Modelling of a pervaporation membrane reactor during esterification reaction coupled with separation to produce ethyl acetate

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ABSTRACT

As a follow up to the previous report on the experimental study of esterification reaction to yield ethyl acetate in a pervaporation membrane reactor (PMR), in this study; modelling of PMR during esterification reaction coupled with separation is presented. The analyzed system is the esterification reaction catalysed by sulfuric acid and Amberlyst 15 in a batch PMR in the temperature range of 50–70°C using polydimethylsiloxane (PDMS) membranes permselective to ethyl acetate. In this way, conversions were increased by continuous removal of ethyl acetate from the reaction medium.The theoretical model was developed taking account permeation of the all components in the reaction mixture. The kinetic calculations were made on the assumptions that the reaction obeyed second order kinetics. The model satisfactorily agrees with the experimental results obtained in the previous work, thus allowing the prediction of the conversion variation with the pervaporation time. The coefficient of determination, R^2, was in the range of 0.9798 to 0.9991. This modelling methodology could be used to extrapolate or to scale-up this type of systems as it provides assistance to analyze the effect of the operating parameters on the conversions during the esterification process.

Keywords: Membrane reactor; Pervaporation; Esterification; Ethyl acetate; modelling; PDMS

1. Introduction

Esterification is an industrially important reaction where a carboxylic acid and an alcohol make an ester usually in the presence of an acid catalyst. These reactions often do not proceed to completion, reaching an equilibrium yield. This equilibrium yield can be enhanced towards higher conversions by selectively removing one of the products those are ester and water from the reaction medium by using a selective membrane. Pervaporation, as a membrane process, is an ideal candidate for selective removal of the desired product. In a pervaporation process, the liquid mixture which is in contact with the membrane surface is sorbed by the membrane and selectively diffuses through the membrane to be separated from the other side appearing in vapor form by applying vacuum [1]. The permeate is condensed in cold traps and then removed. The removal of one reaction product by a membrane to shift a liquid phase reaction has gained considerable interest in recent years in terms of process intensification and efficiency [2–4].

An esterification–pervaporation coupling is attractive for the industrial applications. Because the energy consumption is low, the reaction can be carried out at the optimal temperature and the separation efficiency in pervaporation is not determined by the relative volatility as in reactive distillation [5,6]. By using pervaporation aided reactors for esterification reactions,

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considerable savings can also be made in the amount of reactants required (as there is hardly any need for excess amount of one of the starting components) and the reaction time [5–8]. PMR has several advantages over conventional reaction processes; it reduces the cost and the energy consumption, achives separation of the products simultaneously, improves the conversions by shifting the reaction to the desired direction and thus reduces the reaction time.

There are several studies in the literature for pervaporation coupled esterification based on water removal however ester removal was not much investigated [9–16]. This work is centred on the removal of ethyl acetate formed by the reaction between ethanol and acetic acid catalysed by sulfuric acid and Amberlyst 15 using PMR. The influence of process parameters such as temperature, ratios of the reactants and the catalyst type on the reactor performance were analyzed in the previous study [17]. As a follow up to the previous report, in this contribution a mathematical model has been applied to analyze the previous experimental data. Thus, the focus of the current paper is on the development of a theoretical model to formulate a generalized model to describe esterification coupled pervaporation systems in terms of ester removal.

2. Experimental

The membrane used in this work was a cross-linked hydrophobic membrane, polydimethylsiloxane (PDMS) prepared in our labs [18]. The material used was given in the previous work [17].

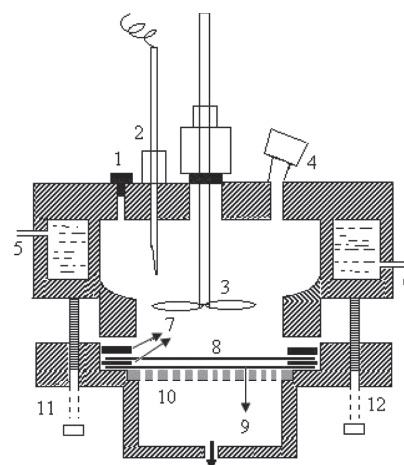Esterification reactions were carried out in batch reactors both with and without membrane under the

Fig. 1. Membrane reactor cell: 1: sample valve, 2: temperature sensor, 3: mechanical stirrer, 4: condenser, 5,6: inlet and outlet of the heating jacket, 7: teflon O-rings, 8: membrane, 9: membrane support, 10: perforated disk, 11,12: screws.

same conditions. Thus, the effect of membrane on the conversions was determined. The operating parameters were summarized in Table 1.

The membrane cell was maintained at constant temperature by a heating jacket. Reaction mixture was stirred by a mechanical stirrer during the pervaporation. The membrane was supported on a perforated stainless steel disk with a hole diameter of 5 mm. Two pairs of teflon O-rings between flanges provided the vacuum seal. The illustration of the membrane reactor cell was presented in Fig. 1.

PMR experiments were performed in a batch mode. The determination of the experimental data was described in the previous work [17]. The experimental setups of the simple batch reactor without membrane and the pervaporation membrane reactor used are illustrated in Fig. 2. As seen in Fig. 2(a), PMR was connected to a vacuum pump at the downstream side. The permeate in the vacuum line was captured in the cold traps

Table 1
Operating parameters used in this system

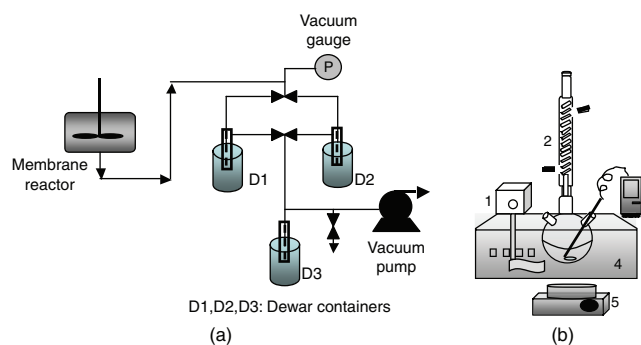| Parameter	Notation and unit	Value/range
Initial mol ratio of ethanol to acetic acid	$M = c_B/c_A$	1–1.5
Ratio of the membrane area to volume of reacting mixture	S/V cm^{-1}	0.1325
Reaction time	T (min)	350
Temperature	T (°C)	50–70
Catalyst concentration		
Amberlyst 15	g catalyst/100 g acetic acid	5
	(g l^{-1})	(2.06–2.6)
Sulfuric acid	g catalyst/100 g acetic acid	1
	(g l^{-1})	(0.41–0.52)

Fig. 2. (a) Batch pervaporation membrane reactor, (b) Batch reactor without membrane; 1: thermostatic circulater 2: condenser 3: temperature sensor, 4: water bath, 5: magnetic stirrer.

filled with liquid nitrogen. Two cold traps were parallel connected to work continuously, and another cold trap was used to protect the vacuum pump. The experiments were also carried out in a batch reactor without membrane as it is illustrated in Fig. 2(b). Reaction was carried out in a three necked flask which was settled in a thermostatic bath to maintain constant temperature. The temperature of the reaction mixture was monitored using a temperature sensor. A magnetic stirrer was used to mix the reaction mixture that was settled under the bath. A condenser was settled into a neck of the flask to prevent over-vaporization of the reaction mixture.

3. Modelling study

3.1. Reactor modelling

The esterification reaction can be represented by:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} E + W \tag{1}$$

where A is acetic acid, B is ethanol, E is ethyl acetate and W is water, k_1 is the forward reaction rate constant and k_2 is the backward reaction rate constant which was performed in a batch pervaporation membrane reactor at a constant temperature. Here, acetic acid is the limiting reactant. The rate of acetic acid conversion is given Eq. (2) where r_A presents the rate of acetic acid conversion and c_A, c_B, c_E and c_W present concentrations of the acetic acid, ethanol, ethyl acetate and water, respectively.

$$r_A = -k_1 c_A c_B + k_2 c_E c_W \tag{2}$$

Considering that the pervaporation membrane permeates some amount of acetic acid, the acetic acid equilibrium in the reactor will be:

$$r_A V = S J_A + \frac{d(V c_A)}{dt} \tag{3}$$

where S is the membrane area, J_A is the acetic acid flux through the membrane and V is the volume of the mixture.

The permeation flux of a component through the membrane depends on the concentration of the component in the mixture. A change in the feed concentration will affect the sorption phenomena of the membrane at the liquid-membrane interface as proved by the solution-diffusion principle [19,20]. The diffusion of the components in the membrane is also dependent on the concentration of the components (or the solubility of the components), and thus, permeation characteristics are related with the feed concentration of the mixture. Since the transmembrane concentration (ΔC) is the driving force for the mass transport in a pervaporation process, the permeation flux is directly depended on the concentration and the permeability of the species in the membrane can thus be defined as the equation below [21].

$$P = DK \tag{4}$$

In Eq. (4) P is the permeability, D is the diffusion coefficient and K is the partition coefficient that gives the ratio of membrane-liquid interface concentration to feed concentration. Clearly, as the feed concentration changes, the concentration at the membrane-liquid interface changes linearly, and consequently this results in a linear change in the permeation fluxes. As a result, it can be assumed that permeation flux of each component is proportional to its concentration. Based on this assumption, the flux of component i can be written as:

$$J_i = K_{p,i} c_i \tag{5}$$

where K_p, a temperature depended constant, gives the correlation between flux and concentration. If the equations (2), (3) and (5) are combined assuming the volume is constant, concentration of acetic acid in the reactor can be written as:

$$\frac{dc_A}{dt} = -(k_1 c_A c_B - k_2 c_E c_W) - \frac{S}{V} J_A \tag{6}$$

Similarly, the concentration of the other components in the reaction can be determined:

$$\frac{dc_i}{dt} = \pm(k_1 c_A c_B - k_2 c_E c_W) - \frac{S}{V} J_i \tag{7}$$

Considering the conversion or formation of the component by reaction and removal of the component by pervaporation, concentration of each component in the reactor can be expressed in a general form as [22]:

$$c_i = c_{i0} \pm \text{reaction} - \text{pervaporation} \tag{8}$$

Since the limiting reactant is acetic acid in this reaction, the starting concentration of acetic acid may be substituted into the concentration terms of each component as follows:

$$c_B = c_{A0}(M - x) - \int \frac{S}{V} J_B dt \tag{9}$$

$$c_E = c_{A0} x - \int \frac{S}{V} J_E dt \tag{10}$$

$$c_W = c_{A0}x - \int \frac{S}{V} J_W dt \tag{11}$$

where x is the conversion and M is the ratio of initial concentrations of ethanol to acetic acid. By substituting Eq. (5) to Eqs. (9), (10) and (11), following equations can be obtained for the concentrations of each component in the reactor:

$$c_B = \frac{c_{A0}(M - x)}{1 + \int \frac{S K_{p,B}}{V} dt} \tag{12}$$

$$c_E = \frac{c_{A0}x}{1 + \int \frac{S K_{p,E}}{V} dt} \tag{13}$$

$$c_W = \frac{c_{A0}x}{1 + \int \frac{S K_{p,w}}{V} dt} \tag{14}$$

The simultaneous integration of Eqs. (12), (13) and (14) with substituting them into Eq. (6), allows the determination of conversions with time for the esterification reaction coupled with pervaporation.

3.2. Reaction modelling

The kinetic calculations were made on the assumptions that the reaction obeyed second order kinetics. Amberlyst 15 may be considered that the pores of the macro-porous resin have a diameter such there is no resistance to the diffusion of the reagents or the products within the resin. The concentrations of the film reagents and of the pore interiors are practically equal, and therefore a homogeneous model may be assumed for the reaction catalyzed by Amberlyst 15 [22]. Thus, a homogenous model was considered for the Amberlyst 15 catalyzed reaction. The properties of catalysts used in this work are given in Table 2.

If we substitute the equations of $r_A = dc_A/dt$ and $K_e = k_1/k_2$ to the Eq. (2) which is the general rate expression of acetic acid conversion, the equation becomes as follows:

$$-\frac{dc_A}{dt} = (k_1)(c_A c_B - \frac{c_E c_W}{K_e}) \tag{15}$$

Since there is catalyst in the reaction medium, k_1 changes with the influence of the catalyst on the reaction rate. Taking account the influence of the catalyst on k_1, forward reaction rate constant can be presented as k_{obs}, which is the observed forward rate constant in the presence of catalyst. Thus, the rate of homogeneous catalyzed esterification reaction can be written as follows due to the general kinetic expression for second-order reversible reaction:

$$-\frac{dc_A}{dt} = (k_{obs})\left(c_A c_B - \frac{c_E c_W}{K_e} \right) \tag{16}$$

Here, the observed rate constant, k_{obs}, is calculated directly from the initial stage of the conversion lines which were determined in the presence of catalysts. The rate constants for the esterification reaction of acetic acid and ethanol catalyzed by sulfuric acid and Amberlyst 15 have been measured and are listed in Table 3. K_e is the equilibrium constant which was estimated using different K_e values taken from the literature between 55–80°C [26,27]. The catalysts used in the literature for the K_e determination were similar to Amberlyst 15 or same as Amberlyst 15 [26,27]. In the work of Hangx et Al., the catalyst used was the ion exchange resin Purolite CT179, which is a porous cation exchange resin containing sulfonic acid groups, similar to Amberlyst 15 [27]. The catalytic activity of an ion-exchange resin on the same reaction depends on its three-dimensional structure, which is influenced by the porosity, the internal surface area and the sulfonic acid content. The acidic capacity of Purolite CT179 and Amberlyst 15 are relatively similar which are 5.25 and 4.7 mmolH$^+$ g^{-1}, respectively. On the other hand the average pore diameters of Amberlyst 15 and Purolite CT179 are 300 and 386 Å, respectively where these values can be also considered relatively close to each other [28]. Considering these similar catalyst properties of Amberlyst 15 and Purolite CT179,

Table 2
The properties of catalysts used in this work [23–25]

Acid catalyst	Acid amount (mmolH$^+$ g^{-1})	Surface area (m^2/g)	Particule radius (mm)	Porosity
Amberlyst 15	4.7	40.89	0.3	0.319
Sulfuric acid	19.8	–	–	–

Table 3
Kinetic parameters calculated for the esterification between acetic acid and ethanol at various temperatures

T(°C)	K_e	Sulfuric acid		Amberlyst 15	
		c_{cat} (g/l)	k_{obs} (l/molmin)	c_{cat} (g/l)	k_{obs} (l/molmin)
50	7.174	0.52	0.0010	2.60	0.00042
		0.41	0.0009	2.07	0.00031
60	6.107	0.52	0.0019	2.60	0.00082
		0.41	0.0015	2.07	0.00062
70	5.04			2.60	0.00140
				2.07	0.00092

kinetic parameters of the reaction carried out in the presence of Purolite CT179 can be used for K_e estimation. The other K_e value taken from literature for the K_e estimation was determined by Kırbaşlar et al. in the presence of Amberlyst 15 [26]. These K_e values at different temperatures were plotted versus temperature, and the K_e values at desired temperature were estimated from the model equation determined from the graph.

3.3. Model implementation

The differential equations were solved in a MatCAD sheet. The equations were solved simultaneously for parameters such as process temperature, initial mol ratio of acid over alcohol, the ratio of the effective membrane area to the volume of reacting mixture. The values and range of the various parameters used for simulations are given in Table 1 and 3. The volume of the reaction mixture was simulated as a function of time and embedded to the model. Conversions were estimated for each time interval by modifying the initial process parameters of each experimental condition.

4. Results and discussion

4.1. Evaluation of the fluxes through membrane

In all pervaporation experiments, the membrane showed a relatively higher selectivity towards ethyl acetate. The selectivities of ethyl acetate to total compounds were in the range of 4–5 in terms of separation factor while the fluxes of ethyl acetate through the membrane were in the range of 2379–3350 g m^{-2}h depending on the catalyst used.

The partial flux of a component through the membrane depends on the concentration of the component in the feed mixture. As it was mentioned in the previous sections, permeation flux of each component was assumed to be proportional to its concentration (Eq. 5). $K_{p,i}$ of each component were estimated from the slope of the lines determined by plotting partial flux versus feed concentration. Estimated $K_{p,i}$ coefficients of each component at different temperatures are given in Table 4.

The value of $K_{p,i}$ can be considered as a parameter that shows the affinity of the membrane to a component. The affinity of the membrane to a component increases with increasing $K_{p,i}$ values. As can be seen from Table 4, ethyl acetate has the highest $K_{p,i}$ values indicating that the membrane permeates ethyl acetate much more than the other components. The $K_{p,i}$ values of the components are in the following order: ethyl acetate; ethanol; acetic acid; water.

$K_{p,i}$ values increased with increasing temperature due to a higher swelling of the membrane at a higher temperature. The permeation flux of ethyl acetate increases with increase in temperature. The removal rate of a component from reaction zone by pervaporation is directly depended on the permeation flux of the component through the membrane (Eq. 3,7,8). As the permeation flux increase, the amount of the component that transfers through the membrane per time increases too. Any parameter that affects the quantity of the permeation flux, also affects the removal rate of the compound from the reaction medium. Thus, with the increase of the temperature the permeation flux of ethyl acetate increases, and consequently the removal rate of the ethyl acetate from the reaction zone becomes higher. An increase in the removal rate led to higher conversions. Furthermore, the temperature has also an influence on the reaction kinetics. An increase in temperature induced not only an acceleration of removal rate but also acceleration in esterification. Thus, the increase of the temperature enhances the conversions by means of its coupling effect on reaction kinetics and permeation flux that controls removal rates from the reactor.

4.2. Model output versus experimental results

Fig. 3 (a) and (b) show the comparison of the conversions calculated by the pervaporation model and obtained from experimental results with and without pervaporation catalyzed by Amberlyst 15 at different initial molar ratios of reactants and temperatures. The proposed model adjusts satisfactorily to the obtained experimental data for this system with an average error of 5%.

In Fig. 3, the continuous lines represent the pervaporation model calculated from the corresponding equations. The model output was in good agreement with the experimental values, indicating that the reaction between acetic acid and ethanol can be assumed to obey the simple second order kinetics. The initial molar ratio of ethanol to acetic acid was varied from 1 to 1.5 for the esterification reaction. From Fig. 3 (a) and (b) it can be seen that as the molar ratio was increased to 1.5 from 1, the conversions increase. It is known that an excess amount of one reactant leads to increased conversions by shifting the reaction towards products. As seen in Fig. 3, the conversions increased around 10% by increasing the

Table 4
$K_{p,i}$ coefficients of each component at different temperatures

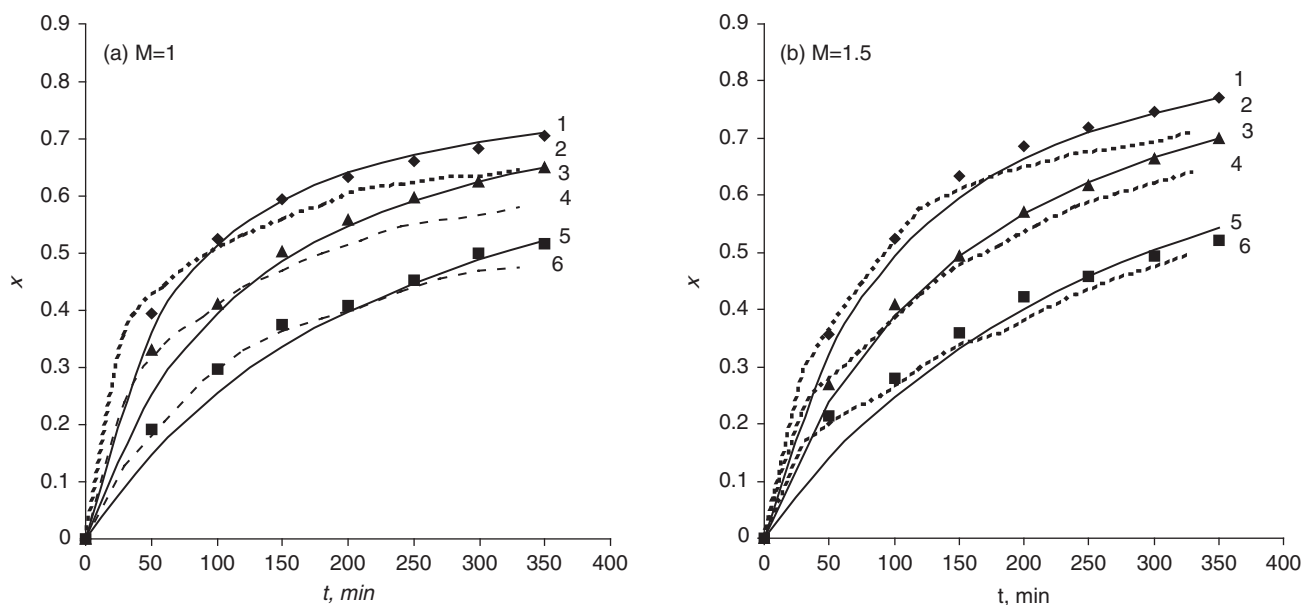| $K_{p,i}$ (10^{-3}g/molh)	50°C	60°C	70°C
$K_{p,\text{water}}$	20.91	27.33	37.79
$K_{p,\text{ethanol}}$	80.70	111.48	147.24
$K_{p,\text{ethyl acetate}}$	518.31	678.37	851.93
$K_{p,\text{acetic acid}}$	62.67	75.65	91.56

Fig. 3. The conversions calculated by the model and their comparison with the experimental results with and without pervaporation (PV) catalyzed by Amberlyst 15 for initial molar ratios, M, of (a) 1 and (b) 1.5 (♦:70°C with PV, ▲:60°C with PV, ■:50°C with PV, line 1: 70°C model, line 2: 70°C without PV, line 3: 60°C model, line 4: 60°C without PV, line 5: 50°C model, line 6: 50°C without PV).

M ratio 1 to 1.5. Thus, increasing *M* to a reasonable value in pervaporation membrane reactor improves the reactor performance in terms of conversion. In all the PMR experiments the conversions obtained from pervaporation were higher than those of without pervaporation. With the use of PV, conversions were enhanced up to 12% compared with the conversions obtained without PV. Enhanced conversions were a result of continuous removal of ethyl acetate from the reaction medium. As can be seen in Fig. 3, the enhancement of conversions by PV is more effective at higher temperatures since both permeation flux and production rate of ethyl acetate increase with temperature. As the production rate increase, the concentration of the ethyl acetate in the reaction zone increases and this leads to higher permeation fluxes because feed concentration of a component has a positive effect on its permeation flux. Also permeation flux increase with increasing temperature. As a result the removal rate becomes higher than the production rate at higher temperatures or in other words the production rate changes less while removal rate changes more at higher temperatures and so, the enhancement of the conversions becomes more distinctive as the temperature increases.

Fig. 4 shows the comparison of the conversions calculated by model and determined by experiments with and without pervaporation catalyzed by sulfuric acid at different temperatures at equimolar condition. The proposed model adjusts to the obtained experimental data acceptably. As the temperature increases from 50°C to

60°C, the average error increases from 5% to 8%. These results show that model may adjust the experimental data much more satisfactorily at a lower temperature for sulfuric acid. This is the fact of sudden change of the conversions with increasing temperatures when sulfuric acid is used as catalyst.
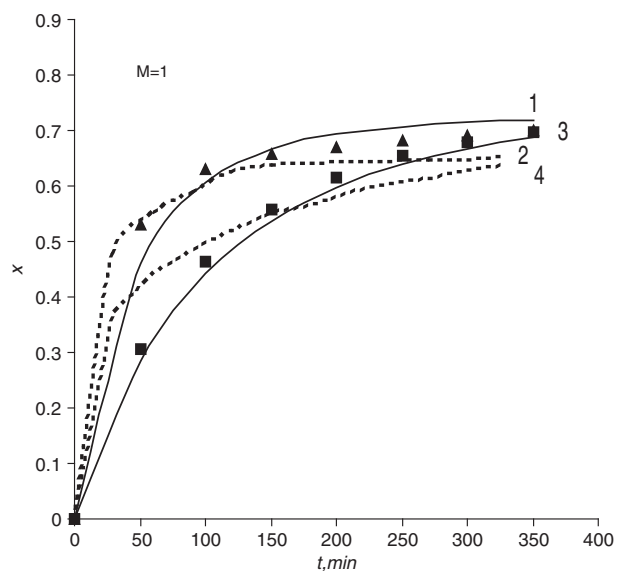

Fig. 4. The conversions calculated by the model and their comparison with the experimental results with and without pervaporation catalyzed by sulfuric acid at equimolar condition (▲:60°C with PV, ■:50°C with PV, line 1:60°C model, line 2: 60°C without PV, line 3: 50°C model, line 4:50°C without PV).

Table 5
Coefficient of determination (R^2) of each experimental condition for experiment-model relation

	Coefficient of determination, R^2					
	$M=1$			$M=1.5$		
	50°C	60°C	70°C	50°C	60°C	70°C
Amberlyst 15	0.9879	0.9868	0.9967	0.9798	0.9980	0.9961
Sulfuric acid	0.9991	0.9834	–	–	–	–

The coefficient of determination (R^2), which is equal to the ratio of the reduction in the sum of squares of deviations obtained by using the linear model to the total sum of squares of deviations about the sample mean (in this case mean of model output), gives a quantitative interpretation of the strength of the relation between two variables of y and x, where y represents model output and x represents experiments here. To obtain the degree of agreement of model output and experimental results, R^2 was calculated for each experimental condition and presented in Table 5. As seen in the table, R^2 was in the range of 0.9798 to 0.9991 indicating a high correlation between experimental results and model output. The experimental results at all experimental conditions were graphed versus their model output and compared with a $y=x$ line to show the strength of the linear relation between experimental and model results. This comparison is presented in Fig. 5. The results show that model predictions are in a good agreement with the experiments. The model developed in this work has good predictive capability under various operating conditions.

As the Figs. 3 and 4 are compared, it can be seen that the conversions obtained with sulfuric acid are markedly higher than those of Amberlyst 15. This is a consequence of the fact that sulfuric acid is a homogeneous acid and also it is much more acidic than Amberlyst 15. As seen in Table 1, acid amounts of Amberlyst 15 and sulfuric acid are 4.7 and 19.8 mmolH$^+$ g^{-1} respectively and therefore, sulfuric acid can be considered to be more efficient than Amberlyst 15. Thus, the reaction is more rapid using sulfuric acid compared to using Amberlyst 15 as a catalyst. On the other hand, the performance of a heterogeneous catalyst is restricted by the diffusion limitation through the pores in liquid phase reactions. Diffusion limitation of liquids within porous solids dictates that effective solid acids for liquid-phase reactions require the use of mesoporous materials where the pore size is 20–500 Å. In that respect, Amberlyst 15 which has an average pore size of 300 Å, is an effective solid acid compared to many sulfonic acid-functionalized meso/macroporous catalysts [23,29]. Although Amberlyst 15 has a drawback of diffusion restrictions when compared to sulfuric acid, it offers several intrinsic advantages over their homogeneous counterparts: product separation is easier; catalyst reuse is available; bifunctional phenomena is achieved involving reactant activation/spillover between support and active phases; the purity of the products is higher as the side reactions can be completely eliminated or are significantly less; and the corrosive environment caused by the discharge of acidcontaining waste is eliminated.

On the comparison of Figs. 3 and 4, it can be seen that when sulfuric acid was used as the catalyst, the

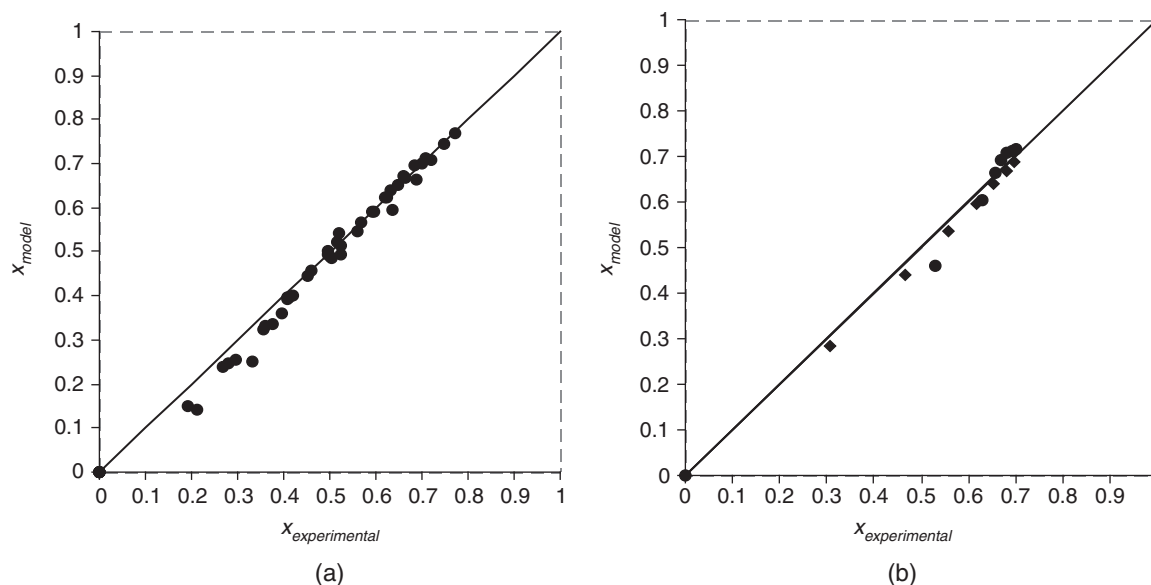(a)   (b)

Fig. 5. Model output versus experimental results for different operating conditions (a) Amberlyst 15, (b) Sulfuric acid.

maximum conversion was achieved in a shorter time compared to the case with Amberlyst 15, and thus the conversion lines using sulfuric acid change sharply. On the other hand the conversion lines of Amberlyst 15 change more slowly during the total experiment time indicating that the calculated kinetic calculations could be more consistent for the Amberlyst 15 for the given experimental period. Nevertheless this modeling methodology could be used for both catalysts to predict the conversions for a given time with an acceptable error margin.

5. Conclusion

The pervaporation separation using polydimethylsiloxane membrane was applied to the esterification of acetic acid with ethanol heterogeneously catalyzed by Amberlyst 15 and homogeneously catalyzed by sulfuric acid. The pervaporation aided esterification process was simulated using a homogeneous second order kinetic model. The pseudo-homogeneous model satisfactorily adjusts the data those obtained from the experiments for the Amberlyst 15 system. The model output agrees with the experimental data obtained for the sulfuric acid in a reasonable range. The described model allows the prediction of the conversions for a given time. The conversions were enhanced in the PMR as compared to a conventional reactor. The results indicate that it is possible to attain almost complete conversion with the use of pervaporation membrane reactor. The model makes possible to determine the optimum operating conditions as it provides assistance to analyze the effect of operating parameters on conversions. This modelling methodology could be used to extrapolate or to scale-up this type of systems.

Acknowledgements

Symbols

C	Concentration, mol l^{-1}
c_{A0}	Initial concentration of acetic acid, mol l^{-1}
c_{cat}	Catalyst concentration, g l^{-1}
D	Diffusion coefficient
J_i	Flux, mol m^{-2}h^{-1}
K	Partition coefficient
K_e	Equilibrium constant
k_1	Forward reaction rate constant, l mol^{-1} min^{-1}
k_2	Backward reaction rate constant, l mol^{-1} min^{-1}
k_{obs}	Observed rate constant, l mol^{-1} min
K_p	The coefficient that gives the correlation between flux and concentration, g mol^{-1} h
M	Initial molar ratios of ethanol to acetic acid
P	Permeability
R	Reaction rate, mol^3 min^{-1}
S	Membrane area, m^2
T	Time, min
T	Temperature, °C
V	Volume, l
X	Conversion

Subscripts and superscripts

A	Acetic acid
B	Ethanol
E	Ethyl acetate
W	Water

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