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Simulation of pervaporation membrane reactors for liquid phase synthesis of ethyl *tert*-butyl ether from *tert*-butyl alcohol and ethanol

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Abstract

The synthesis of ethyl *tert*-butyl ether (ETBE) from a liquid phase reaction between ethanol (EtOH) ethyl and *tert*-butyl alcohol (TBA) in pervaporation membrane reactors (PVMRs) is discussed in this paper. Three modes of PVMR operation; semi-batch reactor (SBR), continuous stirred tank reactor (CSTR) and plug flow reactor (PFR) were modeled using kinetic parameters of the synthesis over β-zeolite and permeability data for a polyvinyl alcohol (PVA) membrane from our previous work. Good agreement between experimental and simulation results for the SBR mode was obtained. The study focused on comparing PVMR performances between two modes of continuous flow operation for various operating parameters, i.e. ratio of catalyst weight to total molar feed rate (ϕ), ratio of membrane area to catalyst weight (δ), operating temperature and feed composition. It was found that the CSTR mode shows superior performance to the PFR mode only within some ranges of operating conditions. To obtain high ETBE yields, it is best to operate the PVMRs at low temperature with a high ratio of membrane area to catalyst weight (δ) and with the feed ratio of EtOH and TBA at the stoichiometric value or slightly higher.
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Keywords: Simulation; Pervaporation membrane reactor; Pervaporation; ETBE synthesis; Activity coefficient

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1. Introduction

Synthesis of a tertiary ether is a typical example of equilibrium-limited reactions. Presence of H_2O has a strong inhibition effect on catalytic activity and conversion is generally low due to limits imposed by thermodynamics. A combined process of separation and chemical reaction in a single unit operation such as reactive distillation or through use of a pervaporation membrane reactor (PVMR) has been proposed to overcome those limitations. For synthesis of ethyl *tert*-butyl ether (ETBE), it is customary to utilize ethanol (EtOH) and isobutene (IB) as reactants. However, IB is obtained from refinery cracking operations so the supply is limited. Alternatively, *tert*-butyl alcohol (TBA), a major byproduct of propylene oxide production from IB and propylene in the ARCO process, can be employed instead of IB [1]. ETBE can be produced from TBA by either a direct or an indirect method. In the direct method

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Abbreviations: ETBE, ethyl *tert*-butyl ether; EtOH, ethanol; H_2O, water; IB, isobutene; TBA, *tert*-butyl alcohol

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Nomenclature

a_i	activity of species i (–)
A	membrane area (m^2)
f_i	dimensionless molar flow rate of species i in the reaction side (–)
F_i	molar flow rate of species i (mol/s)
k_1	reaction rate constant of reaction (1) in the activity-based model (mol/(kg s))
k_2	reaction rate constant of reaction (2) in the activity-based model (mol/(kg s))
K_1	equilibrium constant of reaction (1) in the activity-based model (–)
K_W	water inhibition parameter in the activity-based model (–)
m_i	number of moles of species i (mol)
n_i	permeation rate of species i (mol/s)
N_i	molar flow rate of species i in the permeate side (mol/s)
$\bar{N}_i$	dimensionless molar flow rate of species i in the permeate side (–)
P_i	permeability coefficient of species i (mol/(m^2 s))
r_j	reaction rate of reaction j (mol/(kg s))
t	reaction time (s)
T	temperature (K)
v	dimensionless reactor volume (–)
V	reactor volume (m^3)
W	catalyst weight (kg)
x_i	mole fraction of species i in liquid mixture (–)

Greek letters

γ_i	activity coefficient of species i (–)
δ	ratio of membrane area to catalyst weight (m^2/kg)
λ	ratio of initial mole of EtOH to TBA (–)
ϕ	ratio of catalyst weight to total molar feed flow rate (kg s/mol)

Subscripts

0	initial value at $t = 0$
T	total

ETBE is produced from TBA and EtOH in one reactor whereas TBA is dehydrated to IB in a first reactor and then reacts with EtOH to produce ETBE in a second reactor in the indirect method. The direct method, which is the reaction route of our interest, is favored because it reduces plant size and complexity [2].

Only a few researchers have dealt with the direct synthesis of ETBE from EtOH and TBA. Yang and Goto [1] considered batch reactive distillation using Amberlyst-15 as a catalyst with and without pervaporation. The use of pervaporation helped remove water so that a higher fraction of ETBE could be obtained in the top product. Quitain et al. [3] used Amberlyst-15 as a catalyst in continuous reactive distillation. Conversion of TBA and selectivity to ETBE of 99.9 and 35.9%, respectively, were obtained. The distillate was further purified by solvent extraction with the column bottom, resulting in a product with 95 mol% ETBE. Later, the same authors described a process for synthesizing ETBE on an industrial-scale using the Aspen Plus simulation program [4]. Our previous work [5] proposed a PVMR in which H_2O was simultaneously removed from the reaction zone via a permselective membrane.

PVMRs have been applied to many other reactions such as esterification of oleic acid with EtOH [6], esterification of acetic acid with EtOH [7,8], esterification of lactic acid with EtOH [9], esterification of acetic acid with *n*-butyl alcohol [10] and dehydration of butanediol to tetrahydrofuran [11]. Most of the previous experimental and simulation studies considered a semi-batch operation [5,12,13]. Few studies discussed a continuous flow operation [8] and no one has attempted to compare the performances of PVMRs operated under different modes of continuous flow operation.

Our objective in this paper is to compare performances of the PVMRs operated under two different continuous modes: as a continuous stirred tank reactor (CSTR) and as a plug flow reactor (PFR). Mathematical models of the synthesis of ETBE from TBA and EtOH are developed. Permeation parameters for a polyvinyl alcohol (PVA) membrane and kinetic parameters for a β-zeolite catalyst were adopted from our previous works [5,14]. The effects of various operating parameters such as ratio of catalyst weight to total molar feed flow rate (ϕ), ratio of membrane area to catalyst weight (δ), operating temperature and feed composition are investigated.

2. Mathematical modeling

The reactions taking place in the reactor can be summarized as follows:

$$TBA_{(l)} + EtOH_{(l)} \Leftrightarrow ETBE_{(l)} + H_2O_{(l)} \tag{1}$$

$$TBA_{(l)} \Leftrightarrow IB_{(g)} + H_2O_{(l)} \tag{2}$$

$$IB_{(l)} + EtOH_{(l)} \Leftrightarrow ETBE_{(l)} \tag{3}$$

The major side reaction of this system is the production of isobutene (IB) gas. Although, IB can simultaneously react with EtOH to form ETBE, the low operating pressure in this study results in just a small amount of dissolved IB in our liquid mixtures. Hence, the reverse reaction in Eq. (2) and the reaction in Eq. (3) can be neglected.

In this study, β-zeolite was selected as a catalyst because it showed superior performance compared to Amberlyst-15. The rate models for the reactions in Eqs. (1) and (2) and the kinetic parameters obtained from our previous study can be expressed as follows [14]:

$$r_1 = k_1 \frac{a_{TBA} a_{EtOH} - a_{ETBE} a_{H_2O}/K_1}{1 + K_W a_{H_2O}} \tag{4}$$

$$r_2 = k_2 \frac{a_{TBA}}{1 + K_W a_{H_2O}} \tag{5}$$

where

$$k_1 = \exp\left(3.55 - \frac{2286}{T}\right) \tag{6}$$

$$k_2 = \exp\left(36.57 - \frac{13653}{T}\right) \tag{7}$$

$$K_W = \exp\left(-16.16 + \frac{6636}{T}\right) \tag{8}$$

$$K_1 = \exp\left(1140 - \frac{14\,580}{T} + 232.9 \ln T + 1.087T - 1.114 \times 10^{-3} T^2 + 5.538 \times 10^{-7} T^3\right) \tag{9}$$

k_1 and k_2 are the reaction rate constants, while K_W and K_1 are the water inhibition parameter and the equilibrium constant, respectively.

The activity can be calculated from the following relation:

$$a_i = \gamma_i x_i \tag{10}$$

where x_i is the mole fraction of species i in the liquid mixture and γ_i the activity coefficient which can be estimated by using the UNIFAC method.

The permeation rate of species i through the PVA membrane (PERVAP 2201 from Sulzer Chemtech GmbH-Membrane Systems) can be expressed as follows [5]:

$$n_i = AP_i a_i \tag{11}$$

$$P_{H_2O} = \exp\left(2.07 - \frac{2441}{T}\right) \tag{12}$$

$$P_{EtOH} = \exp\left(3.25 - \frac{4328}{T}\right) \tag{13}$$

$$P_{TBA} = \exp\left(7.67 - \frac{6434}{T}\right) \tag{14}$$

It is noted that the permeation of ETBE is negligibly small so its permeation was not included in the models.

Mathematical models for the PVMRs were obtained from material balances around the reactors, assuming the reactors behaved ideally. In addition, isothermality was assumed so that an energy balance was not necessary. The sets of equations for different operating modes can be summarized as follows.

Semi-batch mode:

$$\frac{d}{dt} m_{TBA} = -AP_{TBA} a_{TBA} - W(r_1 + r_2) \tag{15}$$

$$\frac{d}{dt} m_{H_2O} = -AP_{H_2O} a_{H_2O} + W(r_1 + r_2) \tag{16}$$

$$\frac{d}{dt} m_{EtOH} = -AP_{EtOH} a_{EtOH} - Wr_1 \tag{17}$$

$$\frac{d}{dt} m_{ETBE} = -AP_{ETBE} a_{ETBE} + Wr_1 \tag{18}$$

PFR mode:

$$\frac{d}{dv} f_{TBA} = -\phi\delta P_{TBA} a_{TBA} - \phi(r_1 + r_2) \tag{19}$$

$$\frac{\mathrm{d}}{\mathrm{d}v} f_{\mathrm{H_2O}} = -\phi\delta P_{\mathrm{H_2O}} a_{\mathrm{H_2O}} + \phi(r_1 + r_2) \tag{20}$$

$$\frac{\mathrm{d}}{\mathrm{d}v} f_{\mathrm{EtOH}} = -\phi\delta P_{\mathrm{EtOH}} a_{\mathrm{EtOH}} - \phi r_1 \tag{21}$$

$$\frac{\mathrm{d}}{\mathrm{d}v} f_{\mathrm{ETBE}} = -\phi\delta P_{\mathrm{ETBE}} a_{\mathrm{ETBE}} + \phi r_1 \tag{22}$$

$$\frac{\mathrm{d}}{\mathrm{d}v} \bar{N}_i = \phi\delta P_i a_i$$

CSTR mode:

$$f_{\mathrm{TBA,0}} - f_{\mathrm{TBA}} - \phi\delta P_{\mathrm{TBA}} a_{\mathrm{TBA}} - \phi(r_1 + r_2) = 0 \tag{23}$$

$$f_{\mathrm{H_2O,0}} - f_{\mathrm{H_2O}} - \phi\delta P_{\mathrm{H_2O}} a_{\mathrm{H_2O}} + \phi(r_1 + r_2) = 0 \tag{24}$$

$$f_{\mathrm{EtOH,0}} - f_{\mathrm{EtOH}} - \phi\delta P_{\mathrm{EtOH}} a_{\mathrm{EtOH}} - \phi r_1 = 0 \tag{25}$$

$$f_{\mathrm{ETBE,0}} - f_{\mathrm{ETBE}} - \phi\delta P_{\mathrm{ETBE}} a_{\mathrm{ETBE}} + \phi r_1 = 0 \tag{26}$$

where $f_i = F_i/F_{\mathrm{T,0}}$, $v = V/V_{\mathrm{T}}$, $\phi = W/F_{\mathrm{T,0}}$, $\bar{N}_i = N_i/F_{\mathrm{T,0}}$ and $\delta = A/W$.

EQUATRAN-G (All-purpose equation solver, Omega Simulation) was employed to solve the equations.

3. Experimental

The experimental setup for the semi-batch PVMR is shown in Fig. 1. The membrane with an effective area of 54 cm^2 was placed between two chambers. A frame holding four catalyst baskets was mounted on a rotating shaft and a disk turbine in the upper chamber while the lower chamber was fed with a N_2 sweep gas at a constant molar flow rate of 7.2×10^{-5} mol/s. The system was maintained at a constant temperature by circulating hot water in jackets around the chambers. A heater with a temperature controller was used to control water temperature while a condenser was attached to the system to condense all vapors leaving the reaction chamber. The frame of the catalyst baskets was held above the liquid level by upper hooks. The disk turbine fully stirred the reaction mixture. After the nitrogen gas flow rate and temperature of the reactant mixture were maintained at a desired value, the reaction was started by changing the direction of agitation so that the catalyst baskets dropped into the liquid mixture. The lower hooks were securely connected with slots on the disk turbine and the frame was rotated without slip. In this way, a start-up time

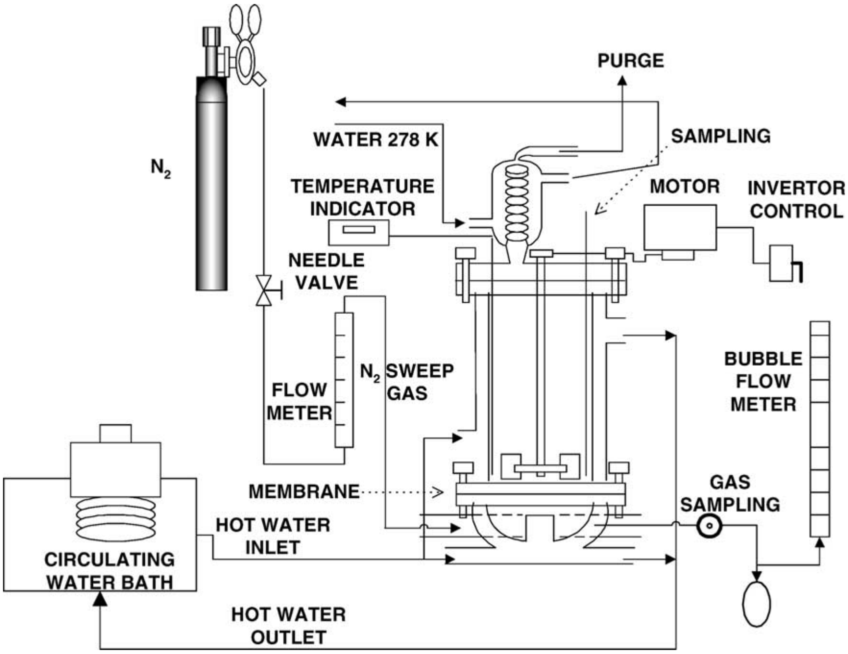

Fig. 1. Experimental setup.

could be accurately measured. The stirring speed was fixed at 1210 rpm to ensure negligible external mass transfer resistance.

4. Results and discussion

4.1. Comparison between simulation and experimental results

The mathematical model was verified by comparing simulation results with the experimental results. Fig. 2 shows the concentration profiles of liquid mixture as a function of time for the PVMR operated under the SBR mode. It is obvious that the model (continuous lines) predicts the experimental results (symbols) very well. Unfortunately, due to the limitation of the equipment, the PVMR models for both the CSTR and PFR modes could not be verified.

4.2. Comparison between PVMRs and conventional reactors

Figs. 3 and 4 show the yield and the selectivity, respectively, as a function of ratio of catalyst weight to total molar feed flow rate (ϕ). The ETBE yield and ETBE selectivity are defined as follows:

$$\text{yield} = \frac{F_{\text{ETBE}} - F_{\text{ETBE},0}}{F_{\text{TBA},0}}$$

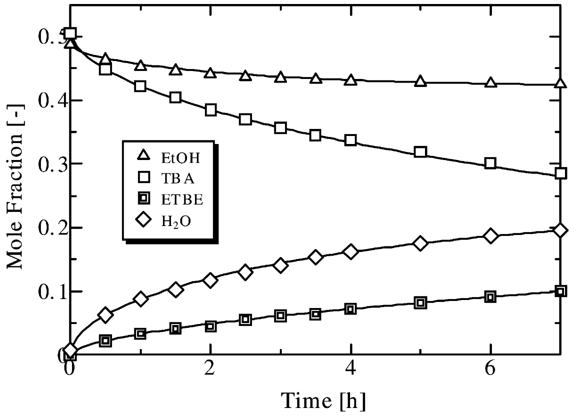

Fig. 2. Concentration profiles with reaction time in the SBR mode (β-zeolite catalyst weight = 0.0015 kg, $m_{\text{TBA},0} = 2.02$ mol, $m_{\text{EtOH},0} = 1.95$ mol, $m_{\text{ETBE},0} = 0$ mol, $m_{\text{H_2O},0} = 0.03$ mol, $A = 0.0054\,\text{m}^2$ and $T = 343$ K).

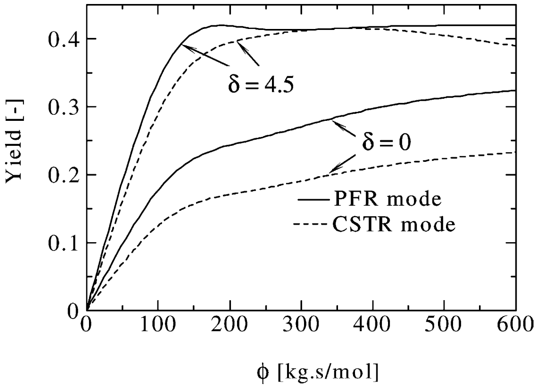

Fig. 3. Comparison between conventional reactors and PVMRs operated in the PFR and CSTR modes on ETBE yield at various ratios of catalyst weight to total molar feed flow rate (ϕ) ($F_{\text{TBA},0} = 3.3 \times 10^{-5}$ mol/s, $F_{\text{EtOH},0} = 3.3 \times 10^{-5}$ mol/s, $F_{\text{ETBE},0} = 0$ mol/s, $F_{\text{H_2O},0} = 0$ mol/s and $T = 343$ K).

$$\text{selectivity} = \frac{F_{\text{ETBE}} - F_{\text{ETBE},0}}{F_{\text{TBA},0} - F_{\text{TBA}}}$$

The case when the ratio of membrane area to catalyst weight $\delta = 0$ represents the conventional reactors without a membrane. It is obvious that the PVMRs showed superior performances to that of a conventional reactor. Removal of H_2O from the reaction system through the membrane improved the ETBE yield by shifting the equilibrium conversion and increasing

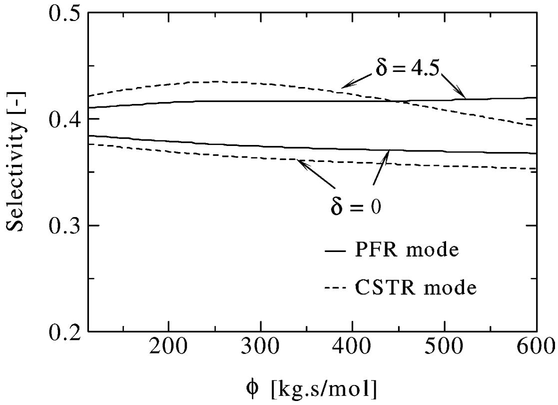

Fig. 4. Comparison between conventional reactors and PVMRs operated in the PFR and CSTR modes on the ETBE selectivity at various ratios of catalyst weight to total molar feed flow rate (ϕ) ($F_{\text{TBA},0} = 3.3 \times 10^{-5}$ mol/s, $F_{\text{EtOH},0} = 3.3 \times 10^{-5}$ mol/s, $F_{\text{ETBE},0} = 0$ mol/s, $F_{\text{H_2O},0} = 0$ mol/s and $T = 343$ K).

the reaction rate through suppressing the backward reaction and water inhibition. In addition, because the forward rate of the undesired side reaction was promoted to a relatively lower extent than the rate of the desired reaction, PVMRs offered higher ETBE selectivity than a conventional reactor as may be observed in Fig. 4. It should be noted that the conventional PFR provided a higher ETBE yield than the conventional CSTR as expected because reactant concentrations were at their minimum values in the reactor so that, the reaction proceeds at the lowest rate. However, differences in yield between these modes were less pronounced in the PVMR because of the effect of product removal and/or reactant loss.

4.3. Effect of ratio of membrane area to catalyst weight

Figs. 5 and 6 show the effect of the ratio of membrane area to catalyst weight ($\delta = A/W$) at three ratios of catalyst weight to total molar feed flow rate ($\phi = 112.5$, 272 and 600 kg s/mol). It can be seen that for the PFR mode, the yield and selectivity increased with increasing the ratio of membrane area to catalyst weight (δ) and then leveled off at high values. For the CSTR mode, yield and selectivity increased initially to maximums and then dropped at high values of δ. The drop of ETBE yield was not observed in the PFR mode due to the complete conversion of TBA in the reaction chamber. After the complete consumption of TBA, the rest of the reactor behaved as a separator. The existence of optimum ratios of membrane area to catalyst weight (δ) was especially obvious for the case with high value of catalyst weight to total molar feed flow rate (ϕ) for the CSTR mode. The optimum resulted from the well-mixed characteristic of the CSTR. Increasing the ratio of membrane area to catalyst weight (δ) initially improved the selectivity because more H_2O was removed from the reaction system and, as a result, the selectivity increased. However, further increase of the ratio enhanced reactant losses, leading to the decrease in selectivity. It should be noted that at high values of ratio of catalyst weight to total molar feed flow rate ($\phi = 600$ kg s/mol), there were ranges of operating conditions where the CSTR mode offered higher yield than the PFR mode.

Generally, a PVMR is more complicated than a conventional reactor because reaction and separation functions take place simultaneously in the reactor. As a result, various competing effects need to be taken into account. Considering the case with $\phi = 600$ kg s/mol, at low value of the ratio of membrane area to catalyst weight (δ), the system behaves much like a conventional reactor in which a PFR is superior to a CSTR due to the small membrane area. At moderate values of this ratio, the effect of H_2O removal and reactant losses play more important roles. Figs. 7 and 8 show

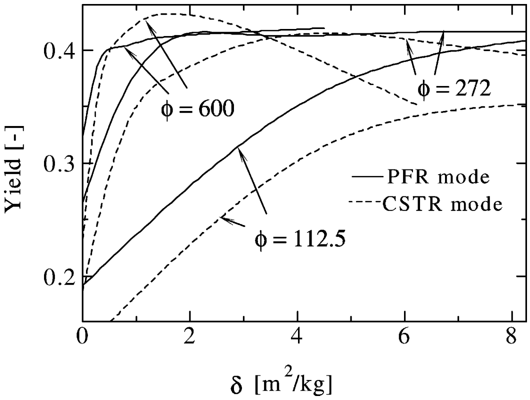

Fig. 5. Effect of the ratio of membrane area to catalyst weight (δ) at different ratios of catalyst weight to total molar feed flow rate (ϕ) on ETBE yield ($F_{TBA,0} = 3.3 \times 10^{-5}$ mol/s, $F_{EtOH,0} = 3.3\times10^{-5}$ mol/s, $F_{ETBE,0} = 0$ mol/s, $F_{H_2O,0} = 0$ mol/s and $T = 343$ K).

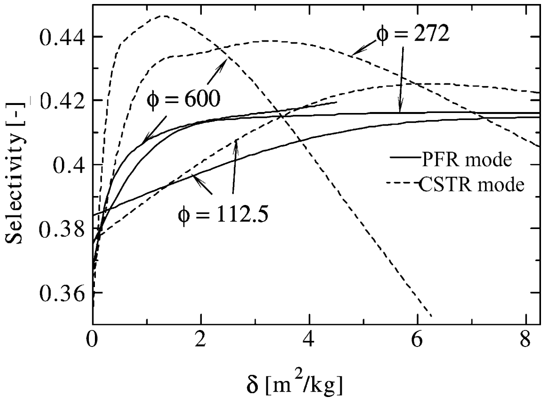

Fig. 6. Effect of the ratio of membrane area to catalyst weight (δ) at different ratios of catalyst weight to total molar feed flow rate (ϕ) on ETBE selectivity ($F_{TBA,0} = 3.3 \times 10^{-5}$ mol/s, $F_{EtOH,0} = 3.3\times10^{-5}$ mol/s, $F_{ETBE,0} = 0$ mol/s, $F_{H_2O,0} = 0$ mol/s and $T = 343$ K).

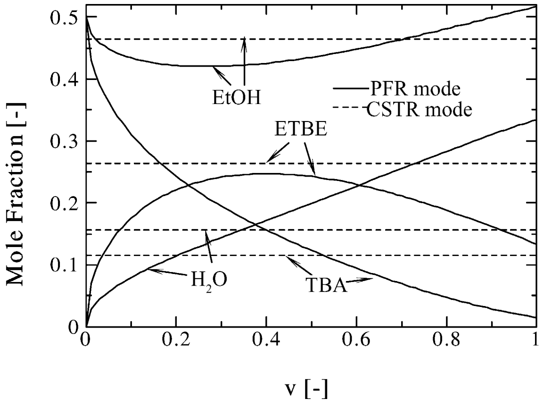

Fig. 7. Mole fraction profiles with reactor volume ($\phi = 600$ kg s/mol, $\delta = 0.25\,\text{m}^2/\text{kg}$, $F_{\text{TBA},0} = 3.3 \times 10^{-5}$ mol/s, $F_{\text{EtOH},0} = 3.3 \times 10^{-5}$ mol/s, $F_{\text{ETBE},0} = 0$ mol/s, $F_{\text{H}_2\text{O},0} = 0$ mol/s and $T = 343$ K).

the mole fraction profiles of each species as functions of reactor volume for the cases with $\delta = 0.25$ and $1.75\,\text{m}^2/\text{kg}$, respectively. The continuous lines represent results for the PFR mode while the dashed lines show these values at the exit of the CSTR mode. It can be seen that for the PFR mode, the H_2O concentration increased with the reactor volume for $\delta = 0.25\,\text{m}^2/\text{kg}$; however, at higher membrane area ($\delta = 1.75\,\text{m}^2/\text{kg}$) it increased and then deceased due to H_2O removal through the membrane. Comparing operating modes, the mole fraction of H_2O in the PFR mode is usually higher than for the CSTR before the complete disappearance of TBA in the reaction mixture. This explains the superior selectivity for the CSTR mode found in Fig. 6, since in the CSTR mode the water concentration remains at its lowest value throughout the reactor. Then, the forward reaction to form ETBE is promoted to a higher extent than in the PFR mode. When the membrane area is further increased while the catalyst weight remained unchanged, the rate of reactant loss predominates and, consequently, the poor performance is observed.

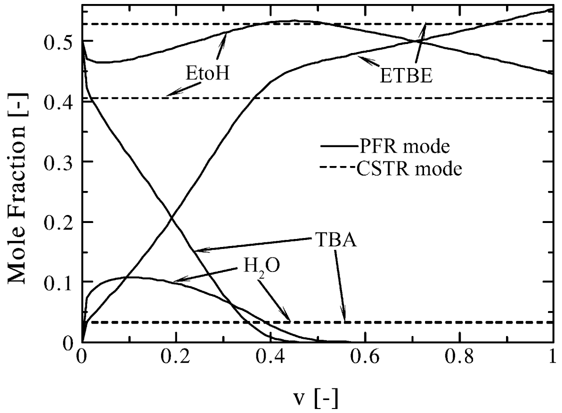

Fig. 8. Mole fraction profiles with reactor volume ($\phi = 600$ kg s/mol, $\delta = 1.75\,\text{m}^2/\text{kg}$, $F_{\text{TBA},0} = 3.3 \times 10^{-5}$ mol/s, $F_{\text{EtOH},0} = 3.3 \times 10^{-5}$ mol/s, $F_{\text{ETBE},0} = 0$ mol/s, $F_{\text{H}_2\text{O},0} = 0$ mol/s and $T = 343$ K).

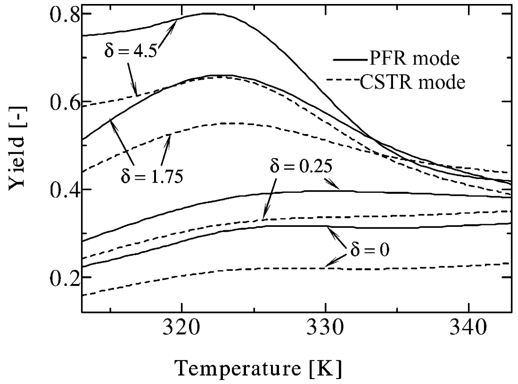

Fig. 9. Effect of temperature on the ETBE yield at different ratios of membrane area to total molar feed flow rate (δ) ($\phi = 600$ kg s/mol, $F_{\text{TBA},0} = 3.3 \times 10^{-5}$ mol/s, $F_{\text{EtOH},0} = 3.3 \times 10^{-5}$ mol/s, $F_{\text{ETBE},0} = 0$ mol/s and $F_{\text{H}_2\text{O},0} = 0$ mol/s).

4.4. *Effect of operating temperature*

The effect of operating temperature is shown in Fig. 9. Within the range studied, it can be seen that at high values of the ratio of membrane area to catalyst weight ($\delta \geq 1.75\,\text{m}^2/\text{kg}$), there is an optimum operating temperatures for each value of δ. Operating temperature influences the rates and selectivities of both the reactions and permeation. Reaction selectivity dropped significantly with increasing temperature (not shown) because the activation energy of the side reaction ($E_a = 113.5$ kJ/mol) was higher than that of the desired reaction ($E_a = 19$ kJ/mol). The rate of H_2O removal improves with increasing temperature but the reactant loss (EtOH) is greatly enhanced as shown in Fig. 10 for the case with $\delta = 4.5\,\text{m}^2/\text{kg}$. Thus, optimum values of operating temperature are observed. From these results, it should be noted that it is better

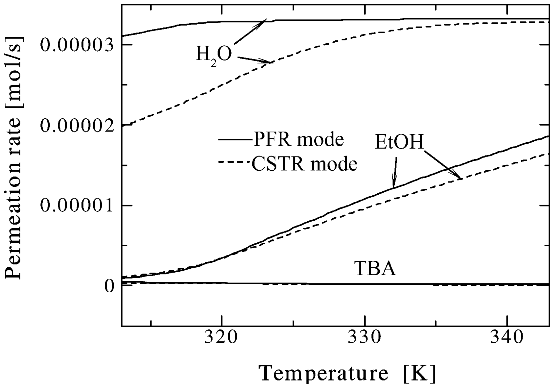

Fig. 10. Effect of temperature on permeation rate ($\phi = 600$ kg s/mol, $\delta = 4.5\,\text{m}^2/\text{kg}$, $F_{\text{TBA},0} = 3.3 \times 10^{-5}$ mol/s, $F_{\text{EtOH},0} = 3.3 \times 10^{-5}$ mol/s, $F_{\text{ETBE},0} = 0$ mol/s and $F_{\text{H}_2\text{O},0} = 0$ mol/s).

to operate PVMRs at low temperature with a high ratio of membrane area to catalyst weight (δ) to obtain high yield.

Comparison between modes of operation reveal that at low operating temperature ($T < 333$ K), the PFR mode always provided higher yield than the CSTR mode for all ranges of the ratio of membrane area to catalyst weight (δ). However, at high operating temperature, there are some ranges of the ratio of membrane area to catalyst weight (δ) in which the CSTR mode offers higher yield than the PFR mode but the difference is not large and the corresponding yields are low.

4.5. *Effect of reactant feed ratio*

Because the dehydration of TBA to IB takes place in parallel to the ETBE reaction, it is possible to improve the ETBE selectivity and yield by increasing the EtOH concentration. Fig. 11 shows the effect of reactant feed ratio ($\lambda = F_{\text{ETOH},0}/F_{\text{TBA},0}$) on the ETBE yield at various ratios of membrane area to catalyst weight (δ). The molar feed rate of TBA was fixed at 3.3×10^{-5} mol/s. It was found that the ETBE yield increased with increasing reactant feed ratio (λ) for both operation modes but the improvement was less pronounced after reaching the stoichiometric ratio ($\lambda = 1$). Slight decrease of ETBE yield can be seen at high ratio of membrane area to catalyst weight (δ). This behavior may be due to decreased rates of reaction and H_2O removal because of dilution.

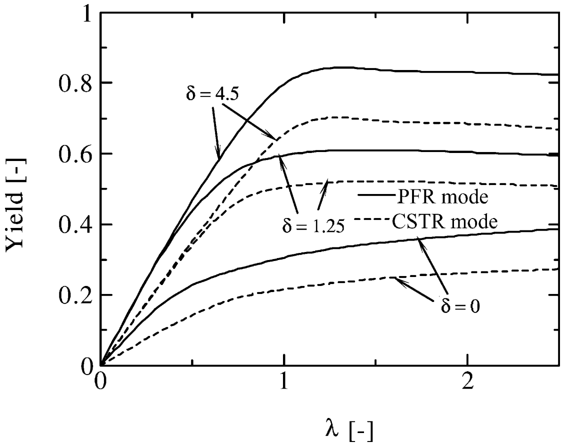

Fig. 11. Effect of the ratio of initial mole of EtOH to TBA (λ) on ETBE yield at different ratios of membrane area to total molar feed flow rate (δ) (β-zeolite catalyst weight = 40 g, $F_{\text{TBA},0} = 3.3 \times 10^{-5}$ mol/s, $F_{\text{ETBE},0} = 0$ mol/s, $F_{\text{H}_2\text{O},0} = 0$ mol/s and $T = 323$ K).

5. Conclusion

Modeling the synthesis of ETBE from TBA and EtOH in PVMRs demonstrates:

(1) PVMRs are superior to the conventional reactors due to selective removal of H_2O from the reaction mixture.
(2) PFR mode of PVMR operation is preferable to the CSTR mode although there are some ranges of operating conditions where the CSTR mode offered higher yield but this occurred at low yields.
(3) Operating temperature is a key parameter determining reaction selectivity. Operation of PVMRs at low temperature with a high ratio of membrane area to catalyst weight (δ) is desirable.
(4) Feed ratios of EtOH and TBA at the stoichiometric value or slightly higher leads to higher ETBE yields.

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