

## 전산모델링을 통한 투과증발-촉진 에스테르화 반응에 대한 연구

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### A Parametric Study of Pervaporation-facilitated Esterification

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**요 약:** 본 연구에서는 물과 함께 에스테르화 반응물 및 생성물 일부가 친수성 막을 투과하는 비완전 분리를 고려한 투과증발-촉진 에스테르화 반응모델을 확립하였으며, 이 모사모델에 막 분리 효율 및 물 제거능력을 설명하는 항들을 포함시킴으로써 막 투과분리가 에스테르화 반응에 어떻게 영향을 끼치는가를 공정모사를 통해서 체계적으로 살펴보았다. 모사결과 막을 통한 비완전 분리 즉, 분리막을 통한 반응물의 투과는 역반응을 유발시켜 전체 반응을 지연시키며 그 결과 반응 전환율은 투과증발 공정을 사용하지 않은 반응보다는 높으나 물에 대한 완전한 투과선택도를 갖는 투과증발 공정을 사용하는 반응시스템보다는 낮음을 알 수가 있었다. 반응 시스템 내에서 장착된 막을 통한 투과로 인한 반응부피의 변화가 반응 속도에 끼치는 영향을 살펴보았는데 반응 초기에는 반응물 농축효과가 지배적이어서 반응을 촉진시키며, 반응이 진행되어 생성물이 형성됨에 따라 생성물 농축효과가 점점 중요해지고 이 효과가 반응의 속도를 감소시킴을 알 수가 있었다. 에스테르화 반응공정 중에 투과증발공정을 적용하는 시점에 따라 반응속도, 반응 전환율이 달라짐을 공정모사를 통해 관찰하였다. 반응 모델 식으로부터 분리막의 성능과 반응 인자들 간의 상관관계는 확립하고 이 상관관계를 주어진 막 분리능력 하에서 반응 인자 조건 설정, 혹은 주어진 반응조건 하에서 막 분리능력을 설계하는 도구로 사용할 수 있다.

**Abstract:** A parametric study on pervaporation-facilitated esterification was performed by using a practical model based on non-perfect separation through membrane which is not perfectly permselective to water. Thus, membrane selectivity as well as membrane capability to remove water should be taken into account in establishing the simulation model to explain how the membrane separation influence the esterification reaction process. It was shown by simulation that in the reaction systems with non-perfect separation, the permeation of reactants which are acid or/and alcohol retards the reaction by inducing the backward reaction so that reaction conversion curve is located between a reaction system coupled with pervaporation process having a perfect permselectivity to water and a reaction system without pervaporation process. The volume change of reaction system occurs as a result of the permeation through the membrane. The reaction volume change which can be characterized by the reaction ratio of  $r_p$  to  $r_{p=1}$  affects reaction kinetics by concentrating reactants and products, respectively, with different extent with time; reactant-concentrating effect is dominant during the initial stage of reaction, resulting in facilitating the reaction, and then product-concentrating effect is exerted more on reaction, causing to slow down the reaction. When pervaporative dehydration is applied to the reaction system plays an important role in the reaction as well. The effect of timing to impose pervaporation on reaction system affected the reaction kinetics in terms of reaction rate and reaction conversion. A relationship was derived to explain membrane unit capacity and reaction parameters that will be used as a design tool to determine membrane unit capacity at a given reaction conditions or reaction parameters at a membrane unit capacity.

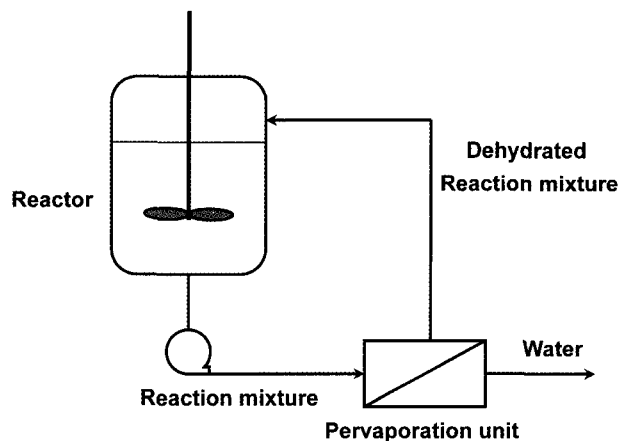
**Keywords:** membrane reactor, esterification, pervaporation, facilitated reaction, dehydration

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## 1. Introduction

Currently, there is a great deal interest in the application of a membrane reactor to various chemical reaction processes. The membrane reactor system combines the reaction and separation in a single process, so that both the chemical reaction and the membrane separation of products can take place simultaneously during a process. 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]. Among the membrane processes, pervaporation (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.

Most of the models [6-8] presented so far of PV membrane reactors has been based on the reaction kinetics and membrane permeation under an assumption of a perfect dehydration separation in which only water permeates through membrane. However, it was reported [3,8,9] that the permeation of reactants takes place through membrane and affects reaction kinetics in real PV membrane reactors even though the reactant permeation is not as significant as the water permea-



**Fig. 1.** A batch-wise membrane reactor that integrates a batch reactor with a membrane unit.

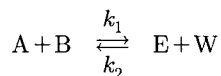
tion. In the previous study [10], pervaporation-facilitated esterification of carboxylic acid and alcohol had been theoretically characterized by using a practical simulation model, considering non-perfect separation through membrane which is not perfectly permselective to water. It was shown from a series of simulations that in the reaction system with non-perfect separation, reaction can hardly be achieved when any reactant in equal molar reactants or less abundant reactant at initial molar ratio  $> 1$  permeates through membrane, while the permeation of ester accelerates the forward reaction and increases reaction conversion at any instant through removal of product species like water.

This work is a continuation of the previous study to provide a fundamental understanding of the practical behavior of PV membrane reactor with membrane separation performance. A simple reactor configuration (Fig. 1) was chosen as model membrane reactor system, consisting of a batch reactor integrated with pervaporation. A predictive model of PV-aided esterification established by incorporating a more realistic description of reaction kinetics and membrane performance with separation characteristics was used in simulation. In the model, a non-perfect separation system where the membrane is not perfectly permselective to water was applied to the model to investigate how it influences the membrane-facilitated reaction process

and improves the reactor performance. The timing effect of when the pervaporation is imposed on the reaction system was also studied with relation to reaction rate and reaction conversion. From the model, a relationship between membrane unit capacity and reaction parameters was derived. With help of the relationship, reaction parameters for a given membrane unit capacity or membrane unit capacity at certain reaction condition can be determined. The relationship can be used as a design tool to provide a proper combination of the reaction parameters for a given membrane capacity or a combination of membrane area, membrane permeability and reaction mixture volume for a given operating conditions. The esterification reaction between ethanol and oleic acid was chosen as model reaction and investigated theoretically, by using reaction parameters available in publications [9].

## 2. Theory

Taking into consideration the esterification reaction that can be schematically represented by;



where  $A$  and  $B$  refer to acid and alcohol, 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 Fig. 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;

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

$$\begin{aligned} r_i &= \pm (k_1 C_A C_B - k_2 C_E C_W) \\ &= \pm k_1 \left( C_A C_B - \frac{C_E C_W}{K_e} \right) \end{aligned} \quad (2)$$

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.  $K_e$  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. According to the general expression for a second order reversible reaction, the reaction rate with respect of any species  $i$  is expressed by Eq. (2)

Considering that the PV module consists of a hydrophilic membrane through which water permeates preferentially, the permeation fluxes of water and species  $i$  through the membrane are approximately given, respectively, as;

$$J_W = P_W C_W \quad (3)$$

$$J_i = \frac{y_i}{y_W} \frac{C_W}{C_i} P_W C_i = \alpha_{i/W} P_W C_i \quad (4)$$

$$\alpha_{i/W} = \frac{y_i / y_W}{C_i / C_W} \quad (5)$$

where  $y$  denotes the mole fraction in permeate,  $\alpha_{i/W}$  denotes the selectivity to species  $i$  over water component, and 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]. 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.

From the equations described above, the number of moles or concentration of species with the extent of re-

action is given by

$$C_i V / V_0 = C_o (R_i \pm X) - \vartheta_W \alpha_{i/W} \int_0^t C_i dt \quad (6)$$

where

$$\vartheta_W = \frac{P_W A_m}{V_o} \quad (7)$$

$$R_i = \frac{C_{i0}}{C_{A0}} \quad (8)$$

$C_{i0}$  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  $\vartheta_W$  that constitutes membrane parameter  $P_W$  and operating parameters  $A_m$  and  $V_o$  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  $A$ .  
Defining the dimensionless parameters

$$Y_i = \frac{C_i}{C_0} \quad (9)$$

$$\psi = \frac{V}{V_0} \quad (10)$$

and differentiating Eqs (2) and (6) with respect to reaction time  $t$  can give,

$$\frac{dX}{dt} = \psi k_1 C_0 \left( Y_A Y_B - \frac{Y_E Y_W}{K_e} \right) \quad (11)$$

$$\frac{dY_i}{dt} = \frac{1}{\psi} \left( \pm \frac{dX}{dt} - Y_i \frac{d\psi}{dt} - \vartheta_W \alpha_{i/W} Y_i \right) \quad (12)$$

The volume of the reaction mixture at time  $t$  can be calculated by addition of each species volume;

$$V = \sum_i N_i \frac{M_i}{\rho_i} \quad (13)$$

where  $N_i$ ,  $M_i$  and  $\rho_i$  are the number of moles, molar

mass and density of species  $i$ , respectively. Then from Eqs (10) and (13), the dimensionless parameter  $\psi$  is derived as follows;

$$\psi = \frac{\sum_i (R_i \pm X) \frac{M_i}{\rho_i} - \vartheta_W \sum_i \alpha_{i/W} \frac{M_i}{\rho_i} \int_0^t Y_i dt}{\sum_i R_i \frac{M_i}{\rho_i}} \quad (14)$$

$$\frac{d\psi}{dt} = - \frac{\vartheta_W \sum_i \left( \alpha_{i/W} \frac{Y_i M_i}{\rho_i} \right)}{\sum_i R_i \frac{M_i}{\rho_i}} \quad (15)$$

Eq (14) 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. The permeation amount of species  $i$ ,  $Q_i$ , for permeating time  $t$  can be obtained as follows

$$\begin{aligned} Q_i &= A_m \int_0^t J_i dt \\ &= C_0 V_o \vartheta_W \alpha_{i/W} \int_0^t Y_i dt \end{aligned} \quad (16)$$

Thus at a given time the parameters  $X$ ,  $Y_i$  and  $\psi$  can readily be obtained by solving Eqs (11)~(14) numerically. The initial conditions are at  $t = 0$ ;

$$\begin{aligned} X_0 &= 0 \\ Y_{A0} &= 1, \quad Y_{B0} = R_B, \quad Y_{W0} = 0 \\ \psi_0 &= 1 \end{aligned}$$

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. The reaction rate involving the catalyst concentration is given as follows (10);

$$\frac{dX}{dt} = k_{C1} C_{C0} C_0 \left( Y_A Y_B - \frac{Y_E Y_W}{K_e} \right) \quad (17)$$

**Table 1.** Molar Volumes of Each Species at 75°C

| Species      | Molar volume (m <sup>3</sup> /mol) |
|--------------|------------------------------------|
| Oleic acid   | 0.3315                             |
| Ethanol      | 0.0621                             |
| Ethyl oleate | 0.3755                             |
| Water        | 0.0186                             |

where  $k_{Cl}$  denotes rate constant for forward reaction and  $C_{C0}$  initial catalyst concentration. Eq. (17) indicates that reaction rate is more likely to be dependent on the initial catalyst concentration rather than the catalyst concentration at any instant.

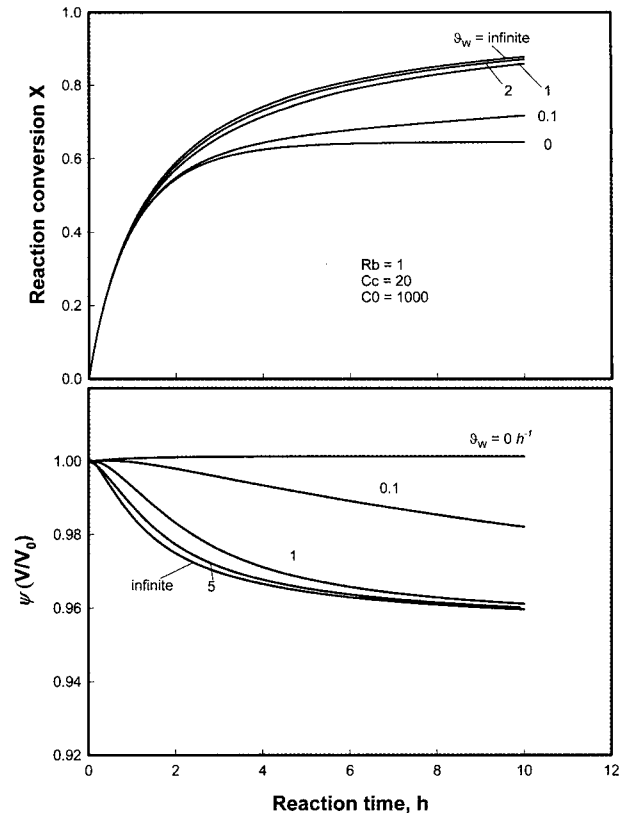
Now, reaction volume change, membrane selectivity and membrane capability to remove water are included in the simulation model to explain how they influence the membrane-facilitated reaction process and improve the reactor performance.

### 3. Results and Discussion

To demonstrate esterification reaction behavior with membrane unit capacity and separation efficiency in the simulation, the esterification reaction between ethanol and oleic acid catalyzed by p-toluenesulfonic acid is taken as model reaction, by using the parameters,  $k_{Cl} = 3.4 \times 10^{-5} \text{ m}^3/(\text{mol} \cdot \text{h})$ ,  $K_e = 3.3$ ,  $\rho_A = 852$ ,  $\rho_B = 741$ ,  $\rho_E = 827$ ,  $\rho_W = 970 \text{ kg/m}^3$ , which are representative of the esterification of oleic acid and ethanol at 75°C [9]. These kinetic parameters will be used throughout this study unless specified otherwise. The molar volumes of each species at 75°C are given in Table 1.

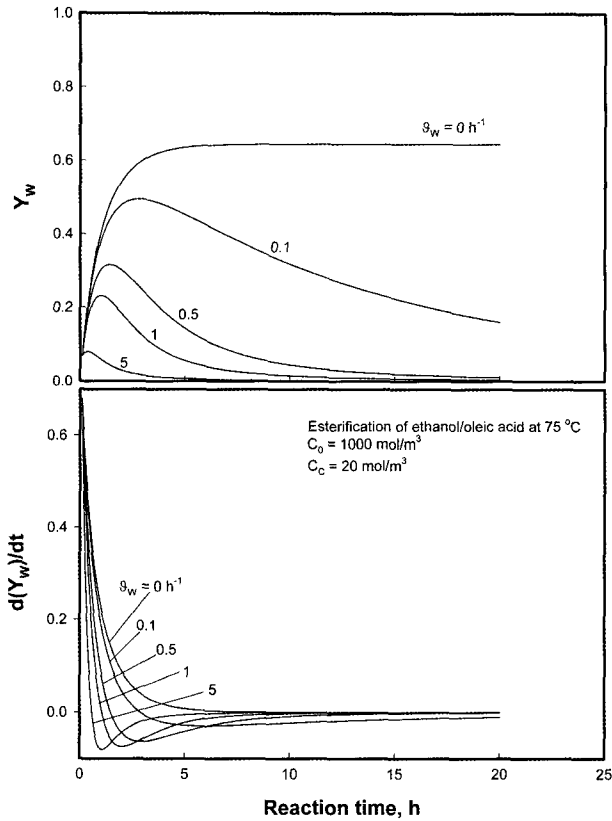
#### 3.1. PV-aided Reaction with Perfect Separation

Fig. 2 shows the plots of reaction conversion and reaction volume 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



**Fig. 2.** Plots of reaction conversion and dimensionless reaction volume with reaction time in PV-aided reaction with perfect separation at different membrane unit capacities.  $C_0 = 1000 \text{ mol/m}^3$ ,  $C_{C0} = 20 \text{ mol/m}^3$ , and  $R_b = 1$ .

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, 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. Here increasing of membrane unit capacity is obtainable by increasing of membrane permeability and/or larger membrane area per unit reaction mixture volume. Looking at the plots of dimensionless reaction volume with reaction time at different membrane unit capacities, as assumed in previous section, reaction volume is ob-

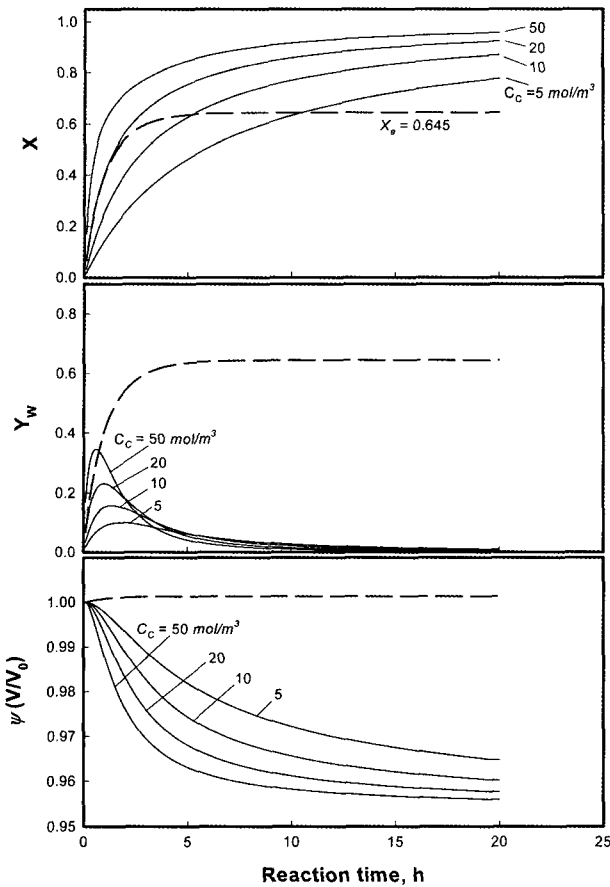


**Fig. 3.** Dimensionless water concentration and water formation rate with reaction time in PV-aided reaction with perfect separation at different membrane unit capacities.  $C_0 = 1000 \text{ mol/m}^3$ ,  $C_{C0} = 20 \text{ mol/m}^3$ , and  $R_b = 1$ .

served 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 volume decreases less and less and finally leveled off with reaction time for a given reaction system. When the membrane unit capacity is larger, the reaction volume is reduced more at any instant due to removing more water and thereby facilitating reaction by pervaporation. Like the conversion curve in Fig. 2, as the value of membrane unit capacity increases, the curve of reaction volume moves asymptotically to the curve labeled with infinite. Selective removal of water con-

centrates 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.

Fig. 3 shows the plots of water concentration in the reactor and water formation rate with reaction time at various membrane unit capacities. 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 and so does water removal rate correspondingly until the concentration reaches the maximum when its removal rate and formation rate are equal. Thereafter, water removal is faster than its formation, so that water becomes depleted in the reactor; a negative value of the water formation rate as can be seen in its curve, resulting in increasingly facilitating the reaction. As membrane unit capacity is larger, the concentration curve has its maximum point shifted into shorter reaction time and decreasing the value of the point as a result of removing more water as shown in the water formation rate curve. In other word, larger membrane unit capacity causes a lesser accumulation of water in the reactor, i.e. a smaller area under the curve representing water concentration versus time; 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.



**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  $\partial_w = 1 \text{ h}^{-1}$ . Broken lines are reaction parameters calculated for the reaction without PV at  $C_{C0} = 20 \text{ mol/m}^3$ .

optimization of them in design step to achieve the best membrane reactor performance for a given circumstance.

Fig. 4 exhibits the variations of reaction conversion, dimensionless water concentration and reaction volume with reaction time in PV-aided reaction at different catalyst concentrations. All of the reaction conversions in the reaction go beyond the equilibrium conversion with increasing reaction time. Usually, increasing catalyst concentration accelerates the esterification reaction. Thus, it is found in this figure that at higher catalyst concentration, the reaction proceeds and reaches faster completion. As mentioned before, the pervaporative dehydration is slower than the reaction during the early

period of reaction. With increasing catalyst concentration, the reaction is accelerated to produce more products, resulting in increasing faster water content with reaction time. 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 and located 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, 0.95 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 Fig. 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 labeled-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 de-

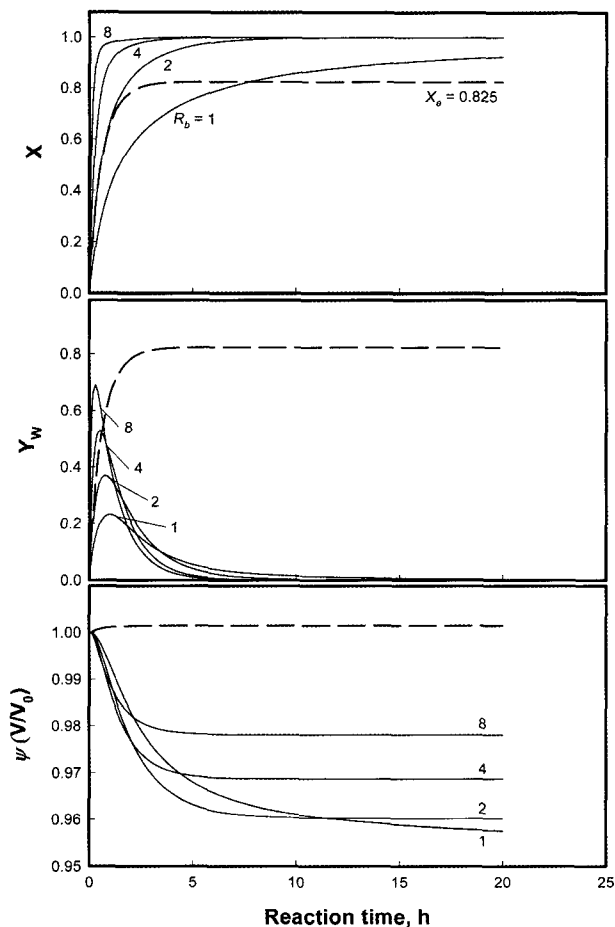


Fig. 5. Reaction parameters with reaction time in PV-aided reaction with perfect separation at different initial molar ratios.  $C_0 = 1000 \text{ mol/m}^3$ ,  $C_{C0} = 20 \text{ mol/m}^3$  and  $\delta_w = 1 \text{ h}^{-1}$ . Broken lines are reaction parameters calculated for the reaction without PV at  $R_b = 2$ .

clines the extent of mixture volume reduced as much as the produced water which is removed by PV.

### 3.2. 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 explain more practical reaction behavior on the PV-aided reaction, separation efficiency in the permeation of species though membrane should be tak-

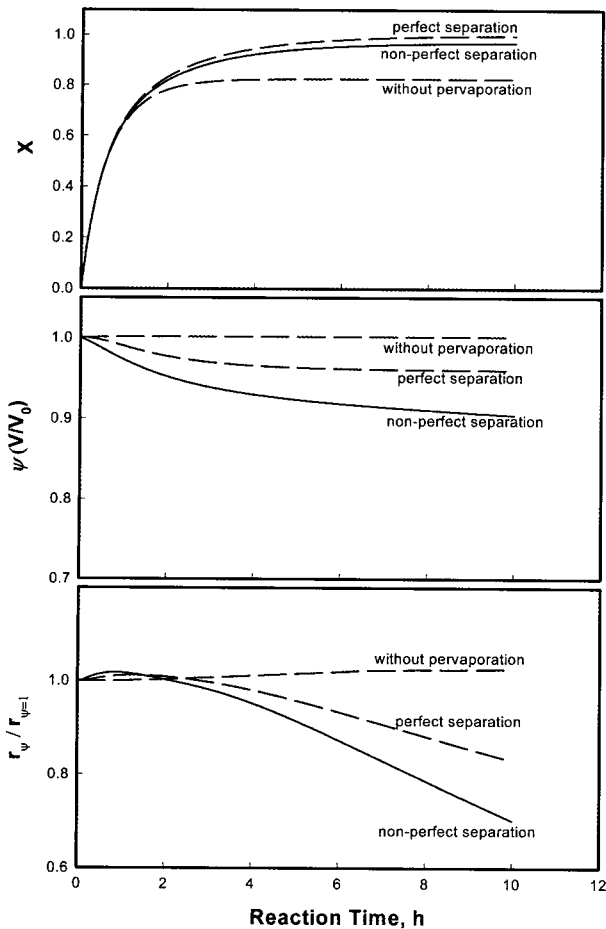
en into account.

There will be three cases for permeation through the hydrophilic membrane in real PV-aided reaction system:

- Case 1: the permeation of binary components (called binary permeation hereafter) through membrane in which water and component  $i$  permeates which is one of reactants with a separation factor  $\alpha_{i/W}$  and others else are blocked completely by the membrane.
- Case 2: the permeation of ternary components (called ternary permeation hereafter) through membrane in which water and both reactants  $A$  and  $B$  with separation factors  $\alpha_{A/W}$  and  $\alpha_{B/W}$ , respectively, and ester is blocked completely by the membrane.
- Case 3: the permeation of all species through membrane in which water and both reactants  $i$  and  $j$  with water with separation factors  $\alpha_{A/W}$ ,  $\alpha_{B/W}$  and  $\alpha_{E/W}$ , respectively. However, this case has an equivalent effect on reaction with Case 2 because the permeation of ester influence the reaction in the same way as water permeation does.

Let's consider the permeation effect of ternary components on the reaction as an example of non-perfect separation. 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 ( $\alpha_{E/W} = 0$ ). Here, 0.025 of  $\alpha_{i/W}$  means that the permeability of species  $i$  is 0.05 of water permeability. In the model reaction, the alcohol is used in excess ( $R_b = 2$ ). When one or both of reactants permeates with water through membrane, in the PV-aided reaction with non-perfect separation, conversion line lies between two lines labeled with "perfect separation"

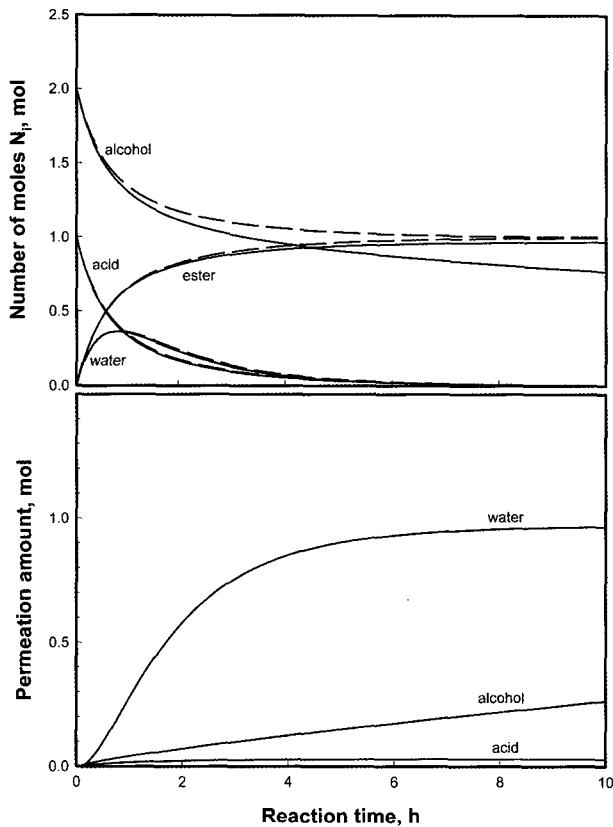




**Fig. 6.** Reaction parameters with reaction time in PV-aided reaction with non-perfect separation at permeation of ternary components (reactants-water).  $C_0 = 1000 \text{ mol/m}^3$ ,  $C_{C0} = 20 \text{ mol/m}^3$ ,  $R_b = 2$  and  $\vartheta_W = 1 \text{ h}^{-1}$ . The non-perfect separation has  $\alpha_{A/W} = \alpha_{B/W} = 0.025$ ,  $\alpha_{E/W} = 0$ .

and “without pervaporation”. The line of “perfect separation” is designated for conversion in the PV-aided reaction with perfect separation and “without pervaporation” for conversion in the reaction without PV. With the permeation of reactant, the PV-aided reaction system continuously loses the reactant during the reaction depending on its separation factor, leading 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 due to water permeation. Reaction volume ( $V/V_0$ ) decreases fast at initial and then reduces slower and slower as the reactants are depleted, as shown in Fig. 6. Reaction vol-

ume with non-perfect separation at any instant is below one with perfect separation. More decreasing of reaction volume in non-perfect separation system is obviously attributed to the additional permeation of organic species besides water permeation. To characterize volume change effect caused by the permeation of species on the reaction, the ratios of the reaction rate  $r_\psi$  to a reaction rate  $r_{\psi=1}$  that is determined under 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  $r_\psi$  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. As discussed in previous study [10], the magnitude of the ratio can tell how the volume change contributes to the reaction rate; ratio  $< 1$  for more product-concentrating effect than reactant-concentrating effect, ratio = 1 for no effect of volume change, and ratio  $> 1$  for more reactant-concentrating effect. 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 PV-aided reaction with non-perfect separation has a larger reaction ratio than the other two reaction systems at the incipient stage of reaction. It reveals that reactant-concentrating effect by removal of the reactant is dominant over product-concentrating effect during the beginning period of reaction when the concentrations of products are low. However, as the reaction progresses further and the concentration of product increases as well, the ratios decrease below 1, decreasing faster for the reaction system with non-perfect separation. It can be noted from these observations that the reactant-concentrating effect exerts to a great deal of extent during an incipient es-



**Fig. 7.** Moles of and cumulative permeation amount of each species in the reactor with reaction time in PV-aided reaction with non-perfect separation at permeation of ternary components (reactants-water).  $C_0 = 1000 \text{ mol/m}^3$ ,  $C_{C0} = 20 \text{ mol/m}^3$ ,  $R_b = 2$  and  $\partial_w = 1 \text{ h}^{-1}$ . The non-perfect separation has  $\alpha_{A/W} = \alpha_{B/W} = 0.025$ ,  $\alpha_{E/W} = 0$ . Broken lines are for perfect separation and solid lines for non-perfect separation.

terification in PV-aided reaction at non-equal molar reactants, and as product concentration increases with reaction time, the product-concentrating effect becomes important and then eventually predominant over the reactant-concentrating effect as approaching reaction completion.

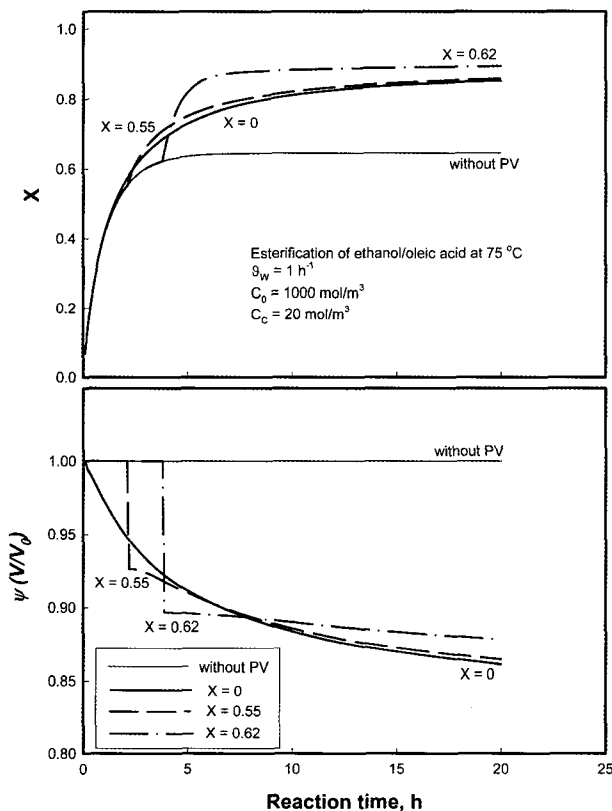
Fig. 7 shows the moles of each species in reaction mixture and its cumulative permeation amount of with reaction time. Since the alcohol and acid are consumed in the reaction and also removed simultaneously by permeation through membrane, their moles in the reaction mixture decrease faster with time than in the reaction system with perfect 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 from the simulation of the model equations in the reaction without PV and PV-aided reactions at different initial molar ratios and separation efficiencies are summarized 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. Oleic acid has a larger molar volume than ethanol, as shown in Table 1. Reaction volume decreases more in binary permeation of oleic acid-water than in that of ethanol-water at any initial molar ratio. More decreasing of reaction volume will cause to more concentrate reactants to such an extent that higher reaction conversion can be obtained due to faster reaction rate, as can be seen Table 2. 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

**Table 2.** Equilibrium Reaction Conversion in the Reaction without PV and PV-aided Reaction at Different Initial Molar Ratios and Different Separation Efficiencies,  $C_0 = 1000 \text{ mol/m}^3$ ,  $C_C = 20 \text{ mol/m}^3$  and  $75^\circ\text{C}$ 

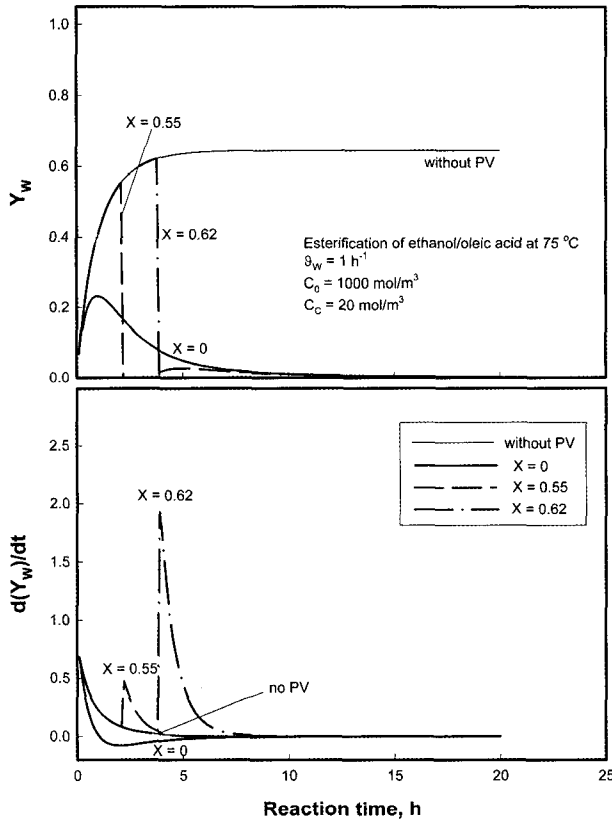
| Reaction system                           | $R_b$  | $X_{eq}$ |       |
|---|--|----------|-------|
| Reaction without PV                       | 1  | 0.645    |       |
| PV-aided reaction with perfect separation | 1  | 1.000    |       |
| Permeation of binary species              | $\alpha_{A/W} = 0.05$ , $\alpha_{B/W} = \alpha_{E/W} = 0$  | 1        | 0.851 |
|   | $\alpha_{B/W} = 0.05$ , $\alpha_{A/W} = \alpha_{E/W} = 0$  | 1        | 0.846 |
|   | $\alpha_{E/W} = 0.05$ , $\alpha_{A/W} = \alpha_{B/W} = 0$  | 1        | 1.000 |
| Reaction without PV                       | 2  | 0.825    |       |
| PV-aided reaction with perfect separation | 2  | 1.000    |       |
| Permeation of binary species              | $\alpha_{A/W} = 0.05$ , $\alpha_{B/W} = \alpha_{E/W} = 0$  | 2        | 0.947 |
|   | $\alpha_{B/W} = 0.05$ , $\alpha_{A/W} = \alpha_{E/W} = 0$  | 2        | 1.000 |
|   | $\alpha_{E/W} = 0.05$ , $\alpha_{A/W} = \alpha_{B/W} = 0$  | 2        | 1.000 |
| Permeation of ternary species             | $\alpha_{A/W} = \alpha_{B/W} = 0.025$ , $\alpha_{E/W} = 0$ | 2        | 0.971 |
| Permeation of all species                 | $\alpha_{A/W} = \alpha_{B/W} = \alpha_{E/W} = 0.02$        | 2        | 0.977 |

**Fig. 8.** Plots of reaction conversion and dimensionless reaction volume with reaction time in PV-aided reaction with non-perfect separation at different timings to impose on pervaporation.  $C_0 = 1000 \text{ mol/m}^3$ ,  $C_{C0} = 20 \text{ mol/m}^3$ ,  $R_b = 1$  and  $\partial_W = 1 \text{ h}^{-1}$ . The non-perfect separation has  $\alpha_{A/W} = 0.05$  and  $\alpha_{B/W} = \alpha_{E/W} = 0$ .

be somewhat allowed.

### 3.3. Effect of Timing to Impose Pervaporation Process on Reaction System

Fig. 8 shows plots of reaction parameters with reaction time obtained at different timing of imposing pervaporation to facilitate the Esterification. It is found that the later is pervaporation imposed, the more is the reaction facilitated. The facilitation of reaction is accomplished by pervaporation removing water cumulatively produced before imposing pervaporation. As pervaporation is imposed at higher reaction conversion, the accumulated amount of water produced during a period of reaction time till pervaporation is larger, that is, higher water concentration in reaction system at an instant of imposing pervaporation. Since flux through hydrophilic membrane is proportional to water concentration in liquid mixture, larger water permeate through the membrane at the instant of imposing pervaporation at higher reaction conversion. Thus, reaction volume reduces more rapidly due to faster permeation of water as shown in the plot of reaction volume with reaction time in Fig. 8, and thereby the forward reaction is more accelerated and more reaction facilitation is experienced (Fig. 9). In addition, it is observed that a loss of reactant species by permeation is less when perva-



**Fig. 9.** Dimensionless water concentration and water formation rate with reaction time in PV-aided reaction with non-perfect separation at different timings to impose on pervaporation.  $C_0 = 1000 \text{ mol/m}^3$ ,  $C_{C0} = 20 \text{ mol/m}^3$ ,  $R_b = 2$  and  $\vartheta_w = 1 \text{ h}^{-1}$ . The non-perfect separation has  $\alpha_{A/W} = 0.05$  and  $\alpha_{B/W} = \alpha_{E/W} = 0$ .

poration is imposed later, resulting in less reduction of reaction volume as can be seen in Fig. 8. However if pervaporation is imposed at too high reaction conversion, water concentration in the reaction solution can be too high to likely damage the hydrophilic membrane. Thus, timing to impose pervaporation should be determined by compromising the undesirable risk.

### 3.4. Relationship between Reaction Parameters and Membrane Unit Capability

At a critical membrane unit capability,  $(\vartheta_w)_{cr}$  beyond which water removed as fast as it is formed, so that the reverse reaction rate can be negligible in compared with the forward reaction rate because, the resulting reaction rate is approximated to the forward reaction

rate. Then the differential equation Eq. (17) can be solved analytically to give the following relation;

$$t_r = \frac{1}{C_0 k_1 (R_b - 1)} \ln \frac{R_b - X}{R_b (1 - X)} \quad (18)$$

where  $t_r$  is a time required to reach a conversion  $X$ . In this case, the total amount of water removed through membrane would be equal to the water amount produced by the reaction. Note that  $C_0$  is equal to the water concentration that would be obtained at complete reaction in a simple batch reactor. Thus, the total cumulative permeation amount  $Q_w$  and average permeation rate,  $\dot{Q}_w$  of water for the permeating time are given, respectively,

$$\begin{aligned} Q_w &= X C_0 V_0 = \int_0^{t_r} J_w A_m dt \\ &= \dot{Q}_w t_r \end{aligned} \quad (19)$$

where

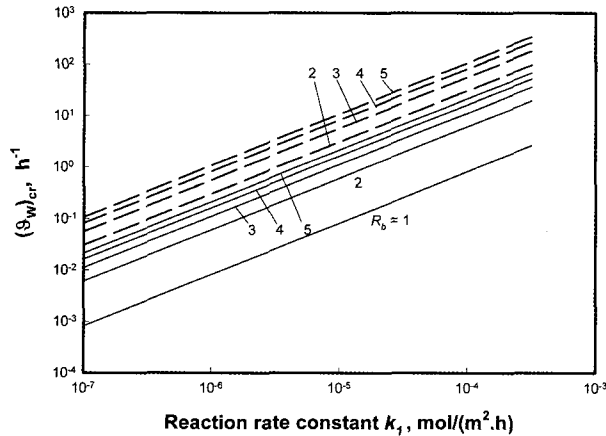
$$\dot{Q}_w = C_0 V_0 (\vartheta_w)_{cr} Y_w \quad (20)$$

$$Y_w = \frac{\int_0^{t_r} Y_w dt}{\int_0^{t_r} dt} \quad (21)$$

Thus, combining Eqs (18)~(21) yields the relationship between reaction parameters and membrane unit capability  $(\vartheta_w)_{cr}$ ;

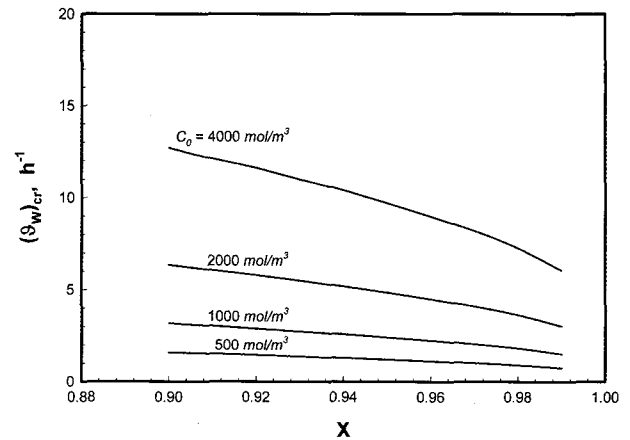
$$(\vartheta_w)_{cr} = \frac{C_0 (R_b - 1) X}{Y_w \ln \frac{R_b - X}{R_b (1 - X)}} \quad (22)$$

The above equation is very important relationship to explain how the membrane unit capacity is dependent on the reaction parameters. Fig. 10 shows the plots of the membrane unit capacities with reaction rate at different initial molar ratios and different average water concentrations. The membrane unit capacity has an in-



**Fig. 10.** Plots of membrane unit capacities against reaction rate constant to obtain 0.98 of reaction conversion at different initial molar ratio of reactants.  $C_0 = 1000 \text{ mol/m}^3$  and  $C_{C0} = 20 \text{ mol/m}^3$ . Broken lines are for average dimensionless water concentration of 0.001 and solid lines for average dimensionless water concentration of 0.005.

crease with increasing the reaction rate constant and/or with initial molar ratio because reaction rate is larger. Eq. (22) gives 5.9 as the value of membrane unit capacity at  $R_b = 1$ ,  $C_0 = 1000 \text{ mol/m}^3$ ,  $X = 0.99$ ,  $k_1 = 6.8 \times 10^{-4}$ ,  $C_C = 20 \text{ mol/m}^3$  and reaction temperature =  $75^\circ\text{C}$ , which are the operating conditions used in Fig. 2. Conversion curve at  $\vartheta_w > 2$  is very close to the upper limit curve and water concentration approximates to the lower limit curve at  $\vartheta_w > 5$ , as can be seen in Fig. 2. Thus, from the comparison of the calculated value from Eq. (22) and those calculated from the model, one can see that the calculation from Eq. (22) yields a reasonable value for the membrane unit capacity. Fig. 11 presents the calculated membrane unit capacity value with reaction conversion at different initial reactant concentrations. The membrane unit capacity is smaller to reach higher reaction conversion. The longer reaction time is required to obtain higher reaction conversion for given reaction conditions. Thus smaller membrane area is needed for longer reaction time, i.e. longer permeation time. It is also natural that larger membrane unit capacity is necessary for larger initial concentration, as can be seen in this figure. As a result, the relationship can be used as a design tool



**Fig. 11.** Plots of membrane unit capacities against reaction conversion obtained at different initial concentrations of reactant A.  $k_1 = 3 \times 10^{-5} \text{ mol/m}^3$ ,  $R_b = 2$  and  $C_{C0} = 20 \text{ mol/m}^3$ . Average dimensionless water concentration is 0.005.

to provide a proper combination of the reaction parameters for a given membrane capacity or a combination of membrane area, membrane permeability and reaction mixture volume for a given operating conditions.

#### 4. Conclusions

PV-aided esterification was studied by using a practical model based on non-perfect separation through membrane. It was illustrated 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 obtained 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 can 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 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. The

volume change effect caused by the permeation on the reaction was characterized by the reaction ratio of  $r_\psi$  to  $r_{\psi=1}$  that was determined under assumption of negligible volume change. 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. It is found that the later is pervaporation imposed, the more is the reaction facilitated. The facilitation of reaction is accomplished by pervaporation removing water cumulatively produced before imposing pervaporation. A relationship between membrane unit capacity and reaction parameters was derived. With help of the relationship, reaction parameters for a given membrane unit capacity or membrane unit capacity at certain reaction condition can be determined.

### Notation

|            |   |
|------------|---|
| $A_m$      | 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                 |
| $\partial_W$   | measure of membrane unit capacity to remove water, $s^{-1}$                   |
| $\psi$         | ratio of reaction mixture volume at time $t$ to initial volume, dimensionless |
| $\rho$         | 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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