



## Advances in Environmental Technology

journal homepage: <http://aet.irost.ir>

## Modeling of esterification in a batch reactor coupled with pervaporation for production of ethyl acetate catalyzed by ion-exchange resins

Araz Tofigh Kouzekonani, Majid Mahdavian\*

Department of Chemical Engineering, Quchan University of Advanced Technology, Quchan, Iran

## ARTICLE INFO

*Article history:*

Received 1 March 2015  
 Received in revised form  
 28 December 2015  
 Accepted 30 December 2015

**Keywords:**

Membrane reactor  
 Pervaporation  
 Esterification  
 Ethyl acetate  
 Modeling  
 Green chemistry

## ABSTRACT

In the chemical industry, process intensification is needed to meet important goals such as sustainable and eco-friendly processes. For esterification reaction the “produce more with less pollution” objective can be achieved by coupling reaction and separation in a so called integrated process. In this work a model for describing the esterification reaction of ethyl acetate in pervaporation membrane reactor using Amberlyst 15 as a heterogeneous catalyst and polydimethylsiloxane (PDMS) membrane was developed. The validity of the model was tested by comparing the calculated results with experimental data reported in the literature. It was shown rate of conversion increased by removing ethyl acetate from the reaction mixture. A parametric study was carried out to evaluate the effects of operating conditions on the performance of the pervaporation membrane reactor. Conversion increased by increasing the temperature, molar ratios of reactants and catalyst concentration. According to the calculation the best conditions for the operation of the reactor in the event of temperature  $\sim 343$  K, catalyst concentration 10 g, excess amount of acetic acid relative to ethanol 50% were shown.

**Nomenclature**

$a_i$	activity of species $i$
$C$	concentration (mol/m <sup>3</sup> )
$E_p$	activation energy for pervaporation (kJ/mol)
$J$	permeation flux (mol/ (m <sup>2</sup> ·h))
$K_p$	permeability coefficient of species $i$ (mol/ (m <sup>2</sup> s))
$k_1$	rate constant of the forward esterification reaction(m <sup>3</sup> /
$k_{-1}$	reaction rate constant of the reverse esterification
$M$	molar mass (kg/mol)
$N$	chemical quantity (mol)
$N_0$	initial quantity (mol)
$P_{i0}$	pre-exponential factor (m/h)
$Q_i$	molar flow rate of species $i$ in the permeate side (mol/s)
$R$	universal gas constant (8.314 J/ (mol.K))
$r$	reaction rate (mol/(kg. s))
$S$	membrane area (m <sup>2</sup> )
$T$	temperature (K)
$t$	time (h)
$V_0$	initial volume of reaction mixture (m <sup>3</sup> )

$V$	volume of reaction mixture (m <sup>3</sup> )
$\rho$	density (kg/m <sup>3</sup> )
$\gamma$	activity coefficient (dimensionless)

**1. Introduction**

The importance of membrane separation processes is well known. Rarely can a chemical process be found in which the purification of raw materials or separation of products from reaction side products is not required. The coupling of reaction with pervaporation is simple and straight forward. This “membrane reactor” shows important benefits in the green synthesis of esters and in water detoxification. For esterification processes where water is produced along with ester as a by-product during the reaction, pervaporation can be used for separating the ester and water from each other [1]. This earth-friendly method with low pollution and high yield is an alternative

\*Corresponding author. Tel: 051-47344001

E-mail address: m.mahdavian@qiet.ac.ir

to hazardous methods because using pervaporation membrane reactor reduces both waste and energy consumption. Pervaporation processes are known as one of the newest and most important separation processes in the field of membrane separation processes. A simultaneous separation of the reaction products in the reversible processing in that reaction can be returned with increasing the product concentration (according to Le Chatelier-Braun principle) enabling the limitations of existing thermodynamic to be overcome, thus causing an increase in the percentage of conversion reaction [2,3]. Several separation methods are performed by creating a second phase and mass transfer between the two phases. Methods such as distillation and crystallization of these are considered. Creating a second phase requires considerable energy. But in pervaporation the enthalpies of vaporization are provided by the feed mixture heat. Because the reaction and purification can be done together, a smaller device will be needed [4]. Thus, lower power consumption, lower investment and higher efficiency products make pervaporation membrane reactor an interesting alternative to conventional processes. This process has been compared with distillation process and it has been found that 75% reduction in energy input can be achieved and a 50% reduction in investment and operational costs [5]. A modeling study on a pervaporation membrane reactor for the esterification of n-butanol with acetic acid was carried out by Li et al [6]. However, the effects of temperature and concentration of water were taken into full consideration. Hydrophilic membrane was used and it was assumed only water permeated through the membrane. A kinetic model describing the reactor.pervaporation hybrid process has also been studied by David et al [7], who did not consider the effects of temperature and variations in feed concentration in the reaction mixtures on the esterification of propionic acid with propanol. A parametric study of a pervaporation membrane reactor was done by Feng et al [8] and the effect of membrane area, membrane permeability on performance of the system was analyzed. Hasanoglu et al. [9,10] studied on the esterification of acetic acid and ethanol catalyzed by both sulphuric acid and Amberlyst 15 using polydimethylsiloxane (PDMS) membranes. Experiments and simulations were conducted. They showed the performance of reactor increases with increasing temperature and increasing the initial molar ratio of acetic acid to ethanol and indicated the conversion of system in the presence of sulfuric acid is higher than amberlyst 15. In this study, a model on the synergistic mechanisms was developed to investigate integration of reaction with membrane separation processes for production of ethyl acetate catalyzed by ion- exchange resin with polydimethylsiloxane (PDMS) membrane due to many positive features: lower power consumption, lower

investment, higher efficiency products and also amberlyst 15, as heterogeneous catalysts play an important role in the catalytic elimination of environmental pollutants. Equation for describing the permeation flux of mixture components was calculated with the available experimental data. Also, the non-ideal thermodynamic effects of the component in the mixture were taken into account using the UNIFAC method. Finally, the effects of various operating parameters on pervaporation membrane reactor are investigated to achieve optimal operating condition.

## 2. Mathematical modeling

A view into the industrial design and the optimal operating condition of the membrane pervaporation reactor can be achieved by mathematical modeling. Mathematical models using kinetic parameters of the reaction over Amberlyst 15 and permeation data for a polydimethylsiloxane (PDMS) membrane are developed and effects of various operating parameters are investigated. The model takes into account the non-ideal effect by expressing the reaction and permeation rates in terms of the activities. In this work an Arrhenius equation for expressing the relationship between the permeability coefficients and operating temperature were used which has been gained by experimental data of Ayca Hasanoglu et al [9, 10]. This schematic representation of pervaporation membrane reactor is shown in Figure 1.

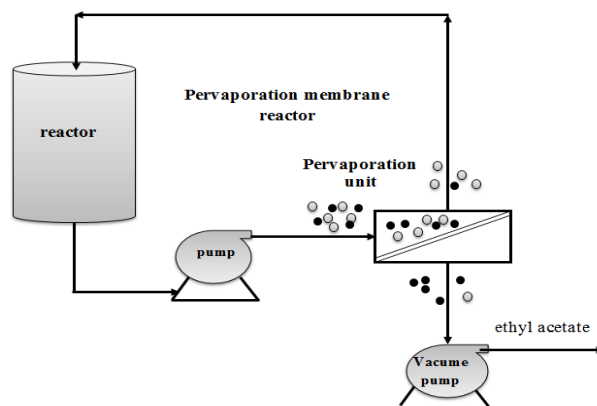
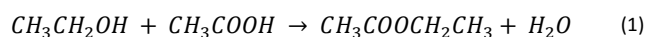


Fig. 1 . schematic diagram of a pervaporation membrane reactor.

### 2.1. Kinetics of the reaction:

The reaction of the esterification of acetic acid with ethanol can be summarized as follows:



Different kinetic models are used to describe esterification reactions catalyzed by ion-exchange resins, in this work to consider non-ideal effect of component and overlook the absorption effect of the components in the reactant medium to simplify kinetic model, the

pseudohomogeneous model has been used [11]. The rate model and the kinetic parameters of the reaction over amberlyst15 are expressed as follows:

$$r = \frac{1}{m_{cat}} \frac{1}{v_i} \frac{dn_i}{dt} = -k_1 \left( \alpha_A \alpha_B - \frac{\alpha_C \alpha_D}{K_a} \right) \quad (2)$$

$$k_e = k^0_e * \exp\left(\frac{-E_{A,e}}{RT}\right) \quad (3)$$

$$K_a = \frac{k_1}{k_{-1}} \quad (4)$$

where  $m_{cat}$  is the catalyst mass,  $v_i$  the stoichiometric coefficient of the  $i$ th component,  $n_i$  the number of moles of the  $i$ th component,  $t$  the time,  $k_1$  the forward reaction rate constant,  $k_{-1}$  the backward reaction rate constant,  $K_a$  the equilibrium constant  $a_i$  the activity of the  $i$ th component,  $T$  temperature of mixture,  $k^0_e$  is the pre-exponential factor,  $E_{A,e}$  the activation energy and  $R$  the gas constant. The kinetic parameters of the reaction over amberlyst-15 are expressed in table 1 The ASOG and UNIFAC procedures are explained in detail in Calvar *et al*'s work [12].

**Table 1.** Preexponential factors and activation energies of esterification and hydrolysis calculated by ASOG and UNIFAC [12]

	ASOG	UNIFAC
$E_{A,1}$ (kJ mol <sup>-1</sup> )	38.40	28.49
$E_{A,-1}$ (kJ mol <sup>-1</sup> )	35.07	26.70
$k^{0,1} \cdot 10^3$ (mol s <sup>-1</sup> kg <sup>-1</sup> )	161.29	2.811
$k^{0,-1} \cdot 10^3$ (mol s <sup>-1</sup> kg <sup>-1</sup> )	8.34	0.051

**2.2. Rates of pervaporation**

Hasanoglu *et al*'s experimental data [9, 10] are used to find an accurate equation of component through the Polydimethylsiloxane membrane. Determining diffusion coefficient of species through the membrane is difficult; many parameters can influence it such as temperature, concentration of the component, membrane thickness and so on. By assuming that partial pressures of the component, in permeate side are negligible the following equation is used for describing the component flux through the membrane [13].

$$Q_i = A * k_{p_i} * a_i \quad (5)$$

Where  $k_{p_i}$  is the permeability coefficient, which is related to temperature and  $a_i$  is the activity coefficient of each compound. Table 2 summarizes permeability coefficients for the permeation experiments of quaternary mixtures at three temperature levels [9,10].

**Table 2.**  $K_p$  experimental permeability coefficients of each component at different temperatures [9, 10]

Kp: Permeability coefficient $g/(m^2 * h)$				
Temperature (K)	Ethyl acetate	Water	ethanol	Acetic acid
323	4963	260	1466	564
333	6495	340	1780	780
343	8157	470	2142	1029

Good relationship between permeability coefficients of each component through the membrane with temperature was obtained with an Arrhenius equation. Ethyl acetate is clearly the dominant component in the total flux because of the high selectivity of the PDMS membrane for ethyl acetate. the expressions are as follows:

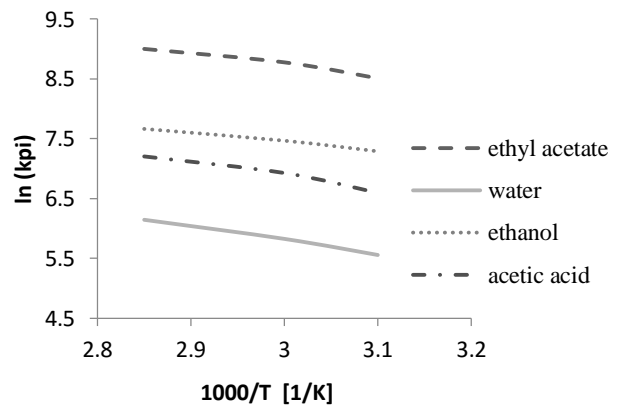
$$kp_{ethylacetate} = 3.23 * 10^7 \exp(-2840/T) \quad (6)$$

$$kp_{water} = 8.6 * 10^6 \exp(-3272/T) \quad (7)$$

$$kp_{ethanol} = 1.2 * 10^6 \exp(-2171/T) \quad (8)$$

$$kp_{acetic\ acid} = 2.95 * 10^7 \exp(-3428/T) \quad (9)$$

The variation of permeability coefficient with temperature is shown in Figure 2. Water permeation through the membrane is low, but permeation of ethyl acetate is significantly high. This is due to the tendency of PDMS membrane to ethyl acetate.



**Fig. 2.** Arrhenius plot of permeability.

For the non-ideal mixture, concentration term must be corrected to show the departure from the ideal case. Usually a phase model like UNIFAC, UNIQUAC or NRTL models are used to describe this non- ideality factor [14]. In this paper the UNIFAC group contribution method is used to calculate the activity coefficient. The volume, surface, and interaction parameters of all components in

the mixture are shown in Tables 3 and 4, data obtained from Dortmund data bank.

**Table 3.** UNIFAC parameters for the four compounds in the mixture (UNIFAC – VLE Subgroup Parameters)

Main Group	Subgroup	R <sub>k</sub>	Q <sub>k</sub>
CH <sub>2</sub>	CH <sub>3</sub>	0.9011	0.8480
CH <sub>2</sub>	CH <sub>2</sub>	0.6744	0.5400
H <sub>2</sub> O	H <sub>2</sub> O	0.9200	1.4000
OH	OH	1.0000	1.2000
CCOO	CH <sub>3</sub> COO	1.9031	1.7280
COOH	COOH	1.3013	1.2240

**Table 4.** UNIFAC parameters for the four compounds in the mixture (UNIFAC – VLE Interaction Parameters)

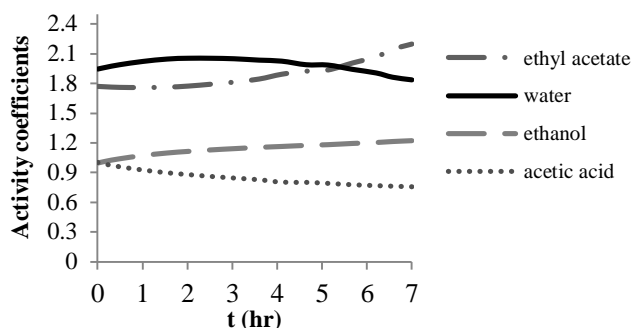
Group	CH <sub>3</sub>	CH <sub>2</sub>	OH	H <sub>2</sub> O	COOC	COOH
CH <sub>3</sub>	0.00	0.00	986.5	1318	232.1	507
CH <sub>2</sub>	0.00	0.00	986.5	1318	232.1	507
OH	156.4	156.4	0.00	353.5	101.1	267.8
H <sub>2</sub> O	300	300	-229.1	0.00	72.87	233.87
COOC	114.8	114.8	245.4	200.8	0.00	-241.8
COOH	329.3	329.3	139.4	124.63	1167	0.00

Activity coefficient changes with time as shown in Figure 3, which shows the non-ideality of the quaternary mixtures. The activity coefficient of ethyl acetate increases as ethyl acetate permeates through the membrane because its content in the mixture decreases during the reaction.

### 2.3. Modeling of pervaporation membrane reactors

The required equations for modeling of the pervaporation membrane reactor were obtained with mass balance around the reactor by considering production or consumption of reaction components in the reactor and their removal through the pervaporation membrane. The concentration of the reaction components can be written as follows [14]:

$$c_i = c_{i0} + \text{reaction} - \text{pervaporation}$$



**Fig. 3.** Activity coefficients of the components in the reaction mixture calculated using the UNIFAC model. Operating conditions: T = 333 K, S/V<sub>0</sub> = 13.25 m<sup>-1</sup>.

The sets of equations can be summarized as follows:

$$\frac{dN_A}{dt} = c_{cat} * k_1 \left( a_A a_B - \frac{1}{K_a} a_C a_D \right) - S * kp_A \quad (10)$$

$$\frac{dN_B}{dt} = c_{cat} * k_1 \left( a_A a_B - \frac{1}{K_a} a_C a_D \right) - S * kp_B \quad (11)$$

$$\frac{dN_C}{dt} = c_{cat} * k_1 \left( a_A a_B - \frac{1}{K_a} a_C a_D \right) - S * kp_C \quad (12)$$

$$\frac{dN_D}{dt} = c_{cat} * k_1 \left( a_A a_B - \frac{1}{K_a} a_C a_D \right) - S * kp_D \quad (13)$$

$$a_i = x_i * \gamma_i \quad (14)$$

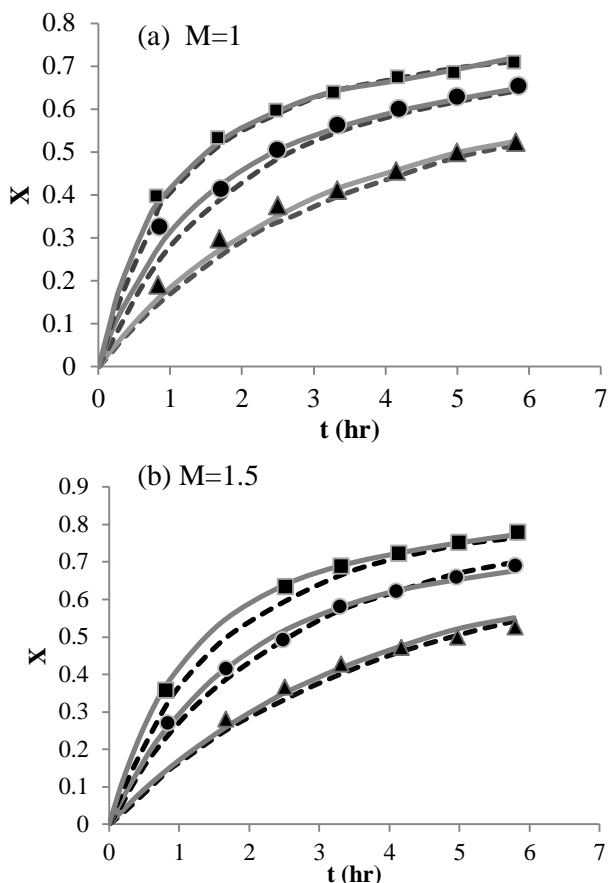
The above equations (Esq. (10) – (14)) are the fundamental equations for describing of modeling of esterification in a batch reactor coupled with pervaporation. The concentration is defined as:

$$C_i = \frac{N_i}{V} \quad (15)$$

$$V == \sum N_i \frac{M_i}{\rho_i} \quad (16)$$

## 3. Results and discussion

The experimental data and model calculations for the conversion are shown in Fig. 4 (a) and (b) where the dotted line represents the calculated results based on the model of Hasanoglu *et al.*'s. [9, 10]. The solid line represents the calculations based on our Work. Both models appear to agree well with the experimental data. However, the reaction conversion is slightly underestimated by the Hasanoglu's model [10] because the non-ideal thermodynamic behavior of the reaction mixtures was not considered in their work.

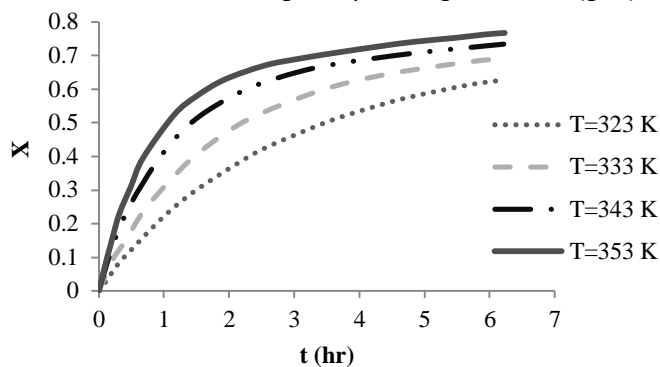


**Fig. 4.** Conversion versus time: a comparison of model calculations with experimental data with pervaporation (PV) catalyzed by Amberlyst 15 for initial molar ratios,  $M$ , of (a) 1 and (b) 1.5 (■: Experimental data 70°C, ●: Experimental data 60°C, ▲: Experimental data 50°C, line 1: 70°C Results of this model, line 2: 70°C Results of Hasanoglu's model [9,10], line 3: 60°C Results of this model, line 4: 60°C Results of Hasanoglu's model [9,10], line 5: 50°C Results of this model, line 6: 50°C Results of Hasanoglu's model [9,10]).

Figures 4 (a) and (b) show the effect of initial mole ratio of acetic acid to ethanol,  $M$ , on the performance of the pervaporation membrane reactor for esterification of acetic acid with ethanol in the presence of Amberlyst 15 as catalyst under the following conditions:  $S/V_0 = 13.25 \text{ m}^{-1}$ ,  $C_{\text{cat}} = 2.6 \text{ g catalyst}/100 \text{ g acetic acid (g l}^{-1}\text{)}$ .  $M$  was changed from 1 to 1.5 for this reaction. Production was increased by increasing  $M$ . An excessive amount of one reactant by progressing the forward reaction leads to an enhancement in conversions. Also a higher yield of ethyl acetate in the reactor was obtained because ethyl acetate formation is increased with the use of an excessive amount of reactant. This caused an increase in permeation flux of ethyl acetate because of the relatively high ethyl acetate concentration at a higher  $M$ . However, if this ratio is high the purification of ethyl acetate will be challenged due to the extra volume of residual acetic acid at the end of the reaction. Appropriate value of  $M$  is considered 1.5 according to the

experimental work. Thus, in the pervaporation membrane reactor increasing the value of  $M$  improves the reactor performance in terms of conversion. Also, it has been shown that a rise in the temperature increases the esterification reaction, because a higher temperature is suitable for removing ethyl acetate through the membrane and increasing the rate of reaction.

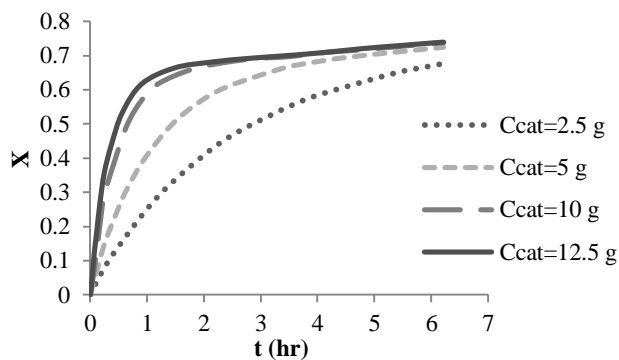
Figure 5 shows the effect of increasing temperature on the performance of the pervaporation membrane reactor for esterification of acetic acid with ethanol in the presence of Amberlyst 15 as catalyst under the following conditions:  $S/V_0 = 13.25 \text{ m}^{-1}$ ,  $C_{\text{cat}} = 2.6 \text{ g catalyst}/100 \text{ g acetic acid (g l}^{-1}\text{)}$ .



**Fig. 5.** Effect of temperature on the esterification performance of the pervaporation-coupled reactor. Operating conditions:  $m = 1.5$ ,  $S/V_0 = 13.25 \text{ m}^{-1}$ ,  $C_{\text{cat}} = 10 \text{ g}$

The calculation results in Fig. 5 show that at temperatures above 343 K, a further increase in temperature will not enhance the reaction conversion considerably. So, according to the operating costs in connection with heating and cooling of component, a convenient temperature of around 343 K seems suitable for esterification coupled with pervaporation.

Figure 6 shows the effect of catalyst concentration on the esterification performance of the pervaporation membrane reactor. Under the following conditions:  $S/V_0 = 13.25 \text{ m}^{-1}$ ,  $M = 1.5$ , and  $T = 343 \text{ K}$ .



**Fig. 6.** Effect of catalyst concentration on the esterification performance of the pervaporation-coupled reactor. Operating conditions:  $S/V_0 = 13.25 \text{ m}^{-1}$ ,  $M = 1.5$ ,  $T = 343 \text{ K}$ .

As expected, enhancement of the catalyst concentration promotes the formation of ethyl acetate and also of water in the reactor; an increase in ethyl acetate content increases the rate of ethyl acetate removal. Maximum conversion of acetic acid ( $X_A$ ) occurs within the first 2 h of the reaction. There is little change in the product yield when the catalyst concentration is above 10 g for a reaction time of 7 h under the conditions studied. This should be considered when selecting a suitable amount of catalyst concentration.

Figure 7 illustrates the effect of  $S/V_0$  on the esterification performance in the pervaporation-coupled reactor under the following conditions:  $M = 1$ ,  $C_{cat} = 10$  g and  $T = 323$  K. For a given reactor volume, enhancement of the membrane area will increase the rate of ethyl acetate removal and the reaction equilibrium will shift toward the product side, because as soon as ethyl acetate formatted continuously is removed through the membrane, the reactant concentration will increase resulting in an enhancement in the reaction rate. However, selecting a suitable  $S/V_0$  is necessary because an enhancement in surface increases the operating cost. So for selecting the appropriate value of  $S/V_0$ , the gain in the enhanced conversion versus the cost associated with the membrane should be taken into account.

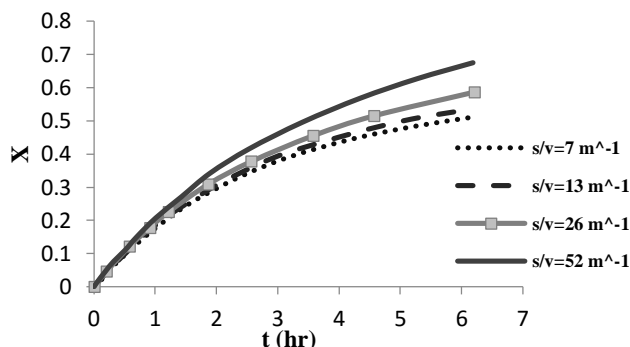


Fig. 7. Effect of ( $S/V_0$ ) on the esterification performance of the pervaporation - coupled reactor. Operating conditions:  $M = 1$ ,  $C_{cat} = 10$  g,  $T = 323$  K.

#### 4. Conclusions

Simulation and selecting the optimal conditions for modeling of pervaporation membrane reactors is very important. The model of esterification of acetic acid with ethanol, catalyzed by Amberlyst 15 has been developed. This model takes into account the non-ideality of the reaction mixtures. It is shown that removal of ethyl acetate through the membrane from the mixture increased the conversion of reaction, because in reversible reactions necessary potential synergies are provided for overcoming the equilibrium limitations. Also Amberlyst 15 as heterogeneous catalyst plays an important role in the catalytic elimination of environmental pollutants and production of clean energy. The development of ion

exchange resins would definitely contribute to the environmental improvement and efficient utilization of energy resources. The model validation is done with available experimental data. Results showed that, there is good agreement between the model and experimental data. The effect of different parameters such as temperature, catalyst concentration and excess amount of acetic acid relative to ethanol on the reaction conversion rate was investigated and, according to the calculation of the model, the best conditions for the operation of the reactor in the event of temperature  $\sim 343$  K, catalyst concentration 10 g, excess amount of acetic acid relative to ethanol 50% were shown. Also, with the use of pervaporation membrane reactor, it is possible to achieve 100% conversion. Thus, the prevention of waste can be achieved if the majority of reagents and the solvent are recyclable. For example, ion exchange resin can be regenerated (if needed) and reused in a subsequent run. So, using pervaporation membrane reactor coupled with ion exchange resin can provide the conditions to move towards green chemistry. This method would also help balance environmental concerns with economic development.

#### Acknowledgements

The authors would like to acknowledge the support and help of 4 th refinery of South Pars Gas Company (SPGC).

#### References

- [1] Lipnizki, F., Field, R. W., Ten, P. K. (1999). Pervaporation-based hybrid process: a review of process design, applications and economics. *Journal of membrane science*, 153(2), 183-210.
- [2] Lipnizki, F., Field, R. W. (2001). Pervaporation-based hybrid processes in treating phenolic wastewater: technical aspects and cost engineering. *Separation science and technology*, 36(15), 3311-3335.
- [3] Datta, R., Tsai, S. P. (1998). *Esterification of fermentation-derived acids via pervaporation* (No. US 5723639). Argonne national laboratory (ANL), Argonne, IL.
- [4] Dutta, B. K., Sikdar, S. K. (1991). Separation of azeotropic organic liquid mixtures by pervaporation. *AIChE journal*, 37 (4), 581-588.
- [5] Waldburger, R. M., Widmer, F. (1996). Membrane reactors in chemical production processes and the application to the pervaporation-assisted esterification. *Chemical engineering technology*, 19(2), 117-126.
- [6] Li, X., Wang, L. J. (2001). The esterification of acetic acid with n-butanol for the production of n-butyl acetate, *Membrane science*, 186, 19-24.
- [7] David, M. O., Nguyen, T. Q., Neel, J. (1991). Pervaporation-esterification coupling. II: Modelling of the influence of different operating parameters.

- Chemical engineering *research & design*, 69(A4), 341-346.
- [8] Feng, X., & Huang, R. Y. (1996). Studies of a membrane reactor: esterification facilitated by pervaporation. *Chemical engineering science*, 51(20), 4673-4679.
- [9] Hasanoğlu, A., Salt, Y., Keleşer, S., Dinçer, S. (2009). The esterification of acetic acid with ethanol in a pervaporation membrane reactor. *Desalination*, 245(1), 662-669.
- [10] Hasanoğlu, A., Dinçer, S. (2011). Modelling of a pervaporation membrane reactor during esterification reaction coupled with separation to produce ethyl acetate. *Desalination and water treatment*, 35(1-3), 286-294.
- [11] Yixin, Q., Shaojun, P. E. N. G., Shui, W., Zhang, Z., & Jidong, W. A. N. G. (2009). Kinetic study of esterification of lactic acid with isobutanol and n-butanol catalyzed by ion-exchange resins. *Chinese journal of chemical engineering*, 17(5), 773-780.
- [12] Calvar, N., Gonzalez, B., Dominguez, A. (2007). Esterification of acetic acid with ethanol: Reaction kinetics and operation in a packed bed reactive distillation column. *Chemical engineering and processing: Process Intensification*, 46(12), 1317-1323.
- [13] Assabumrungrat, S., Phongpatthanapanich, J., Praserttham, P., Tagawa, T., Goto, S. (2003). Theoretical study on the synthesis of methyl acetate from methanol and acetic acid in pervaporation membrane reactors: effect of continuous-flow modes. *Chemical engineering journal*, 95(1), 57-65.
- [14] Aage, F., Petter, R. (1977). Vapour-liquid equilibria using UNIFAC a Group-contribution method.
- [15] Domingues, L., Recasens, F., Larrayoz, M. (1999). Studies of a pervaporation reactor: kinetics and equilibrium shift in benzyl alcohol acetylation. *Chemical engineering science*, 54(10), 1461-1465.