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Esterification of acetic acid with isopropanol coupled with pervaporation
Part II. Study of a pervaporation reactor

Maria Teresa Sanz[a], Jürgen Gmehling[b,*]

[a] Department of Chemical Engineering, University of Burgos, 09001 Burgos, Spain
[b] Department of Industrial Chemistry, University of Oldenburg, D-26111 Oldenburg, Germany

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Abstract

The combination of the chemical reaction step with a pervaporation process can increase the conversion of reversible reactions such as esterification by removing selectively the water formed from the reacting mixture. The esterification of acetic acid with isopropanol was carried out in a reactor combined with a pervaporation unit. The conversions achieved are distinctly higher than the equilibrium conversion. Kinetic and pervaporation parameters obtained in a previous study were used to describe the behavior of the hybrid process. The influence of different operating parameters such as reaction and pervaporation temperature, ratio of membrane area to initial reaction volume, initial molar reactant ratio and amount of catalyst on the process performance has been analyzed in this work.

Keywords: Isopropyl acetate; Esterification; Pervaporation; PERVAP®; Hybrid process

1. Introduction

The combination of the chemical reactor with a pervaporation unit is an interesting alternative to increase the conversion of equilibrium-limited reactions such as esterification reactions. By removing selectively the products from the reacting mixture the conversion can be continuously shifted beyond the thermodynamic equilibrium conversion. The use of pervaporation reactors is attractive because the efficiency of the process is not limited by the phase equilibrium and the production costs can be reduced due to the higher conversion obtained and the lower separation effort caused by this fact [1]. In membrane reactors two basics layouts can be distinguished [2]: (1) the reactor and the membrane are two physically distinct units (2) or both unit operations are integrated into a single unit. In esterification processes, usually the pervaporation unit is built as an external unit. This means, the pervaporation unit is integrated in the recycle to remove water continuously from the reactor [3].

In the literature there are several examples of equilibrium-limited systems where the application of reaction coupled with pervaporation can be beneficial. Assabumrungrat et al. [4] obtained much higher conversions compared to the classical reactor system in the study of the synthesis of methyl acetate from methanol and acetic acid by using pervaporation membrane reactors. To model the performance of the hybrid process they considered the kinetic parameters of the catalytic reaction using Amberlyst 15 and the permeation rates for the four components through the polymeric membrane PERVAP® 2201. In the esterification of acetic acid with 1-propanol, 2-propanol [5] and benzyl alcohol [6] catalyzed by *p*-toluenesulfonic acid, quasi-complete conversions were reached by using a commercial polyvinyl alcohol-based composite membrane (GFT). Laboratory prepared cross-linked polyvinyl alcohol membranes were also used to study the combination of pervaporation with esterification of acetic acid with *n*-butanol catalyzed by $Zr(SO_4)_2{\cdot}4H_2O$ [7,8]. Zeolite membranes were successfully applied for the selective removal of water by pervaporation for the esterification of lactic acid with ethanol catalyzed by *p*-toluenesulfonic acid obtaining yields higher than 90% [9]. Membrane reactors also find increasing application in the biotechnology area. The hydrophilic membrane PERVAP 1005 (GFT) was used in the study of an integrated esterification pervaporation process for the enzymatic esterification of oleic-acid with *i*-amyl alcohol [10]. In this reaction, the water removal improves the effective-

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[*] Corresponding author. Tel.: +49 441 7983831; fax: +49 441 7983330.
E-mail address: gmehling@tech.chem.uni-oldenburg.de (J. Gmehling).

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Nomenclature

a	activity
A	membrane area (m^2)
A/V_0	ratio of membrane area to initial reacting volume (m^{-1})
F	molar permeate flux ($mol\,min^{-1}\,m^{-2}$)
J	mass permeate flux ($kg\,h^{-1}\,m^{-2}$)
m_{cat}	mass of catalyst (g)
n	number of moles
r	reaction rate ($mol\,g\,cat^{-1}\,min^{-1}$)
R	general gas constant ($kJ\,mol^{-1}\,K^{-1}$)
t	time (min)
T	absolute temperature (K)
w	weight fraction
x	mole fraction

Subscripts

HOAc	acetic acid
i	components
iPrOAc	isopropyl acetate
IPA	isopropanol
W	water

ness of the process since water not only has a disadvantageous effect on the reaction rate but also on the enzymatic activity. The same membrane (PERVAP 1005) was employed in the hybrid process for the esterification of acetic acid with ethanol catalyzed by *p*-toluenesulfonic acid coupled with pervaporation [11].

Other examples different from esterification systems are the synthesis of tertiary ethers. Kiatkittipong et al. [12] investigated the synthesis of ethyl-tert-butyl ether from ethanol and tert-butyl alcohol catalyzed by β-zeolite in a pervaporation membrane reactor.

The objective of this work was the study of the esterification of acetic acid with isopropanol catalyzed by Amberlyst 15 coupled with a pervaporation unit. Experiments were carried out in a batch reactor coupled with an external pervaporation unit using the commercial polymeric membrane PERVAP® 2201 for the water removal. The pervaporation performance of this membrane has already been tested for the quaternary mixture involved in this esterification system. It was shown that this membrane presents high selectivity towards water.

Based on the previous kinetic and pervaporation studies [13] a model has been developed to describe the hybrid esterification–pervaporation process. Good agreement was obtained between the experimental and simulated values obtained with the model proposed in this work. This model was used to analyze the influence of four operating parameters, such as operating temperature, ratio of membrane area to initial reaction volume, initial molar reactant ratio, and catalyst concentration on the process performance [14].

2. Theory

2.1. Reaction–pervaporation coupled model

The reaction–pervaporation coupled process can be modeled by combining the equations of the reaction rate and the permeation rates. By performing the material balance for the reactor-pervaporation system, the following expression is obtained for each of the components in the reaction mixture:

$$\frac{dn_i}{dt} = m_{cat} r_i - A F_i \qquad (1)$$

where n_i is the number of mole of species i in the reactor, r_i the reaction rate of component i in the catalytic reaction (mol/g of catalyst min), m_{cat} the mass of catalyst in the reactor (g), F_i the molar permeate flux of species i (mol/min m^2) through the membrane, and A the area of the membrane (m^2).

The parameters obtained in the previous [13] kinetic study of the reaction catalyzed by Amberlyst 15 and permeation rates through the membrane PERVAP® 2201 were used to simulate the behavior of the esterification reactor coupled with the pervaporation step. The pseudohomogeneous model was used to describe the reaction rate for the esterification of acetic acid with isopropanol using Amberlyst 15:

$$r_i = \frac{1}{m_{cat}}\frac{1}{\nu_i}\frac{dn_i}{dt} = 1.02 \times 10^7 \exp\left(\frac{-64.59}{RT}\right) a_{HOAc} a_{IPA} - 1.90 \times 10^7 \exp\left(\frac{-73.63}{RT}\right) a_{iPrOAc} a_{W} \qquad (2)$$

whereby the activity coefficients are calculated using the UNIQUAC equation [13]. The relationship between the reaction rates of the four components can be expressed by the stoichiometric factors:

$$r_W = r_{iPrOAc} = -r_{HOAc} = -r_{IPA} \qquad (3)$$

The permeation fluxes of the different components in the mixture were calculated through the expressions proposed in the previous work [13], where it was shown that the water permeate flux was close to the total permeate flux. The total flux of the three other components was always less than 5 wt.% of the total permeate flow. The expression obtained for the water flux ($kg\,h^{-1}\,m^{-2}$) through the membrane PERVAP® 2201 was:

$$J_W = 2.0 \times 10^6 \exp\left(\frac{-45.8}{RT}\right) [\exp(6.5 w_W) - 1] \qquad (4)$$

The expressions of the flux for the other three components can also be found in our previous work [13].

The set of conversion equations obtained from the material balance for all the components present in the reaction mixture, were solved numerically by using a fourth-order Runge–Kutta method to obtain the concentration profile for all the four components in the reactor as a function of time. In the model used in this work, there are no additional adjustable parameters. All required parameters have been obtained from independent kinetic measurements and pervaporation studies.

3. Experimental section

3.1. Materials

The PVA membrane, PERVAP® 2201, used in this work was supplied by Sulzer Chemtech. For the esterification reaction the ion exchange resin, Amberlyst 15 (Rohm&Haas) was used as heterogeneously catalyst. All reactants were purchased with purity higher than 99%. The chemicals were dried over molecular sieve. No further purification was carried out for the experiments.

3.2. Procedure

The experimental set-up used for the reaction–pervaporation experiments is shown in Fig. 1. The esterification reaction combined with the pervaporation step was performed in a semi-batch operation mode. The membrane was placed in a specially designed stainless steel permeation cell, which provides an effective membrane area in contact with the feed mixture of 100 cm^2 [13,15]. Isopropanol was added to the reactor together with Amberlyst 15 and heated to the reaction temperature. Acetic acid was heated separately. After the reaction temperature was reached for acetic acid it was added to the reactor. At the same time, the reaction mixture was pumped continuously through the pervaporation unit with a feed rate of 16.6 kg/h. This time was taken as the starting time for the experiments. Water was continuously removed from the feed stream through the membrane and the retentate stream with reduced water content was returned to the reactor. The reaction temperature was kept constant within ±0.5 K by using a thermostat. On the permeate side, kept at low pressure with the help of a vacuum pump, the water rich vapor stream is condensed using a glass trap cooled with liquid nitrogen. During the experiments the downstream pressure was always maintained below 1 mbar. Periodically, samples were withdrawn from the reactor to follow the composition of all the components in the reaction mixture. The permeate flux was determined gravimetrically by weighing the mass of the permeate collected.

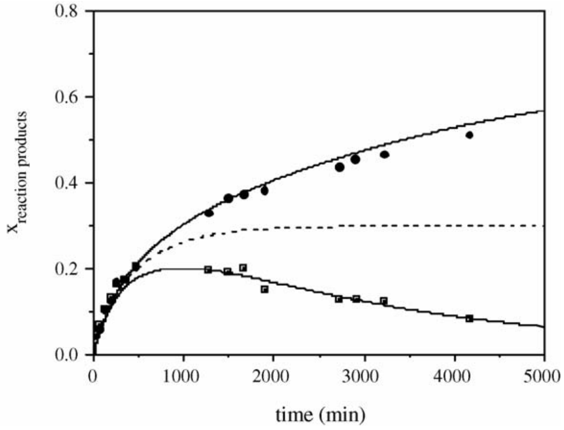

Fig. 2. Variation of the mole fraction of isopropyl acetate (●) and water (■) in the pervaporation coupled reactor as a function of time ($n_{\text{IPA}}/n_{\text{HOAc}} = 1.5$; $T_{\text{reaction}} = 337.15$ K; $T_{\text{pervaporation}} = 334.15$ K; $A/V_0 = 30\ \text{m}^{-1}$; catalyst = 6 wt.%). The continuous lines represent the results obtained with the hybrid model. The dotted line corresponds to the esterification reaction without pervaporation.

3.3. Sample analysis

Samples from both, the reactor and the permeate membrane side, were analyzed by gas chromatography using a HP 6890, equipped with a thermal conductivity detector (TCD). The GC column was a HP-FFAP. The method used to analyze the samples has already been described [13].

4. Results and discussion

In Fig. 2 a typical concentration profile for the esterification–pervaporation coupled process together with the corresponding profile in a conventional reactor is presented. The water profile in the reacting mixture for the pervaporation-supported process shows that at the beginning the water content increases continuously until a maximum is reached. After this maximum, the water content decrease continuously and tends to go to zero. This means, that at the beginning of the process, the water production is faster than its removal by pervaporation due to the low water content. As the reaction proceeds, the water concen-

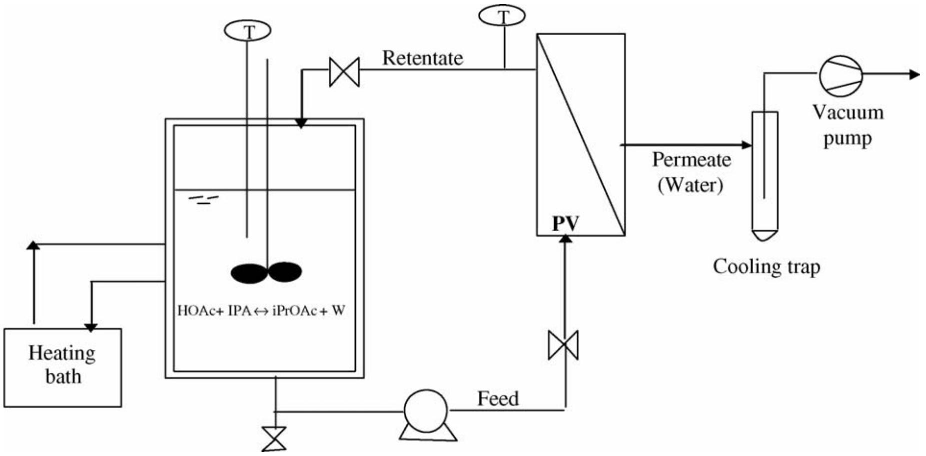

Fig. 1. Experimental set-up for the esterification pervaporation coupled experiments.

tration increases continuously until a maximum is reached in which its removal by permeation rate is equal to its production by esterification [16]. After the water content has reached the maximum value, the water removal by pervaporation from the reaction mixture is faster than its formation rate by esterification. As a consequence, the water concentration in the reactor decreases continuously.

Due to the continuous water removal from the reaction mixture, the conversion obtained with the esterification–pervaporation reactor is distinctly higher than the maximum equilibrium conversion, which can be achieved with a conventional batch reactor without pervaporation unit. Conversions higher than 90% can easily be achieved by combination with a pervaporation unit.

Good agreement between experimental data and the values calculated with the model proposed in this work can be observed, as shown in Fig. 2. Therefore this model was used to study the influence of the different operating parameters on the process performance. In a esterification–pervaporation coupled process there exist mainly four operating variables: operating temperature, initial molar reactant ratio (n_{IPA}/n_{HOAc}), ratio of the membrane area to initial reacting mixture volume (A/V_0) and catalyst concentration. David et al. [14] classified these four parameters in three groups: (1) factors which influence directly the esterification kinetics: catalyst concentration, and initial molar reactant ratio, (2) factors that influence directly pervaporation kinetics: ratio of membrane area to reaction volume and (3) factors that influence simultaneously the esterification and pervaporation kinetics: temperature.

4.1. Effect of initial reactant molar ratio (n_{IPA}/n_{HOAc})

Different experiments were carried out in the esterification pervaporation reactor at different initial reactant molar ratios, n_{IPA}/n_{HOAc}. In Figs. 2 and 3 the experimental results together with the simulated results are presented. For a better comparison of the different performances only the simulation results are plotted in Fig. 4. When the n_{IPA}/n_{HOAc} ratio increases the value of the maximum water content decrease, but the time was found to be nearly the same in the range of n_{IPA}/n_{HOAc} studied in this work. The lower values of the maximum water content are due to the dilution effect by increasing the initial molar reactant ratio [14]. The same behavior has been described in the literature for the study of the coupling effect of esterification with pervaporation [7,14,17]. In conventional reactors higher equilibrium conversions are obtained by increasing the initial molar reactant ratio, but the limited reactant will never react completely.

In Fig. 5 simulation results are plotted for the case that water is already present at the beginning of the reaction for a conventional reactor and for pervaporation coupled reactor. An initial water content of 10 wt.% was used for the simulation. In a conventional reactor, the equilibrium conversion decreases when water is present at the beginning of the process. When a pervaporation unit is used, the effect is less drastic. By increasing the water concentration in the pervaporation coupled reactor, the permeation rate through the membrane increases, and consequently the water content in the reactor will decrease rapidly.

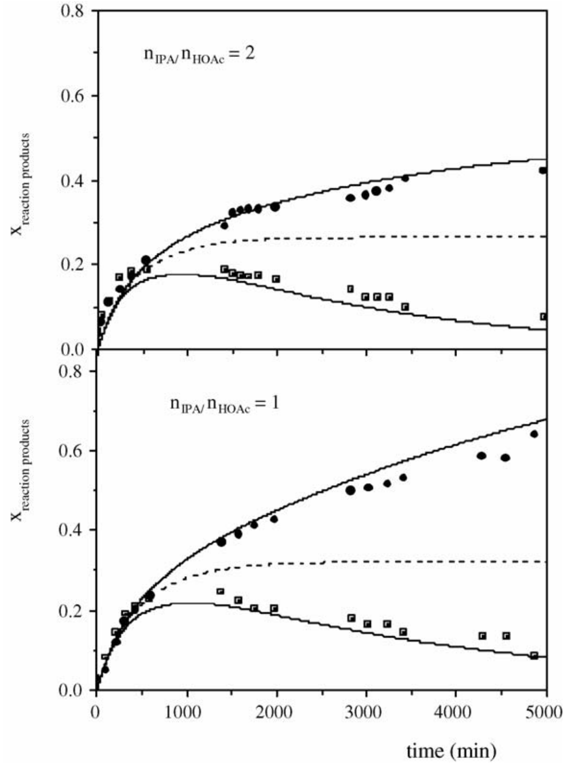

Fig. 3. Variation of the mole fraction of isopropyl acetate (●) and water (■) in the pervaporation coupled reactor as a function of time at different initial molar reactant ratios ($T_{reaction}$ = 337.15 K; $T_{pervaporation}$ = 334.15 K; $A/V_0 = 30\ m^{-1}$; catalyst = 6 wt.%). The continuous lines represent the results obtained with the hybrid model. The dotted line corresponds to the esterification without pervaporation.

4.2. Effect of the membrane area to initial solution volume ratio (A/V_0)

In a esterification–pervaporation reactor a low permeability of the membrane can be compensated by using larger membrane areas [16]. In Fig. 6 the simulation results obtained for the

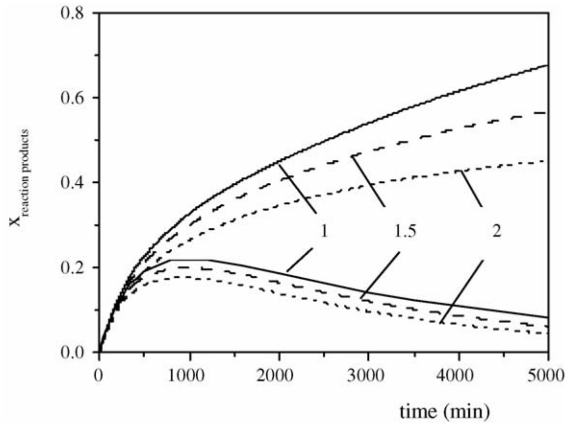

Fig. 4. Effect of the initial molar reactant ratio (n_{IPA}/n_{HOAc}) on the performance of the esterification–pervaporation reactor ($T_{reaction}$ = 337.15 K; $T_{pervaporation}$ = 334.15 K; catalyst = 6 wt.%; $A/V_0 = 30\ m^{-1}$).

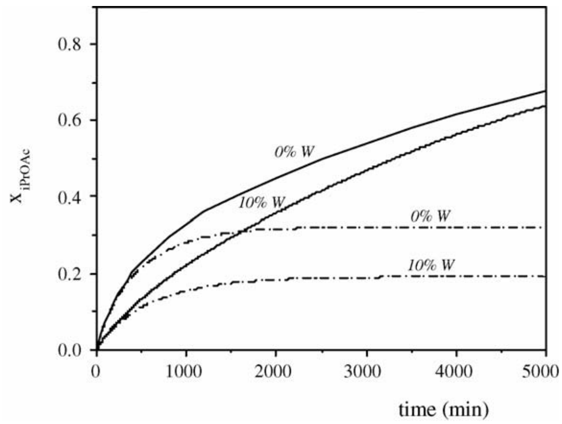

Fig. 5. Effect of the presence of water (10 wt.%) at the beginning of the process ($T_{\text{reaction}} = 337.15$ K; $T_{\text{pervaporation}} = 334.15$ K; catalyst = 6 wt. %; $n_{\text{IPA}}/n_{\text{HOAc}} = 1$; $A/V_0 = 30\ \text{m}^{-1}$) on the performance of a conventional reactor (dotted line) and on a pervaporation coupled reactor (continuous line).

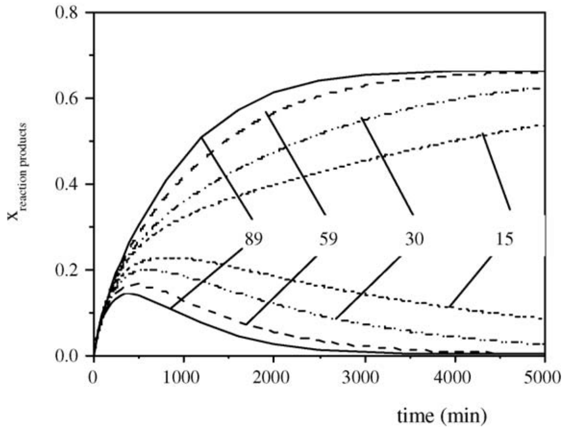

Fig. 6. Effect of the ratio A/V_0 on the performance of the esterification–pervaporation reactor ($T = 343.15$ K; catalyst = 6 wt.%; $n_{\text{IPA}}/n_{\text{HOAc}} = 1.5$).

performance of a esterification–pervaporation reactor at different A/V_0 ratio are presented. With increasing A/V_0 ratio higher isopropyl acetate compositions in the reactor are obtained. The maximum water concentration is reached faster at higher A/V_0 values, but the maximum value decreases with the A/V_0 ratio. Increasing the membrane area per unit of reaction volume, water will be extracted faster and obviously, the water concentration in the reactor will decrease faster.

In Table 1 the different conversions reached in the reactor at a certain operation time are listed. A zero value of this ratio corresponds to a conventional reactor without pervaporation unit. At a certain time, with increasing A/V_0 ratio higher conversions are achieved.

Table 1
Conversion referred to the limited reactant (HOAc) at $t = 50$ h at different values of the ratio A/V_0 ($T_{\text{reaction}} = T_{\text{pervaporation}} = 343.15$ K; $n_{\text{IPA}}/n_{\text{HOAc}} = 1.5$; amount of catalyst = 6 wt.%)

A/V_0	Conversion (%)
0	73.8[a]
15	82.3
30	89.8
59	96.7
89	98.8

[a] Equilibrium conversion.

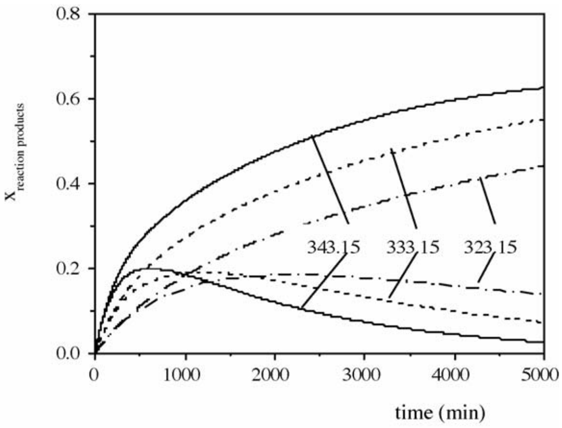

Fig. 7. Effect of the temperature on the performance of the esterification–pervaporation reactor ($A/V_0 = 30\ \text{m}^{-1}$; catalyst = 6 wt.%; $n_{\text{IPA}}/n_{\text{HOAc}} = 1.5$).

From Fig. 6 it can be concluded that no huge improvements can be obtained using a A/V_0 ratio of $89\ \text{m}^{-1}$. The selection of the ratio of the membrane area and the reaction volume will normally be determined from an economical point of view [11].

4.3. *Effect of operating temperature*

The operating temperature has a direct influence on the permeation and reaction rate. From the previous kinetic and pervaporation studies [13] it can be concluded that with increasing temperature both, the permeation rate through the membrane and the water production rate by esterification increase. In Fig. 7 the simulation results obtained at different operating temperatures are presented. From this figure it can be concluded that the maximum water content is reached faster at higher temperatures showing that the effect of the operating temperature on the water production is stronger than on the water permeation rate. After this maximum, the decreasing in water concentration in the reacting medium is faster at higher temperatures due to the higher permeability of the membrane with temperature. A similar temperature dependence has been described by other authors in the study of esterification–pervaporation supported processes [7,14]. The membrane used in our work, PERVAP® 2201 shows a maximum long term temperature of 100 °C. By temperatures above 100 °C the membrane will be damaged, which sets a limit on the vapor pressure that can be used to drive the pervaporation.

4.4. *Effect of catalyst concentration*

In Fig. 8 the simulation results at different amount of catalyst in the esterification–pervaporation coupled reactor are presented. Increasing catalyst concentration of course increases the reaction rate. Consequently, with increasing catalyst concentration the maximum in water concentration in the reacting medium is reached faster. Due to this higher water content in the reactor at high catalyst concentration, the water permeation rate will also

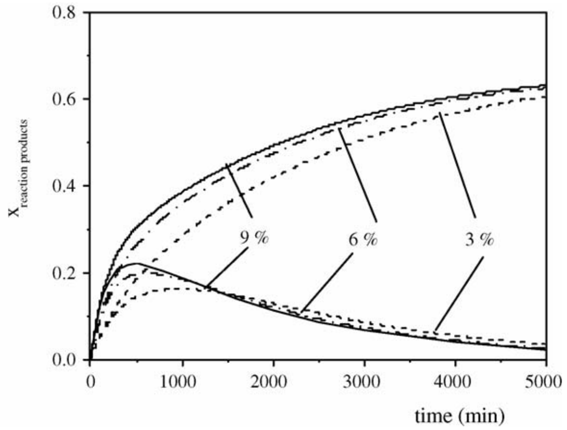

Fig. 8. Effect of the catalyst concentration (wt.%) on the performance of the esterification–pervaporation reactor ($T = 343.15$ K; $A/V_0 = 30\,\text{m}^{-1}$; $n_{\text{IPA}}/n_{\text{HOAc}} = 1.5$).

be increased since permeation flux increase with the water content in the feed, leading to a faster water removal in the reactor [16].

5. Conclusions

The esterification of acetic acid with isopropanol combined with a pervaporation unit has been studied in this work. The experimental conversions achieved in the hybrid process were in all cases distinctly higher than the equilibrium limited conversion reached in a conventional reactor.

The influence of several important operating variables on the esterification–pervaporation reactor performance has been analyzed. Pervaporation and reaction rate are both increased with the operating temperature. Decreasing the initial molar reactant ratio the ester rate formation increases significantly. When the A/Vo ratio increases higher ester conversions are obtained. Finally the effect of catalyst concentration has been considered showing that the final water content decreases with increasing catalyst concentration. From the results it can be concluded the right choice of these parameters has a great influence on the performance of the esterification–pervaporation reactor.

Combining the equations and parameters for reaction kinetics and permeation rate obtained in a previous work, a combined kinetic model has been proposed. The results obtained with the model are in good agreement with the experimental results obtained in this work.

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References

[1] N. Wynn, http://www.cepmagazine.org, 97(10) (2001) 66–72.
[2] J.G. Sanchez Marcano, T.T. Tsotsis, Membrane Reactor, Ullmann’s Encyclopedia of Industrial Chemistry, Wiley–VCH Verlagsgesellchaft, 2002, Article Online.
[3] F. Lipnizki, R.W. Field, P.-K. Ten, J. Membr. Sci. 153 (1999) 183–210.
[4] S. Assabumrungrat, J. Phongpatthanapanich, P. Praserthdam, T. Tagawa, S. Goto, Chem. Eng. J. 95 (2003) 57–65.
[5] M.-O. David, R. Gref, T.Q. Nguyen, J. Neel, Trans. IChemE 69(Part A) (1991) 335–340.
[6] L. Domingues, F. Recasens, M.A. Larrayoz, Chem. Eng. Sci. 54 (1999) 1461–1465.
[7] Q. Liu, Z. Zhang, H. Chen, J. Membr. Sci. 182 (2001) 173–181.
[8] Q.L. Liu, H.F. Chen, J. Membr. Sci. 196 (2002) 171–178.
[9] P.M. Budd, N.M.P.S. Ricardo, J.J. Jafar, B. Stephenson, R. Hughes, Ind. Eng. Chem. Res. 43 (2004) 1863–1867.
[10] Z. Koszorz, N. Nemestothy, Z. Ziobrowski, K. Belafi-Bako, R. Krupiczka, Desalination 162 (2004) 307–313.
[11] R. Krupiczka, Z. Koszorz, Sep. Purif. Technol. 16 (1999) 55–59.
[12] W. Kiatkittipong, S. Assabumrungrat, P. Praserthdam, S. Goto, J. Chem. Eng. Jpn. 35 (6) (2002) 547–556.
[13] M.T. Sanz, J. Gmehling, Chem. Eng. J. in press.
[14] M.-O. David, T.Q. Nguyen, J. Neel, Trans. IChemE 69(Part A) (1991) 341–346.
[15] S. Steinigeweg, J. Gmehling, Chem. Eng. Proc. 43 (2004) 447–456.
[16] X. Feng, R.Y.M. Huang, Chem. Eng. Sci. 51 (20) (1996) 4673–4679.
[17] Y. Zhu, H. Chen, J. Membr. Sci. 138 (1998) 123–134.