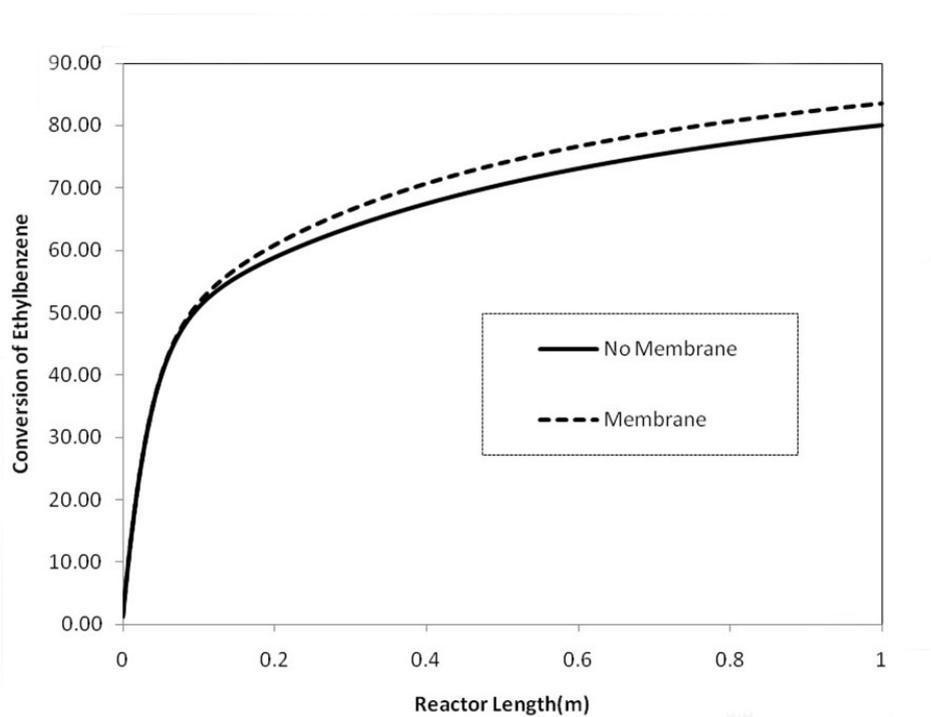


Figure 6: Comparison of ethylbenzene conversions between the conventional PFR and the sodalite membrane reactor

The ethylbenzene conversion and yield of styrene for sodalite membrane reactor and PFR are shown in Figs. 6 and 7. The maximum conversion and yield that can be attained in a conventional PFR at mentioned conditions are about 80% and 44.5% respectively due to thermodynamic limitations. In contrast, the maximum conversion and yield that can be attained in a MR with the characteristics described above, approach 83.45% and 53.49% respectively. So, using sodalite membrane reactor can increase ethylbenzene conversion and yield about 3.45% and 8.99% respectively. The membrane reduces the decreasing of ethylbenzene in MR (due to reduce the side reactions) and increase the yield of styrene in MR in comparison with PFR (Fig. 7).

Fig. 8 shows the temperature of MR and PFR as a function of reactor length. As expected, the temperature decreases with the length of reactors due to the high endothermic reaction of dehydrogenation of ethylbenzene to styrene. As can be seen, the

temperature drop in MR is higher than PFR. This can be explained as membrane performance leads to increase in the conversion of dehydrogenation reaction and so decreases temperature more than PFR.

5. Conclusion

This study focused on the investigation of microporous sodalite membrane, for application of MR in ethylbenzene dehydrogenation. Single gas permeation experiments were used to evaluate the performance of the synthesized membrane. The experimental results revealed that the sodalite membrane has fair potential for dehydrogenation MR applications. A simple model was used to evaluate the MR performance for ethylbenzene dehydrogenation. The modeling results showed that the sodalite membrane reactor is more efficient than a conventional PFR. The magnitude of styrene yield increase which is achieved using sodalite membrane reactor, is appreciable.

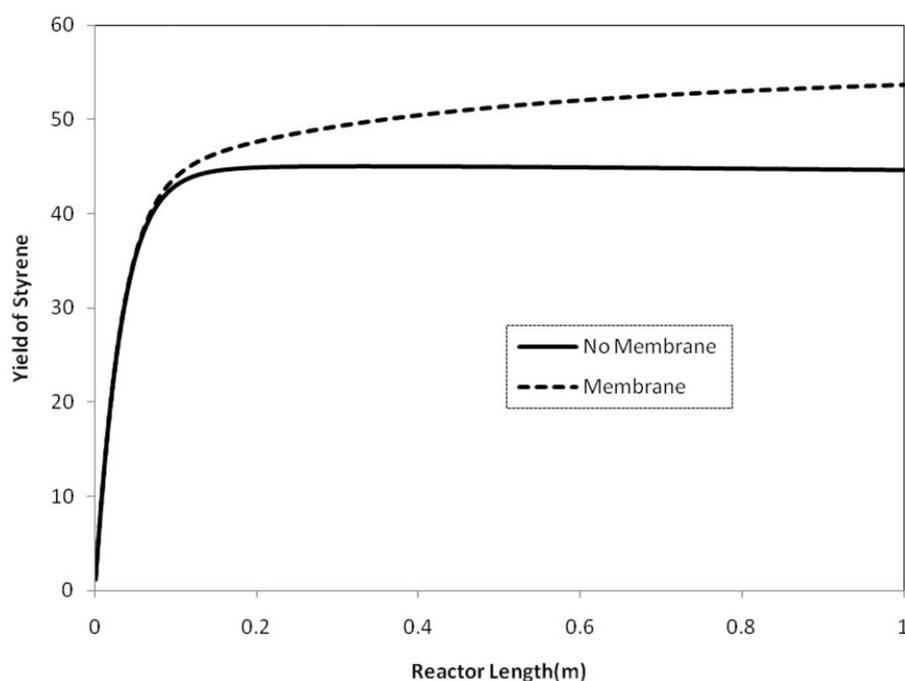


Figure 7: Comparison of styrene yields between the conventional PFR and the sodalite membrane reactor

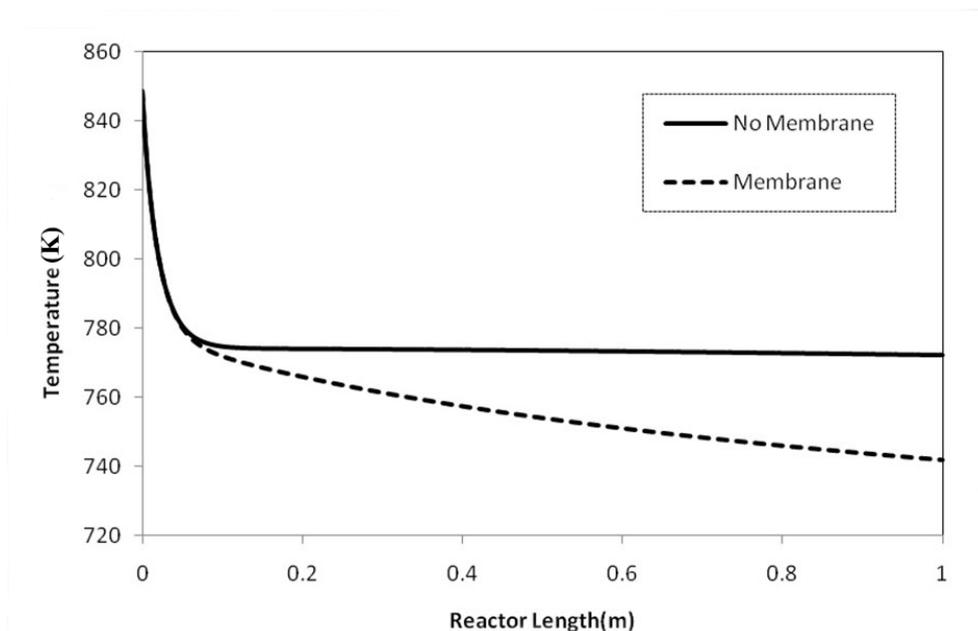


Figure 8: Comparison of temperature drop between the conventional PFR and the sodalite membrane reactor

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Notation

A_i	Frequency Factor, dimensionless
β_{ij}	Stoichiometric coefficient of reactant i in reaction j , dimensionless
C_p	Heat capacity of gaseous mixture in reactor, $J.mol^{-1}.K^{-1}$
E_i	Activation Energy, $kJ.mol^{-1}$
F_{ti}	Molar flow rate of component i at tube side, $mol.s^{-1}$
F_{si}	Molar flow rate of component i at shell side, $mol.s^{-1}$
F_{ti0}	Initial molar flow rate of component i at tube side, $mol.s^{-1}$
F_{si0}	Initial molar flow rate of component i at shell side, $mol.s^{-1}$
F_T	Total molar flow rate of gaseous

	mixture, $mol.s^{-1}$
J_i	Permeance of component i through membrane, $mol.m^{-2}.s^{-1}.bar^{-1}$
ΔH_j	Enthalpy of reaction, $J.mol^{-1}$
N	Number of membrane tube, dimensionless
P_{EB}	Partial pressure of ethylbenzene, bar
P_{SM}	Partial pressure of styrene, bar
P_{H_2}	Partial pressure of hydrogen, bar
P_{si}	Partial pressure of reactant i at shell side, bar
P_{ti}	Partial pressure of reactant i at tube side, bar
P_{sT}	Total pressure at shell side, bar
P_{tT}	Total pressure at tube side, bar
P_{t0}	Initial pressure of tube side at $Z=0$, bar
P_{s0}	Initial pressure of shell side at $Z=0$, bar
ΔP	Pressure difference between shell and tube side, bar
r_i	Rate of reaction i , $mol.s^{-1}.kg$ of cat^{-1}
r_p	Radius of catalyst particle, m
R	Gas constant = $8.314, J.mol^{-1}.K^{-1}$

R_1	Inner diameter of tube, m
T_0	Initial inlet temperature, K
T	Temperature, K
k_i	Rate constant of reaction i , $\text{kmol.kg cat}^{-1}.\text{h}^{-1}$
K_p	Equilibrium constant of main reaction, bar
u_{tz}	Superficial velocity of gas in tube in z direction, m.s^{-1}
y_{si}	Mole fraction of component i in shell, dimensionless
y_{ti}	Mole fraction of component i in tube, dimensionless
Z	Axial direction, m

Greeks Symbol

ϕ	Porosity of catalyst, dimensionless
ϕ_b	Void fraction of packed catalyst bed in reaction side, dimensionless
ρ_{catalyst}	Density of catalyst, kg.m^{-3}
ρ_g	Density of gaseous mixture, kg.m^{-3}
μ_t	Viscosity of gaseous mixture in tube, bar.s

Abbreviation

EB	Ethylbenzene
SM	Styrene monomer

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