

비완전 막분리시 투과증발 막촉진 에스터화 반응 거동 연구

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A Characterization of Pervaporation-facilitated Esterification Reaction with non-perfect Separation

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요 약: 불완전 분리의 실질적인 분리투과 특성을 근거로 하는 모사모델을 이용하여 투과증발 막촉진 에스터화 반응의 실질적인 거동을 연구하였다. 막의 분리효율, 막의 물제거 능력을 모델에 포함시킴으로써 반응모사를 통하여 이들이 막촉진반응에 어떻게 영향을 끼치는지를 체계적으로 관찰할 수 있었다. 막을 통한 비완전분리가 일어날 경우에 초기 반응물 몰비율이 1이 아닐 때 반응 혼합물중 소량으로 존재하는 반응성분이 투과되거나, 혹은 초기 반응물 몰비율이 1인 반응 혼합물중 어느 반응성분이 투과되든지 반응이 완결될 수 없었다. 생성물인 에스터가 물과 함께 일부 투과될 경우 정방향 반응속도를 증가시켜 시간에 따른 반응 전환율을 증가시킨다. 막을 통한 불완전 분리시 막을 통한 투과로 인하여 발생하는 반응혼합물의 부피감소로 인하여 반응성분 뿐 아니라 생성성분의 농도가 증가되는데 이들 농도증가가 반응속도에 상반된 영향을 끼친다; 반응물 농축은 반응속도를 증가시키나 생성물 농축은 역방향의 반응을 촉진시킴으로서 반응속도를 감소시킨다. 반응초기에는 반응물 농축효과가 우세하나 반응이 진행됨에 따라 생성물 농축효과가 우세하여 반응속도를 저하시킴이 모사결과 관찰되었다.

Abstract: Pervaporation-facilitated esterification with slow reaction regime was characterized by using a practical model based on non-perfect separation through membrane. A non-perfect separation in which the membrane is not perfectly permselective to water was applied to the model. Thus, membrane selectivity and membrane capability to remove water were included in the simulation model to explain how they influence the membrane-facilitated reaction process and improve the reactor performance. It was shown by simulation that in the reaction systems with non-perfect separation, reaction completion can hardly be achievable when any reactant at initial molar ratio=1 or the less abundant reactant at initial molar ratio>1 permeates through membrane, and the permeation of ester accelerates the forward reaction and increase reaction conversion at any instant through removal of product species like water. The volume change causes concentrating both reactants and products that affect the reaction with time in opposite ways; reactant-concentrating effect is dominant during the initial stage of reaction, increasing the reaction rate, and then concentrating product influences more reaction by decreasing the reaction rate.

Keywords: membrane reactor, esterification, pervaporation, facilitated reaction, dehydration

1. Introduction

Esterification of carboxylic acid and alcohol is a typical equilibrium-limited reaction that produces water as by-product. The reaction conversion cannot be reached

to a high level because of thermodynamically limited equilibrium. To increase the conversion, the equilibrium point should be shifted by either using an excess of one of reactants or removing products. The use of an excess of reactant causes to increase reaction cost by both usage of more reactant and additional treatments to separate the excess reactant after reaction. Pervapo-

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ration (PV) is a technique that allows the separation of liquid mixtures through a polymeric membrane. Now that membrane process has been proven in the dehydration application of organic compounds, coming of age as a dehydration separation process, attention is turning to separations closer to the chemical reaction step more critical to production and promising much greater benefits. The pervaporative dehydration begins to be applied in the esterification reaction to remove water, one of the products of the esterification reaction "in situ" and enhance the conversion through shifting the equilibrium point. Since separation membranes permit selective permeation of a component from a mixture, the separation of one or more reaction product species can increase the conversion of the reversible reaction that is thermodynamically or kinetically limited, promising quantum improvements in reaction efficiencies, yields and process economics - the reaction runs faster, lower residence times suffice, equipment costs are minimized and side reactions are reduced. The membrane processes widely used in membrane reactor are gas separation[1,2], reverse osmosis, vapor permeation[3] and pervaporation[4-6].

Most of the models[6-8] presented so far of PV membrane reactors describe both the kinetics and membrane permeation under an assumption of a perfect dehydration separation in which only water permeates through membrane. Kita and coworkers[9] have investigated PV membrane reactor, considering the effects of volume change, sampling loss of reaction mixture, and the permeation of water and ethanol on the reaction kinetics in: the esterification of ethanol and oleic acid. In real PV membrane reactors[4,8], 90-97% of accumulated permeate was water and the rest organic species, indicating that some organic reactants (acid and alcohol) were permeated and lost into the permeate side. The loss of reactants might affect the reaction kinetics under a certain operating condition, especially large membrane area, large permeation flux and/or low membrane selectivity. Thus, proper care must be taken for the non-perfect separation effects on PV-aided reaction. In previous study[10], model equation

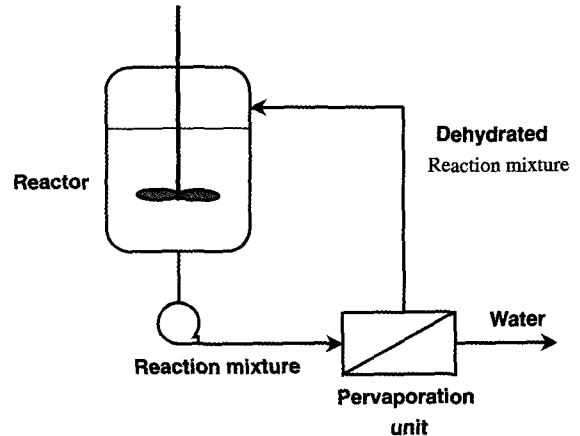


Fig. 1. A batchwise membrane reactor that integrates a batch reactor with a membrane unit.

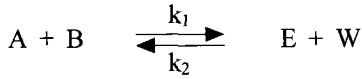
was successfully established to describe the practical reaction behavior of PV-facilitated esterification based on non-perfect separation. The study demonstrated how the permeability and separation efficiency of PV unit influence the reaction rate and conversion in the esterification of ethanol and oleic acid, which is categorized as one of fast reaction systems.

This work is a continuation of PV-aided esterification reaction with non-perfect separation, focused on a parametric study to investigate the practical behavior of a different esterification taking place in slow reaction regime. A simple configuration of batch reactor integrated with pervaporation was chosen as model membrane reactor system as depicted in Figure 1. With help of the established model of PV-aided esterification, more realistic reaction behaviors were investigated with separation characteristics. The model involves the effects of the volume change of reaction mixture due to mass permeation through membrane, the permeation of individual species and membrane selectivity with time. Thus, a non-perfect separation system was applied to the model to investigate how it influences the membrane-facilitated reaction process and improves the reactor performance. Also, The practical reaction behaviors at different reaction conditions were also analyzed with help of the simulation of the established model. The esterification reaction between benzyl alcohol and acetic acid was chosen as model reaction

and investigated theoretically, by using reaction parameters available in publication[8].

2. Theory

A typical esterification reaction can be schematically represented by;



where A and B refer to alcohol and acid, and E and W to ester and water, respectively. k_1 and k_2 denote the rate constants for forward and reverse reactions, respectively. The reaction is carried out in a discontinuous reactor equipped with a pervaporation unit as described in Figure 1. Assume isothermal operation and negligible change in the number of moles of the catalyst. A mass balance on any reactant or product species at any instant is described as follows;

$$\frac{d(C_i V)}{dt} = r_i V - J_i A_m \quad (1)$$

where C denotes the concentration, subscript i species i , t the reaction time, r the reaction rate in the reactor, and V the volume of reaction mixture. J and A_m are the permeation rate and the membrane area, respectively. According to the general expression for a second order reversible reaction, the reaction rate with respect of any species i is expressed as;

$$r_i = \pm k_1 \left(C_A C_B - \frac{C_E C_W}{K_e} \right) \quad (2)$$

where K_e is the equilibrium constant defined as k_1/k_2 . Positive sign is taken for product species to be formed and negative sign is for reactant species to be consumed in the reaction. Considering that the PV module consists of a hydrophilic membrane through which water permeates preferentially, the permeation flux of species i through the membrane is given as;

$$J_i = y_i J_T = \frac{y_i}{y_w} J_w \quad (3)$$

where y denotes the mole fraction in permeate and subscript T refers to the total permeation. Water flux can approximate to the following proportional relationship with water concentration in the mixture mixture.

$$J_w = P_w C_w \quad (4)$$

The proportional coefficient P_w characterizes membrane permeability. This approximation is normally true for dehydration when water content in the mixture is not very high[4-6,9]. Combining Eqs (3) and (4) yields

$$J_i = \frac{y_i}{y_w} \frac{C_w}{C_i} P_w C_i = \alpha_{i/w} P_w C_i \quad (5)$$

$$\alpha_{i/w} = \frac{y_i/y_w}{C_i/C_w} \quad (6)$$

where $\alpha_{i/w}$ denotes the selectivity to species i over water component. Selectivity in pervaporation does not have any specific dependence on feed composition but it is reported[9,11] that the selectivity remains almost constant for a binary system of water-alcohol in esterification of alcohol and carboxylic acid. Thus, for simplicity, the selectivity is assumed to be constant during the process. As a result, the permeation flux of species i can be expressed as a function of water permeability, selectivity over water, and its concentration.

The number of moles of each species in the reactor at any instant N_i is affected by both the formation (or consumption) of the species by chemical reaction and the permeation of the component through membrane;

$$\begin{aligned} N_i &= C_i V \\ &= \text{initial moles} \pm \text{moles produced by reaction} \\ &\quad - \text{moles permeating through membrane} \end{aligned} \quad (7)$$

where negative sign indicates the formation of the species and positive sign the formation of the species. The number of moles or concentration of species with

the extent of reaction is given by

$$C_i V / V_0 = C_{i0}(R_i \pm X) - \vartheta_w \alpha_{i/w} \int_0^t C_i dt \quad (8)$$

where

$$\vartheta_w = \frac{P_w A_m}{V_0} \quad (9)$$

$$R_i = \frac{C_{i0}}{C_{A0}} \quad (10)$$

C_{i0} and C_{A0} are initial concentrations of species i and A , respectively. Let A be less abundant reactant, whose initial concentration is C_0 ($= C_{A0}$), as basis. X is the conversion at any time t . The parameter ϑ_w that constitutes membrane parameter P_w and operating parameters A_m and V_0 is a measure of the capacity of the membrane unit for removing water from the reactor. R_i is defined as initial molar ratio of species i to species A . The membrane parameters, membrane permeability ϑ_w and membrane selectivity are $\alpha_{i/w}$ treated as a constant with reaction time as explained previously. Now, both the membrane unit capacity and its separation factor over water are involved with the other parameters in the relationship to describe the moles or concentration of a species with the extent of reaction, which makes it possible to express the dependence of reaction on these two factors.

Defining the dimensionless parameters

$$Y_i = \frac{C_i}{C_0} \quad (11)$$

$$\Psi = \frac{V}{V_0} \quad (12)$$

and rewriting Eq. (2) and (8) yield, respectively,

$$r_i = \pm k_1 C_0^2 \left(Y_A Y_B - \frac{Y_E Y_W}{K_e} \right) \quad (13)$$

$$Y_i \Psi = (R_i \pm X) - \vartheta_w \alpha_{i/w} \int_0^t Y_i dt \quad (14)$$

Differentiating Eq. (14) with respect to reaction time t and combining Eqs (1), (13) and (14) give,

$$\frac{dX}{dt} = \Psi k_1 C_0 \left(Y_A Y_B - \frac{Y_E Y_W}{K_e} \right) \quad (15)$$

$$\frac{dY_i}{dt} = \frac{1}{\Psi} \left(\pm \frac{dX}{dt} - Y_i \frac{d\Psi}{dt} - \vartheta_w \alpha_{i/w} Y_i \right) \quad (16)$$

The dimensionless concentration of species i , Y_i , can be obtained from Eq. (14). The volume of the reaction mixture at time t can be calculated by addition of each species volume;

$$V = \sum_i N_i \frac{M_i}{\rho_i} \quad (17)$$

where M_i and ρ_i are the molar mass and density of species i , respectively. From Eqs (7), (8) and (17), the dimensionless parameter is derived as follows;

$$\Psi = \frac{\sum_i (R_i \pm X) \frac{M_i}{\rho_i} - \vartheta_w \sum_i \alpha_{i/w} \frac{M_i}{\rho_i} \int_0^t Y_i dt}{\sum_i R_i \frac{M_i}{\rho_i}} \quad (18)$$

Eq (18) indicates that the volume of the reaction mixture changes due to the chemical reaction and mass permeation through membrane as expressed in the first and second terms on the right side of the equation, respectively. In previous study [10], it is found that the volume change due to chemical reaction is negligible;

$$\frac{\sum_i (R_i \pm X) \frac{M_i}{\rho_i}}{\sum_i R_i \frac{M_i}{\rho_i}} \cong 1 \quad (19)$$

Therefore, the differentiation form of Eq. (18) is given by

$$\frac{d\Psi}{dt} = - \frac{\vartheta_w \sum_i \left(\alpha_{i/w} \frac{Y_i M_i}{\rho_i} \right)}{\sum_i R_i \frac{M_i}{\rho_i}} \quad (20)$$

From Eqs (5) and (9), the permeation amount of species i , Q_i , for permeating time t can be obtained as follows

$$Q_i = A_m \int_0^t J_i dt \quad (21)$$

$$= C_0 V_0 \delta_{iW} \alpha_{iW} \int_0^t Y_i dt$$

The concentration of a catalyst may change through changing the reaction mixture volume although the catalyst is not consumed in the reaction or not permeates through membrane. In previous study [10], the reaction rate with a homogeneous catalyst system was obtained as follows;

$$\frac{dX}{dt} = k_{Cl} C_{C0} C_0 \left(Y_A Y_B - \frac{Y_E Y_W}{K_e} \right) \quad (22)$$

where k_{Cl} denotes rate constant for forward reaction and C_{C0} initial catalyst concentration. The above equation indicates that reaction rate is more likely to be dependent on the initial catalyst concentration rather than the catalyst concentration at any instant.

Now at a given time the parameters X , Y_i and ψ can be readily obtained by solving Eqs (15)-(20) numerically. The initial conditions are at $t = 0$;

$$X_0 = 0, Y_{A0} = 1, Y_{B0} = R_b, Y_{E0} = Y_{W0} = 0, \psi_0 = 0$$

Reaction volume change, membrane selectivity and membrane capability to remove water are included in the simulation model to explain how they influence the membrane-facilitated reaction process and improve the reactor performance.

3. Results and Discussion

To demonstrate esterification reaction behavior with membrane unit capacity and separation efficiency in the simulation, the esterification reaction between benzyl alcohol and acetic acid catalyzed by p-toluenesulfonic acid is taken as model reaction, by using the parameters, $k_{Cl} = 1.2 \times 10^{-5} \text{ m}^3/(\text{mol}\cdot\text{h})$, $K_e = 2.7$, $\rho_A = 1014$, $\rho_B =$

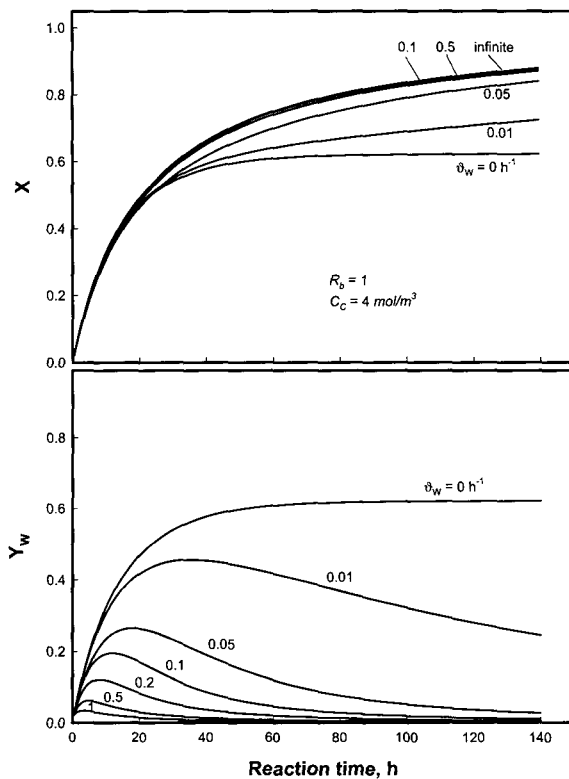


Fig. 2. Plots of reaction conversion and dimensionless water concentration with reaction time in PV-aided reaction with perfect separation at different membrane unit capacities; $C_0 = 1000 \text{ mol/m}^3$, $C_{C0} = 4 \text{ mol/m}^3$, and $R_b = 1$.

989, $\rho_E = 1009$, $\rho_W = 970 \text{ kg/m}^3$, which are representative of the esterification of oleic acid and ethanol at 70°C [8]. These kinetic parameters will be used throughout this study unless specified otherwise.

PV-aided Reaction with Perfect Separation

Figure 2 shows the plots of reaction conversion and water concentration in the reaction mixture against reaction time, which are calculated in PV-aided reaction with perfect separation at different membrane unit capacities. It is observed that the conversion of the PV-facilitated reaction goes beyond the equilibrium conversion that would be obtained as maximum conversion if membrane dehydration were not employed. At a given reaction time, as the value of membrane unit capacity increases, the corresponding conversion increases from the equilibrium value and then asymptotically approaches the curve labeled with "infinite."

This increasing of conversion is obviously attributed to removing of more water that accelerates the forward reaction and then increasingly facilitates the reaction. Thus, the two conversion curves labeled as infinite and 0 in the figure represent the upper and lower limits of the conversion to be reached, respectively, in PV-aided membrane reactor. Looking at the plots of dimensionless water concentration, it undergoes a maximum as reaction proceeds with time in the reactor coupled with pervaporation. The parabolic curve shape of water concentration is a result of two competing opposite processes taking place simultaneously: water formation by reaction, which causes the build-up of water concentration, and water removal by pervaporation, which lowers water concentration in the reactor. At the beginning stage of the reaction, the rate of water formation is at maximum due to the fastest chemical reaction while the rate of water removal is not as high as the water formation because of low water concentration. Consequently, water concentration increases in the reactor. Thereafter, water removal is faster than its formation, so that water becomes depleted in the reactor, resulting in increasingly facilitating the reaction. As membrane unit capacity is larger, the concentration curve changes; shifting its maximum point into shorter reaction time and decreasing the value of the point as a result of removing more water. In other words, the increase in membrane unit capacity leads to a decrease in the area under the curve representing water concentration versus time, i.e. to a lesser accumulation of water in the reactor; this lower accumulation favors increasing forward reaction because it reduces the ester hydrolysis. Since the membrane unit capacity is a parameter that is combined by the three independent parameters, that is, membrane permeability, membrane area and reaction volume, membrane reactor performance can be variable depending on the combination of these three parameters. Thus it is necessary to find a good combination of them, i.e. optimization of them in design step to achieve the best membrane reactor performance for a given circumstance.

Figure 3 shows the plots of dimensionless reaction volume with reaction time at different membrane unit

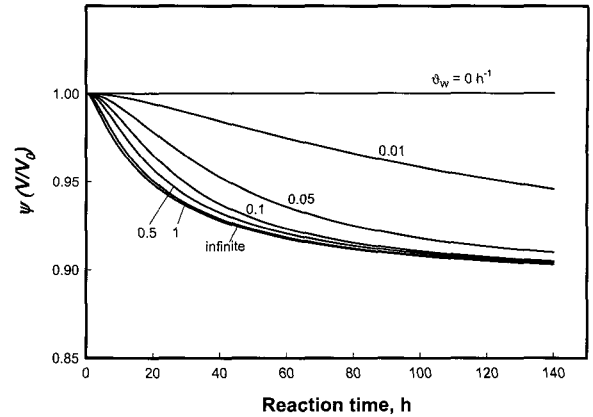


Fig. 3. Reaction volume change with reaction time in PV-aided reaction with perfect separation at different membrane unit capacities; $C_0 = 1000 \text{ mol/m}^3$, $C_{C0} = 4 \text{ mol/m}^3$, and $R_b = 1$.

capacities. As assumed in previous section, reaction volume is observed to be almost constant all the time period of reaction when pervaporation is not applied, whereas reaction volume in PV-aided reaction decreases with reaction time as much as the produced water is depleted by pervaporation. The reaction volume decreases dramatically at the incipient reaction due to the fastest water formation and water removal, and then the decreasing rate slows down with reaction time for a given reaction system. When the membrane unit capacity is larger, the reaction volume is reduced more at any instant. The reduction of reaction volume with membrane unit capacity is also attributed to removing more water and thereby facilitating reaction by pervaporation. Like the conversion curve in Figure 2, the curve of reaction volume moves asymptotically to the curve labeled with "infinite" as the value of membrane unit capacity increases. Selective removal of water concentrates both reactant and product species, that is, increasing their concentrations. Thus, the change of reaction volume influences the reaction rate which is expressed a function of a second order of reactant and product concentrations. The calculation for the perfect separation shows that the pervaporative dehydration yields a decrease in reaction volume by 10% at maximum, indicating that the others than water are concentrated by 10%, respectively. More details on the effect of volume change will be discussed

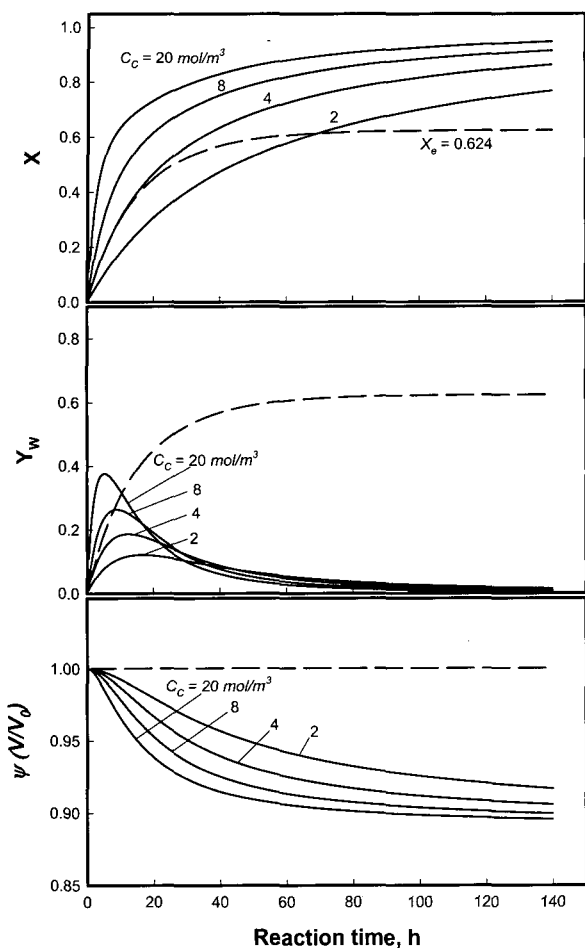


Fig. 4. Reaction parameters with reaction time in PV-aided reaction with perfect separation at different catalyst concentrations; $C_0 = 1000 \text{ mol/m}^3$, $R_b = 1$ and $\theta_w = 0.1 \text{ h}^{-1}$, broken lines = reaction parameters calculated for the reaction without PV at $C_{C0} = 4 \text{ mol/m}^3$.

later.

Figure 4 exhibits the effect of catalyst concentration on the reaction parameters. With reaction time, reaction conversion in the reaction goes beyond the equilibrium conversion due to accelerating and facilitating the reaction by catalyst and PV process, respectively [10]. With increasing catalyst concentration, the reaction is accelerated to produce more water and increase water content faster. Since water permeation rate is higher at larger water content, the removal rate of water can get faster and faster until it is equal to the reaction rate and then decreases. That is why the maximum in the water concentration is larger in height and appears

earlier in reaction time at higher catalyst concentration as shown in this figure. It is natural that reaction volume decreases faster for larger catalyst concentration due to the faster removal of water during the beginning stage. All of the volume curves eventually approach a value, 0.90 when they are extended to sufficiently long reaction time, that is, to reaction completion.

It is commonly known that when one of reactant species is used in excess leads to a quasi-complete conversion of less abundant reactant even without pervaporation. It is because the reaction rate has its dependence on the concentration of reactant species; the higher the reactant concentration, the faster the reaction. In this study, the variations of reaction parameters with reaction time are calculated in PV-aided reaction at different molar ratios of the alcohol to the acid. Apparently, the larger the initial molar ratio is, the faster the reaction is to reach completion, as shown in Figure 5. When initial molar ratio is larger, the maximum of water concentration has a higher amplitude and appears earlier in reaction time due to the same reason as described in the effect of catalyst concentration. At larger initial molar ratio, the volume decreases faster at the incipient reaction, slower with time and then leveled-off to a higher value, showing less final volume reduction. This trend may be explained by the greater dilution of product that goes with the increasing of initial molar ratio of reactant. Regardless of initial molar ratio, the cumulative amount of water produced by the reaction or removed by PV is constant at complete reaction. Consequently, increasing of initial molar ratio cannot only lower the ratio of the produced water amount to initial reaction mixture amount but also declines the extent of mixture volume reduced as much as the produced water which is removed by PV.

PV-aided Reaction with non-perfect Separation

In previous section, reaction behaviors in PV-aided esterification with perfect separation have been examined at various operating conditions. However, perfect separation in which only water permeates through membrane can hardly be obtained in real system. Therefore, to

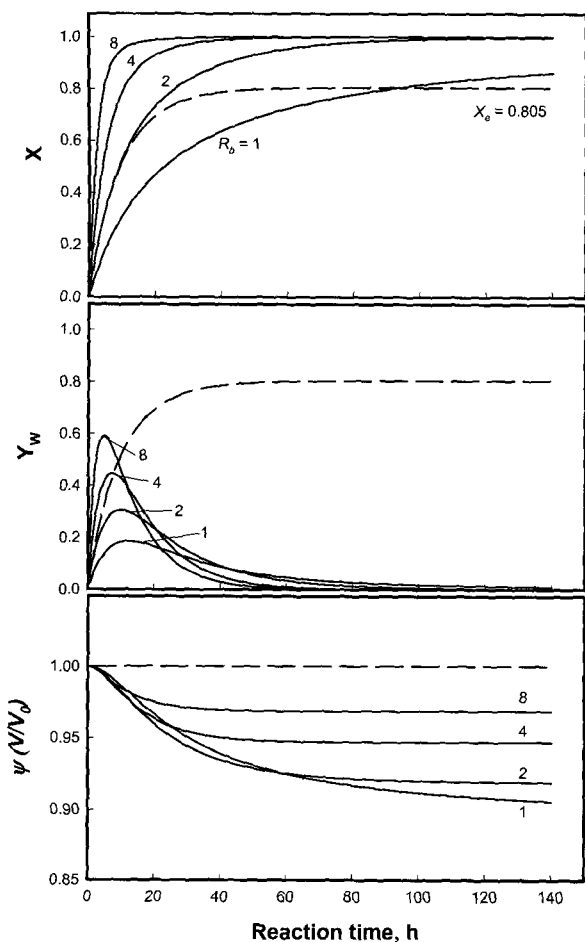


Fig. 5. Reaction parameters with reaction time in PV-aided reaction with perfect separation at different initial molar ratios; $C_0 = 1000 \text{ mol/m}^3$, $C_{C0} = 4 \text{ mol/m}^3$ and $\theta_w = 0.1 \text{ h}^{-1}$, broken lines = reaction parameters calculated for the reaction without PV at $R_b = 2$.

explain more practical reaction behavior on the PV-aided reaction, separation efficiency in the permeation of species through membrane should be taken into account. First, consider the reaction coupled with PV having non-perfect separation where the permeation of binary components (called binary permeation hereafter) occurs through membrane; component i permeates with water with a separation factor $\alpha_{i/w}$ and others else are blocked completely by the membrane. Figure 6 (a) presents the plots of reaction parameters with reaction time obtained at equal molar reactants, i.e., $R_b=1$ under different binary permeations. When $\alpha_{i/w}$ is 0.05, species i permeability is 0.05 fraction of water permeability.

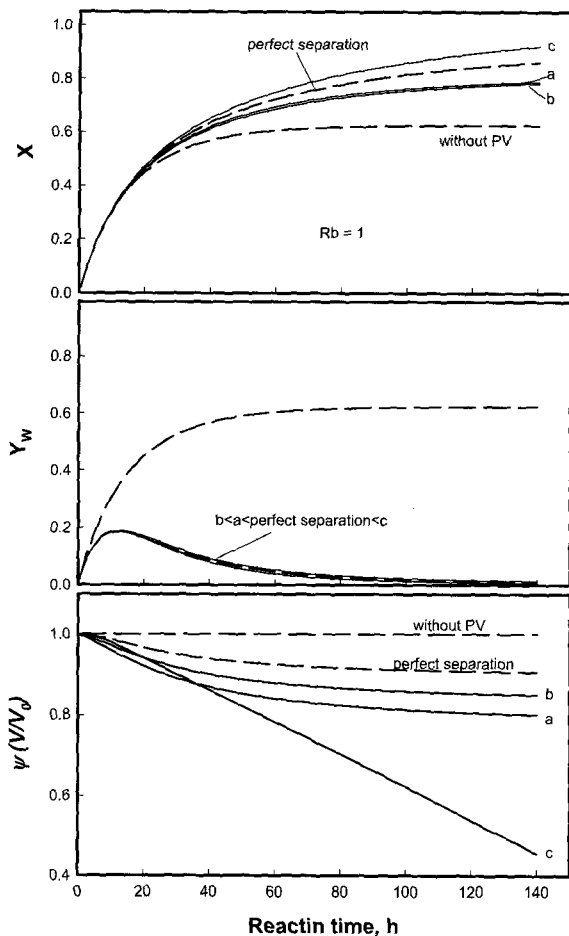


Fig. 6 (a). Reaction parameters with reaction time in PV-aided reaction with non-perfect separation at different permeations of binary components (one of species-water); $C_0 = 1000 \text{ mol/m}^3$, $C_{C0} = 4 \text{ mol/m}^3$, $R_b = 1$ and $\theta_w = 0.1 \text{ h}^{-1}$, lines a = separation efficiency with $\alpha_{A/W} = 0.05$, $\alpha_{B/W} = \alpha_{E/W} = 0$, lines b = separation efficiency with $\alpha_{B/W} = 0.05$, $\alpha_{A/W} = \alpha_{E/W} = 0$, and lines c = separation efficiency with $\alpha_{E/W} = 0.05$, $\alpha_{A/W} = \alpha_{B/W} = 0$.

When one of reactants permeates with water through membrane, in the PV-aided reaction with non-perfect separation (lines a and b), the conversion lines lie between two lines labeled with “perfect separation” and “without pervaporation”. The line of “perfect separation” is designated for conversion in the PV-aided reaction with perfect separation, and the line of without PV for conversion in the reaction “without PV”. With the permeation of a reactant, the PV-aided reaction system continuously loses the reactant during the reaction depending on its separation factor, leading

Table 1. Molar Volumes of Each species at 70°C

Species	Molar volume (m ³ /mol)
Benzyl alcohol	0.1065
Acetic acid	0.0607
Benzyl acetate	0.1487
Water	0.0186

to decrease its concentration in the reactor. Therefore, the reaction is slower than one with perfect separation although the reaction is facilitated by PV process. On the other hand, when ester permeates with water (line c), reaction conversion is found to be higher than even the system with “perfect separation”. Since removal of ester from the reaction mixture causes accelerating the forward reaction as in removal of water, the resulting reaction is facilitated more than one with “perfect separation” and proceeds faster. It is also observed that water concentrations in the reactor are in the same order as in the plots of reaction conversion; $c > \text{perfect separation} > a > b$ even though they are slightly different from each other in PV-aided reactions. The different water concentration is a result of different reaction rate; the faster the reaction, the more the water produced. All of dimensionless reaction volumes with non-perfect separation at any instant are below one which is achievable with perfect separation. The more reduction of reaction volume is obviously attributed to the additional permeation of organic component in addition to water permeation. Acetic acid has a smaller molar volume than benzyl alcohol, as shown in Table 1. Reaction volume decreases more in the permeation of benzyl alcohol-water (line a) than in that of acetic acid-water (line b). The more decrease of reaction volume in line a will cause to concentrate reactants to such an extent that higher reaction conversion can be obtained at a time due to faster reaction rate, as can be seen in the plots of reaction conversion. During the beginning stage of reaction, the permeation rate of ester, one of products, in line c is smaller than those of the two reactants in lines a and b because the concentration of ester is very small. Thus reaction volume in curve c will be larger at the incipient

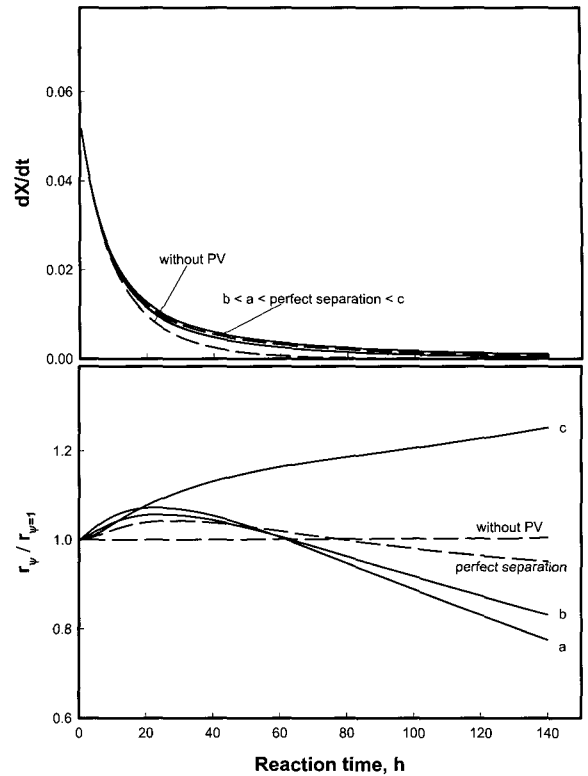


Fig. 6 (b). Reaction rates and reaction rate ratios with reaction time in PV-aided reaction with non-perfect separation at different permeations of binary components (one of species-water); $C_0 = 1000 \text{ mol/m}^3$, $C_{C0} = 4 \text{ mol/m}^3$, $R_b = 1$ and $\vartheta_w = 0.1 \text{ h}^{-1}$, lines a = separation efficiency with $\alpha_{A/W} = 0.05$, $\alpha_{B/W} = \alpha_{E/W} = 0$, lines b = separation efficiency with $\alpha_{B/W} = 0.05$, $\alpha_{A/W} = \alpha_{E/W} = 0$, and lines c = separation efficiency with $\alpha_{E/W} = 0.05$, $\alpha_{A/W} = \alpha_{B/W} = 0$.

reaction. However, as reaction progresses further, ester is accumulated, as a result of its formation of which is much faster than its removal. Consequently, its concentration in reactor increases and thereby its permeation rate increases gradually, whereas the concentration of reactant in line a or b decreases due to its depletion in the reaction and then its permeation rate is reduced and leveled-off near reaction completion. That is why the reaction volume in line c decreases, passing through the two lines a and b with increasing reaction time.

Figure 6 (b) illustrates a comparison of reaction rates between reactions without PV and with PV having different separation efficiencies. From the plots of dX/dt , it can be seen that all the PV-aided esterifications

proceed faster than the reaction without PV, and the reaction rates are also in the order of $c > \text{perfect separation} > a > b$ due to more facilitated reaction as discussed previously. To characterize volume change effect caused by the permeation of species on the reaction, the ratios of reaction rate r_{ψ} at time t to reaction rate $r_{\psi=1}$ that is determined under an assumption of negligible volume change are calculated and plotted in this figure. $r_{\psi=1}$ does not include the effect of volume change by the permeation but r_{ψ} does. Thus, the reaction ratio can tell how the volume change influences the reaction. As the reaction volume is reduced by the permeation, product species get concentrated to the same extent as reactant species do. In this case, two competing opposite effects would be exerted on reaction rate; concentrating reactants would cause to increase the reaction rate by accelerating the forward reaction, while concentrating products decreases the reaction rate by inducing more the reverse reaction. The magnitude of the ratio can tell how the volume change contributes to the reaction rate; ratio < 1 indicates the product-concentrating effect dominant over the reactant-concentrating effect, ratio = 1 means no effect of volume change, and ratio > 1 explains the reactant-concentrating effect prevailing. The ratio of the reaction without PV is found to be almost 1 during all the reaction time, indicating there is no effect of volume change. It is also found that the reactant-concentrating effect by removal of the reactant is dominant over the product-concentrating effect during the incipient reaction in which the concentrations of products are low. However, as the reaction progresses further and the concentration of product increases as much, the ratios decrease below 1, decreasing faster for a reaction system in which a larger molar volume of species permeates through membrane. It can be noted from these observations that as reaction goes on, the product-concentrating effect becomes more significant and then eventually predominant over the reactant-concentrating effect as approaching reaction completion. In PV-aided reaction with the permeation of the product organic-water (line c), the ratio increases continuously with reaction time,

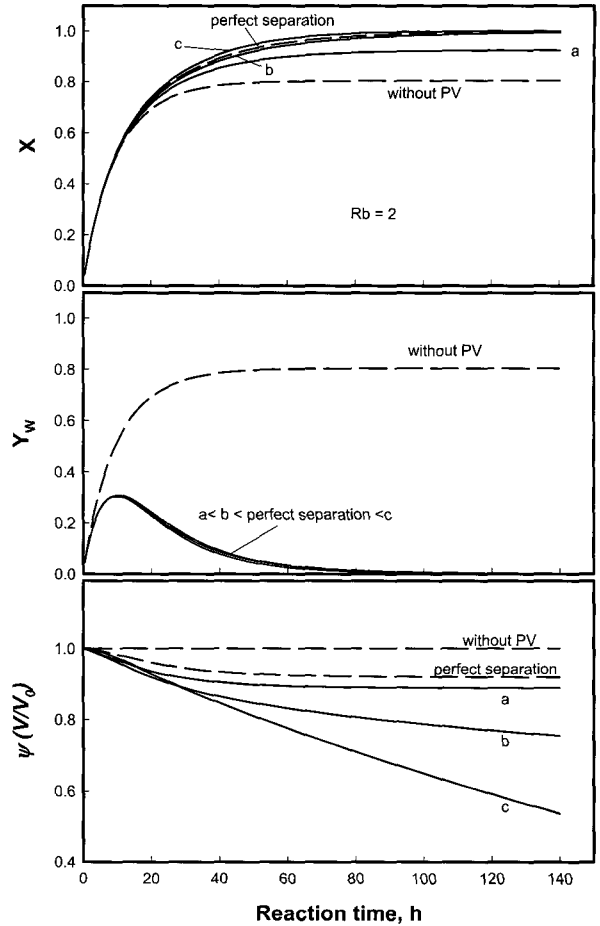


Fig. 7 (a). Reaction parameters with reaction time in PV-aided reaction with non-perfect separation at different permeations of binary components (one of species-water); $C_0 = 1000 \text{ mol/m}^3$, $C_{C0} = 4 \text{ mol/m}^3$, $R_b = 2$ and $\vartheta_w = 0.1 \text{ h}^{-1}$, lines $a =$ separation efficiency with $\alpha_{A/W} = 0.05$, $\alpha_{B/W} = \alpha_{E/W} = 0$, lines $b =$ separation efficiency with $\alpha_{B/W} = 0.05$, $\alpha_{A/W} = \alpha_{E/W} = 0$, and lines $c =$ separation efficiency with $\alpha_{E/W} = 0.05$, $\alpha_{A/W} = \alpha_{B/W} = 0$.

suggesting that concentrating reactant has a more effect on the reaction rate as the product is removed.

Compared to the reaction system with equal molar reactants, the reaction with the acid in excess ($R_b = 2$) is faster and has a higher conversion with time for the same membrane unit capacity, as shown in Figure 7 (a). In the two PV-aided reactions with the binary permeation of reactant-water designated as lines a and b , both of them have a reaction conversion placed between lines labeled with perfect separation and without PV, as in the reaction system with equal molar

reactants. In the system with the acid in excess, the acid has an initial concentration twice larger than the other reactant. Therefore with permeation of the same amount of each reactant, the acid concentration reduces much less, that is, the acid concentration changes less sensitively to its permeation. As a result, the reaction (line *b*) has higher conversion than the reaction (line *a*) with permeation of the less abundant reactant and is close to the reaction with perfect separation, as shown in this figure. The reaction (line *c*) with binary permeation of products obtains the highest conversion with time as explained in Figure 6 (a). Water concentrations in reactor are not much different each other but they are in the same order as in the reaction conversion lines. In the reactions with binary permeation of reactant-water, volume in line *a* decreases faster than in line *b* because of larger molar volume of the acid and then gets leveled-off as the acid is depleted, while volume in line *b* continuously decreases even after reaction completion because the alcohol concentration is still high. In the reaction (line *c*) with the binary permeation of products (ester-water), reaction volume decreases continuously, which continues until all the ester disappears by its permeation.

Looking at the plots of dX/dt with reaction time in Figure 7 (b), the PV-aided reactions are faster than the reaction without PV, and their rate decrease faster than that with equal molar reactants. According to the general expression for a second order reversible reaction that consists of the sum of a reactant concentration term and a product concentration term, reactant concentration determines mainly the reaction rate at the initial stage of reaction, but as reaction proceeds further, reactant concentrations decrease and product concentrations increase, the influence of product concentration becomes significant and then surpasses the effect of reactant concentration on reaction rate. When the initial molar ratio of reactants is larger, reactants are depleted faster and products are formed faster. Thus, reactant concentration tends to be lower and product concentration is higher at any instant under a given operating condition. In this case, as reaction volume decreases

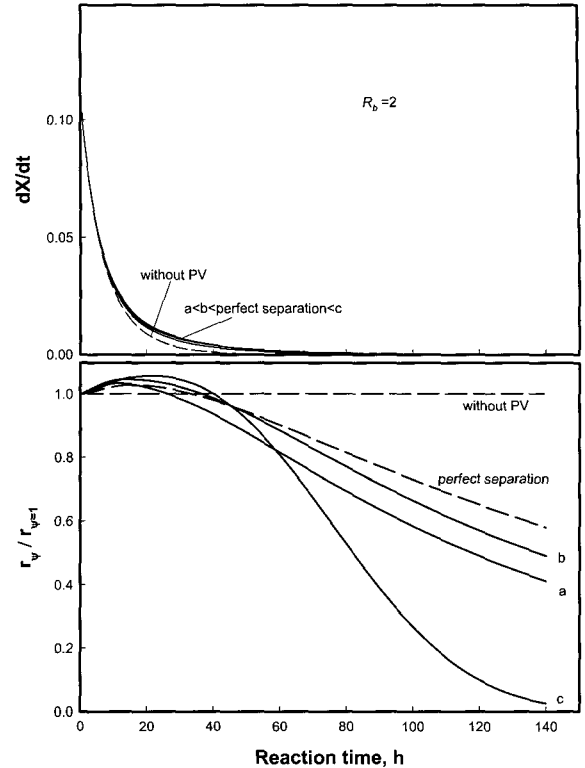


Fig. 7 (b). Reaction rates and reaction rate ratios with reaction time in PV-aided reaction with non-perfect separation at different permeations of binary components (one of species-water); $C_0 = 1000 \text{ mol/m}^3$, $C_{C0} = 4 \text{ mol/m}^3$, $R_b = 2$ and $\vartheta_W = 0.1 \text{ h}^{-1}$, lines *a* = separation efficiency with $\alpha_{A/W} = 0.05$, $\alpha_{B/W} = \alpha_{E/W} = 0$, lines *b* = separation efficiency with $\alpha_{B/W} = 0.05$, $\alpha_{A/W} = \alpha_{E/W} = 0$, and lines *c* = separation efficiency with $\alpha_{E/W} = 0.05$, $\alpha_{A/W} = \alpha_{B/W} = 0$.

due to permeation, a reaction regime dominated by product-concentrating effect would come earlier after a regime dominated by reactant-concentrating effect because of higher product concentration. This postulation is well supported by the fact that the PV-aided reactions have a smaller magnitude of reaction ratio and a shorter period of reaction time holding for reaction ratio larger than 1 in comparison to the reaction with equal molar reactants. In addition, the reaction ratios decrease constantly with time after passing a value of 1, which continues until respective species is removed completely. The smaller value of the ratio during the beginning stage of reaction is because the excess amount of alcohol makes the reactants less concentrated with a given amount of permeation.

During the incipient reaction, the reaction with binary permeation of products (line *c*) has larger reaction ratio and longer time holding for the ratio >1 than in the reaction with binary permeation of reactant-water, more facilitating the reaction by removing ester, and as the reaction proceeds further, it has a faster decrease in the ratio below 1 because of a high concentration of ester, indicating that the volume change negatively affects the reaction rate. Now it can be summarized that when the initial molar ratio of reactants is larger, reactant-concentrating effect is less significant and product-concentrating effect is more remarkable due to faster reaction producing higher concentration of product at a time.

Let's consider the permeation effect of ternary components on the reaction. Usually since ester is less hydrophilic and is bigger in molecular size than any other else component in the mixture, it can hardly permeate through hydrophilic membrane. Thus, a reaction system with permeation of both reactants and water is taken as model to demonstrate the permeation effect of ternary components, which alcohol and acid permeate through membrane with their separation factors over water, $\alpha_{A/W} = \alpha_{B/W} = 0.025$, respectively, and ester is blocked by the membrane ($\alpha_{E/W} = 0$). Like the reactions with binary permeation of reactant-water already discussed previously, as the model reaction goes on, its conversion increases between reactions with perfect separation and without PV, and its reaction volume (V/V_0) decreases fast at initial and then reduces slower and slower as the reactants are depleted, as shown in Figure 8 (a). The reaction rate ratio undergoes the maximum and then decreases below 1, showing reactant-concentrating effect dominant initially and then product-concentrating effect prevailing later.

Figure 8 (b) shows the moles of each species in reaction mixture and its cumulative permeation amount of ternary components with reaction time. Since the alcohol and acid are consumed in the reaction and also removed simultaneously by permeation through membrane, their moles in the reaction mixture decrease faster with time than in the reaction system with perfect

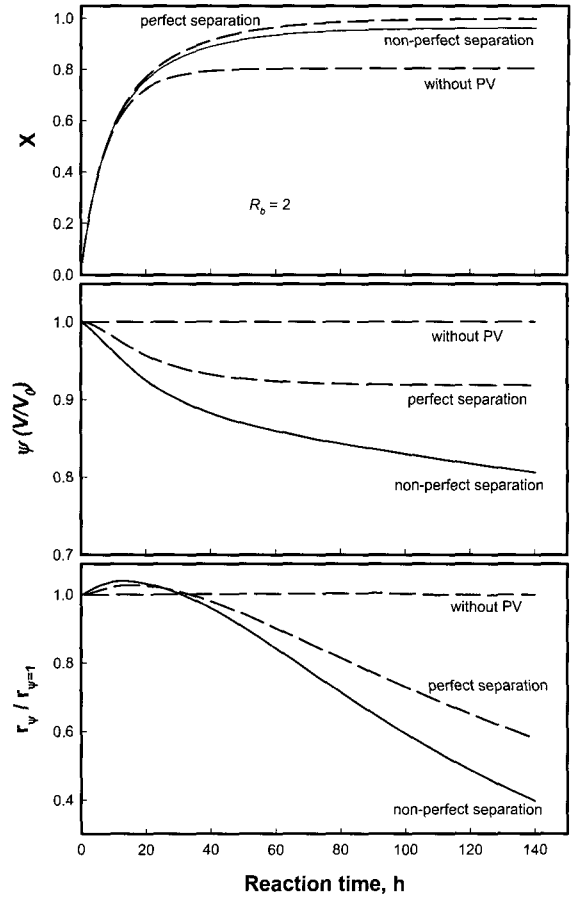


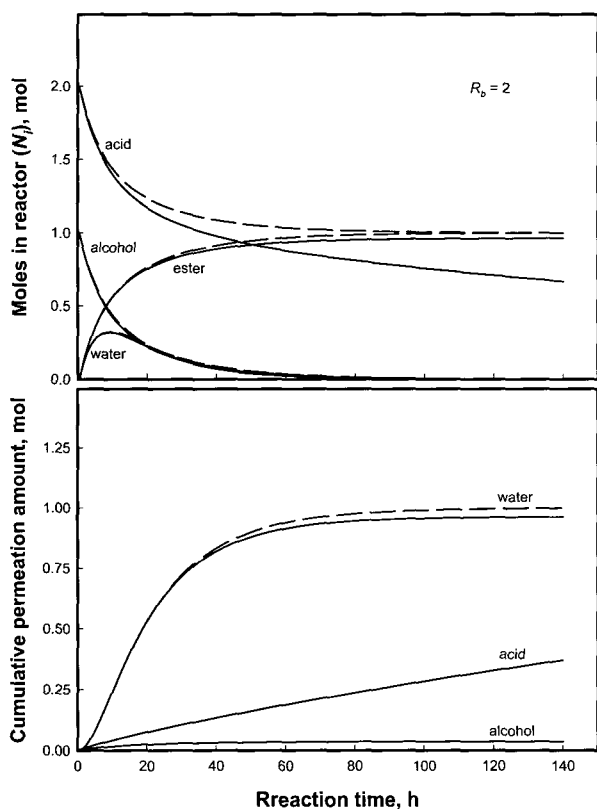
Fig. 8 (a). Reaction parameters with reaction time in PV-aided reaction with non-perfect separation at a permeation of ternary components (reactants-water); $C_0 = 1000 \text{ mol/m}^3$, $C_{C0} = 4 \text{ mol/m}^3$, $R_0 = 2$ and $\vartheta_w = 0.1 \text{ h}^{-1}$, $\alpha_{A/W} = \alpha_{B/W} = 0.025$, $\alpha_{E/W} = 0$.

separation. Especially, the alcohol is continuously depleted even after complete reaction when its concentration is still high enough for permeation. The ester produces less than in the reaction with perfect separation due to slower reaction rate and the loss of reactants by their permeation. The cumulative moles of water permeation are equal to the cumulative mole of the ester production when water is completely removed by PV. The permeation amount of the alcohol is larger than that of the acid because the alcohol concentration is higher in the reactor even though their permeabilities are equal.

The equilibrium conversions calculated in the reaction without PV and PV-aided reactions at different initial

Table 2. Equilibrium reaction conversion in the reaction without PV and PV-aided reaction at different initial molar ratios and different separation efficiencies, $C_0 = 1000 \text{ mol/m}^3$, $C_C = 4 \text{ mol/m}^3$ and 70°C

Reaction system		R_b	X_{eq}
Reaction without PV		1	0.625
PV-aided reaction with perfect separation		1	1.000
Permeation of binary species	$\alpha_{E/W} = 0.05, \alpha_{A/W} = \alpha_{B/W} = 0$	1	1.000
	$\alpha_{A/W} = 0.05, \alpha_{B/W} = \alpha_{E/W} = 0$	1	0.811
	$\alpha_{B/W} = 0.05, \alpha_{A/W} = \alpha_{E/W} = 0$	1	0.808
Reaction without PV		2	0.805
PV-aided reaction with perfect separation		2	1.000
Permeation of binary species	$\alpha_{E/W} = 0.05, \alpha_{A/W} = \alpha_{B/W} = 0$	2	1.000
	$\alpha_{B/W} = 0.05, \alpha_{A/W} = \alpha_{E/W} = 0$	2	1.000
	$\alpha_{A/W} = 0.05, \alpha_{B/W} = \alpha_{E/W} = 0$	2	0.924
Permeation of ternary species	$\alpha_{A/W} = \alpha_{B/W} = 0.025, \alpha_{E/W} = 0$	2	0.958

**Fig. 8 (b).** Moles of and cumulative permeation amount of each species in the reactor with reaction time in PV-aided reaction with non-perfect separation at a permeation of ternary components (reactants-water); $C_0 = 1000 \text{ mol/m}^3$, $C_{C0} = 4 \text{ mol/m}^3$, $R_b = 2$ and $\vartheta_w = 0.1 \text{ h}^{-1}$, $\alpha_{A/W} = \alpha_{B/W} = 0.025$, $\alpha_{E/W} = 0$, broken lines = perfect separation and solid lines = non-perfect separation.

molar ratios and separation efficiencies are listed in Table 2. The equilibrium conversion is a maximum conversion that the reaction can reach when sufficient

reaction time is available. The reactions without PV at the given initial molar ratios never reach completion but the PV-aided reaction accomplishes completion even at $R_b = 1$ due to PV facilitating the reaction. In the reaction systems with non-perfect separation, it should be noted that reaction can be completed when the reactant in excess permeates, whereas it is difficult to reach reaction completion when any reactant at $R_b = 1$ or the less abundant reactant at $R_b > 1$ permeates. The permeation of the organic product can help to increase the equilibrium conversion to 1 but the valuable product is lost as much as it permeates or additional treatments must be necessary to recover it. In selecting membrane material or optimizing operation conditions, the permeation of the less abundant reactant must be minimized although the permeation of the reactant in excess or the product may be somewhat allowed.

4. Conclusions

PV-aided esterification with slow reaction regime was studied by using a practical model based on non-perfect separation through membrane. It was presented how non-perfect separation and membrane unit capacity to remove water can facilitate the reaction and enhance the reaction conversion and reaction rate. The reaction was more facilitated and led to higher reaction conversion at higher catalyst concentration and/or larger initial molar ratio of reactant by removing water through membrane at a given membrane unit capacity. The

PV-aided reaction with perfect separation could reach reaction completion even at initial molar ratio=1, but in the reaction systems with non-perfect separation, complete reaction is achieved only when the reactant in excess permeates. With the non-perfect separation, reaction completion could hardly be achievable when any reactant at initial molar ratio=1 or the less abundant reactant at initial molar ratio>1 permeates through membrane. When ester permeates, reaction conversion also increases due to accelerating the forward reaction through removal of product species like water. Two competing effects due to the volume change affect the reaction; one is reactant concentrating which affect positively the reaction rate, and the other is product concentrating, which tends to cause reverse reaction, decreasing the reaction rate. Initially, the reactant-concentrating effect prevails. With increasing reaction time, the product-concentrating effect becomes more important as more products are produced and more reactants are depleted. When the initial molar ratio of reactants is larger, reactant-concentrating effect is less significant and product-concentrating effect is more remarkable due to faster reaction producing higher concentration of product at a time as well as the dilution of volume change initially by the reactant in excess.

List of Symbols

A_m	membrane area, m^2
C	concentration in reactor, mol/m^3
C_0	initial concentration of limiting reactant, mol/m^3
J	permeation flux through membrane, $mol/(m^2 \cdot s)$
k_1, k_2	forward and reverse reaction rate constant, respectively, $m^3/(mol \cdot s)$
K_e	equilibrium constant, dimensionless
M	molar mass, kg/mol
N	number of moles, dimensionless
r	reaction rate, $mol/(m^3 \cdot s)$
Q	cumulated permeation amount, mol
R	ideal gas constant, $kJ/(mol \cdot K)$

R_i	initial molar ratio of species i to limiting reactant, dimensionless
t	reaction time, s
V	volume of reaction mixture, m^3
V_0	initial volume of reaction mixture, m^3
X	reaction conversion, dimensionless
y	mole fraction, dimensionless
Y	concentration defined by Eq. (11), dimensionless

Greek letters

$\alpha_{i/w}$	membrane selectivity to species i over water, dimensionless
ϑ_w	measure of membrane unit capacity to remove water, s^{-1}
Ψ	ratio of reaction mixture volume at time t to initial volume, dimensionless
ρ	density, kg/m^3

Subscripts

A, B	acid and alcohol, respectively
E, W	ester and water, respectively.
i	species i in membrane mixture
0	initial condition

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