Analysis of a Membrane Reactor: Influence of Membrane Characteristics and Operating Conditions

Nikunj P. Tanna[*]   S. Mayadevi[†]

[*]Larsen and Toubro Limited, Mumbai, India 400 072, Nikunj_Tanna@lntenc.com

[†]CE and PD Division, National Chemical Laboratory, Pune, India 411 008, s.mayadevi@ncl.res.in

Analysis of a Membrane Reactor: Influence of Membrane Characteristics and Operating Conditions

Nikunj P. Tanna and S. Mayadevi

Abstract

Modeling of an esterification reaction in a batch pervaporation membrane reactor (PVMR), and an analysis of the PVMR performance under different reaction conditions for different membrane characteristics are presented. Esterification of ethyl alcohol with acetic acid was considered as the model reaction. The PVMR performance for this reaction could be represented by a 2-step series model. The PVMR performance was similar to that of the batch reactor when both the reactors were in the kinetic regime. However, the performance of the PVMR was superior to that of the batch reactor when both were in the intermediate/equilibrium regime of the reaction. In these regions, the PVMR performance was influenced/limited by the membrane flux and selectivity. The analysis showed that the membrane flux affected the PVMR performance in the intermediate region and the membrane selectivity affected the performance in the equilibrium regime. Further, the limitations introduced by a low-flux membrane could be overcome by appropriate selection of the membrane area and that due to poor selectivity could be compensated to a certain extent by adjusting the feed ratio.

KEYWORDS: membrane reactor, pervaporation membrane, esterification, performance comparison

1. INTRODUCTION:

In recent years there has been an increasing interest in research on reactive separation in multifunctional reactors (R. Krishna, 2002). Among the different ways in which the separation function is integrated within the reactor, the integration of reaction and permeation has been attracting considerable academic interest and a number of reviews have appeared on this subject (Saracco et al., 1999; Sirkar et al., 1999; Julbe et al., 2001; Wőltinger et al., 2001; Dixon, 2001). The use of membrane reactors with membranes performing a variety of functions, their advantages, disadvantages, future potential etc. have been critically analyzed in these reviews. Reports are available on membrane reactors having outperformed the conventional reactors for many reactions such as esterification (Lim et al., 2002; Zhu et al., 1996), hydrogenation, oxidation (Saracco et al., 1999), biochemical reactions (Wőltinger et al., 2001), photo-catalytic reactions for pollutant decomposition (Molinari et al., 2001), and electrochemical reactions (fuel cell) (Sundmacher et al., 1999; Sundmacher et al., 2001).

The concept of carrying out esterification reactions in pervaporation membrane reactor with *in situ* removal of water for a favorable shift in the equilibrium has been proved in the formation of ethyl and butyl acetates (Lim et al., 2002; Zhu et al., 1996; Tanaka et al., 2001), ester of hexanoic acid (Beers et al., 2001), tartaric acid (Keurentjes, 2001) etc. The formation of ethyl acetate (Zhu et al., 1996; Krupiczka et al., 1999) and diethyl tartarate (Keurentjes, 2001) by hybrid process combining esterification and pervaporation in pervaporation membrane reactors (PVMRs) have been modeled to study the sensitivity of different parameters in the reactor performance. In all the cases the PVMR performance was better than the conventional reactor and the performance was reported to be sensitive to the ratio of membrane area to the batch volume. The design issues of PVMR for esterification were analyzed by Tsotsis and coworkers (2002). Their analysis showed that the performance of the batch PVMR is influenced by the ratio of the characteristic reaction time and the transport time and poses optimization issues. A theoretical analysis on the esterification of tartaric acid in batch reactor with internal and external coupling of pervaporation membrane by Nemec and Gemert (2005) led to the conclusion that the performance of a batch reactor with external coupling of membrane separator was better than that of the PVMR. They attributed this finding to the slow kinetics of the reaction. This implies that the relative benefits of using a PVMR in place of a conventional reactor is influenced by the kinetics of the reaction.

A performance analysis of PVMR for the production of propyl propionate by Tanna and Mayadevi (2005) brought out the need for optimizing the design parameters and operating conditions based on membrane characteristics and reaction kinetics. In this paper we extend the analysis to the formation of ethyl acetate. A model for the reaction in a PVMR is proposed and validated by comparing the predicted concentration profile with data from literature (Tanaka et al., 2001). The influence of membrane characteristics and operating conditions on the behavior of PVMR was analyzed in relation to the different reaction regimes to get a better understanding of the factors that decide its performance

2. THEORY:

We have considered a typical batch reactor for the esterification reaction with water being continuously removed through the membrane. The permeation of individual compounds through membrane is governed by the membrane characteristics and operating conditions. Esterification of ethyl alcohol with acetic acid using a cation exchange resin (Amberlyst 15) (Tanaka et al., 2001) was considered as the model reaction for the study. This is a reversible reaction which proceeds with the formation of the products, ethylacetate and water, and no side reaction. The reaction can be represented as:

$$C_2H_5OH + CH_3COOH \longleftrightarrow CH_3COOC_2H_5 + H_2O$$
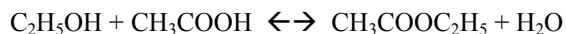
The reaction rate of esterification followed the general kinetic expression for second order reversible reaction is given by:

$$-r_A = k_f.C_A.C_B - k_r.C_C.C_D \tag{1}$$

Here the subscripts *A* and *B* represent the reactants, and *C* and *D* represent the products; r_A is the rate of reaction of reactant *A;* *C* is the concentration in mol/m^3; and k_f and k_r represent rate constant for the forward and reverse reaction, respectively. For the analysis, the values of k_f and k_r were taken as 0.00261 and 0.000816 l/mol.min, which corresponded to a reaction temperature of 70° C (Tanaka et al., 2001).

The general assumptions used in the development of the governing equations were: (1) The reaction is homogeneous and there is no mass transfer gradient existing in the reactor. (2) The operation is isothermal. The reaction temperature and rate remain uniform throughout the reactor at any instant. (3) The membranes used in the reaction do not influence the reaction kinetics. (4) The membrane is permeable only to water and alcohol. The maximum flux through the membrane is decided by the membrane characteristics. (5) The permeation rate of the individual species at any moment is dependent on its concentration at that instant and the membrane characteristics.

The maximum amount of fluid permeating through the membrane at any specific time interval was taken as:

$$M = \Phi.A_m.(t_i - t_{i-1})$$
(2)

where *M* was the total mass of fluid permeated through the membrane in the time interval $t_i - t_{i-1}$; A_m the total mass transfer area of the membrane in m^2 and Φ the membrane flux in kg/m^2.h. It was assumed that the membrane was permeable to only water and alcohol and impermeable to the other species present in the reactor. The permeation of these species varied continuously depending on the change in their concentration due to reaction on the reaction-side of membrane. The permeation of water and alcohol was calculated using the equations (3) and (4) respectively.

$$M_W = \frac{\alpha.(m_w/m_{al}).M.(N_w'/N_{al}')}{1+[\alpha.(m_w/m_{al}).(N_w'/N_{al}')]}$$
(3)

$$M_{al} = M - M_W$$
(4)

Here α is the membrane selectivity, defined as the weight ratio of water to alcohol in permeate to that in the reactor, *m,* the molecular weight and *N'*, the number of moles present in the reactor. The subscripts *w* and *al* represent water and alcohol, respectively.
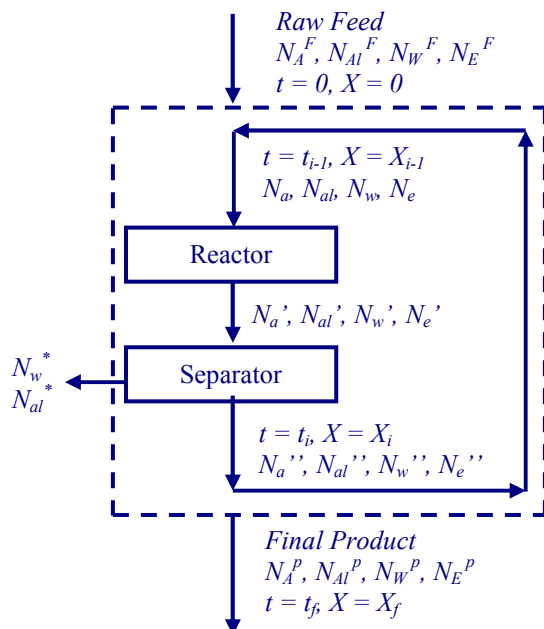

Figure 1. Schematic representation of the sequence of steps

The concentration changes occurring in the reactor during the reaction were perceived to be the result of (1) the reaction proceeding as per the rate equation (the reaction), and (2) the removal of water and alcohol by the membrane (the separation). The model assumes that these two steps occur sequentially in the reactor, and is schematically presented in Fig. 1.

In the figure *N* represents the kmols of different components; *X* is the conversion of limiting component (%); *t* is the time in minutes and X_f is the final conversion at time t_f. The subscripts *A, Al, W, E* represent acid, alcohol, water, ester, before and after the reaction respectively while *a, al, w, e* represent the acid, alcohol, water, ester, during the reaction-separation sequence. The subscript *i* represents the iteration number. The symbols *N'* and *N''* indicate the kilomoles of different components in the reactor at the end of reaction and separation sequence, respectively as shown in Fig.1. *N** in Fig. 1 represents the amount of liquid that permeates through the membrane, superscripts *F* and *P* indicate feed and product, respectively.

The differential equation generated using the model was solved using 4th order Runge Kutta Method. The data generated through the model was compared with the literature data for the same system (Tanaka et al., 2001). The model gave a good fit to the literature data and was used to study the influence of membrane characteristics and operating conditions on the reactor performance. A detailed analysis of the membrane reactor was carried out using this model. The results were useful in establishing the PVMR performance limitations imposed by the membrane/reaction characteristics, and the methods for overcoming the limitations by appropriate selection of operating conditions.

3. RESULTS AND DISCUSSION:

3.1   Model validation

A comparison of the conversion predicted by the model with the experimental data from literature (reaction temperature: 70° C; maximum water flux: 0.5 kg/m^2.h; membrane area: 0.0038 m^2; initial reaction mixture volume: 0.058 m^3 and acid to alcohol molar feed ratio: 1:2; Tanaka et al., 2001) is presented in Fig. 2. The figure shows that the model predictions match well with the experimental data for both batch and membrane reactor. A detailed analysis of the membrane reactor using the model is presented in the next sections. Optimizing the integration step size in numerical analysis leads to reduction in computation time without compromising on the accuracy of prediction. Fig. 3 shows the effect of step size on the prediction of acid conversion. It is observed that for step sizes in time (dT) up to 10 minutes there is negligible difference between the predictions. An increment of 5 minutes was used in all the analyses.
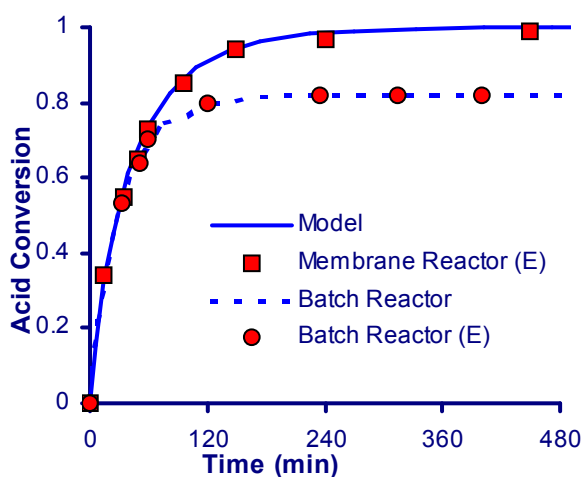

Figure 2. The validation of the model with literature data (maximum water flux: 0.5 kg/m^2.h, membrane area: 0.0038 m^2, selectivity: 200, initial volume of reaction mixture: 0.058 m^3, alcohol to acid feed ratio (molar): 2); symbols represent literature values.
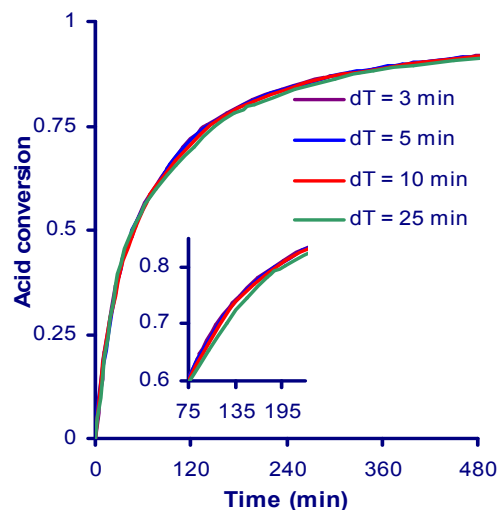
Figure 3. The effect of integration step size, dT (increment of time), on the conversion profile generated by model (membrane flux: 2.15 kg/m^2.h, selectivity: 10000, area: 3.5 m^2, alcohol to acid feed ratio (molar): 1).

3.2   Influence of membrane characteristics on esterification

The thermodynamic limitation of reversible reactions is often overcome through *in situ* removal of product/products in membrane reactors. In this case, the membrane characteristics viz. the flux and selectivity play an important role in the performance of the reactor. During the generation of ethyl acetate in the membrane reactor, the reverse reaction is suppressed by the continuous removal of the byproduct, water. The resulting disturbance in the reaction equilibrium favors the forward reaction leading to an enhancement in conversion. The enhancement in conversion depends upon the reaction kinetics as well as the extent to which the equilibrium is disturbed by removal

of byproduct. The course of a reaction can be divided into three distinct sections/regimes. At the beginning of the reaction, it is completely controlled by the kinetics (kinetically controlled regime), towards the end of the reaction, it is controlled by the thermodynamics (equilibrium controlled regime) and there is an in-between region where the transition from kinetic to equilibrium control occurs (intermediate regime). It will be interesting to analyze the PVMR performance in relation to the reaction regime and membrane characteristics. The rate of removal of byproduct from the membrane reactor is dependent upon two basic membrane characteristics – the membrane flux and the membrane selectivity. The influence of membrane flux and selectivity on acetic acid conversion (acid to alcohol feed ratio: 1; initial reaction mixture volume: 0.12 m^3; membrane area: 3.5 m^2) is presented in figures 4 and 5, respectively.

Figure 4 shows that the conversions in membrane reactor and batch reactor are similar in the initial kinetic controlled regime. In the intermediate and equilibrium regime, the conversions are higher in the membrane reactor. The difference in PVMR and batch reactor conversions increases as the reaction approaches the thermodynamic equilibrium in the batch reactor (64.13% under the reaction conditions). The enhancement in reaction in PVMR becomes noticeable in the intermediate regime where the conversion is found to increase with increase in the membrane flux up to a certain extent (a flux of 1 kg/m^2h, curve C in the figure) beyond which there is marginal/no increase in conversion. The effect of flux disappears in the equilibrium regime where the acid conversions using membranes with different flux converge to a final value indicating that the effect of flux on the PVMR performance is pronounced in intermediate regime.

The sensitivity of acid conversion to changes in membrane selectivity is presented in Fig. 5, along with the conversion in batch reactor under similar operating conditions. The figure shows that the effect of variation of membrane selectivity on final conversion is pronounced when the selectivity values are low (< 100). The conversion is only mildly affected by the variations in membrane selectivity when the selectivity is very high (between 100 and 10000). This is because, the enhancement in the conversion is influenced by the rate of removal of water and high selectivity helps only in reducing the reactant (alcohol) loss through the membrane.

The effect of membrane selectivity and flux on the conversion of acetic acid and the amount of
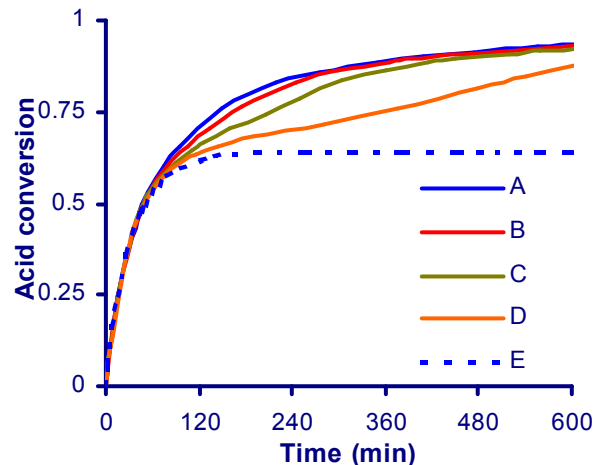

Figure 4. The effect of membrane flux on performance of membrane reactor (membrane selectivity: 10000, area: 3.5 m^2, alcohol to acid feed ratio (molar): 1, membrane flux in $kg/m^2.h$: A: 2.15, B: 1.5, C: 1.0, D: 0.5; E: conventional batch reactor).

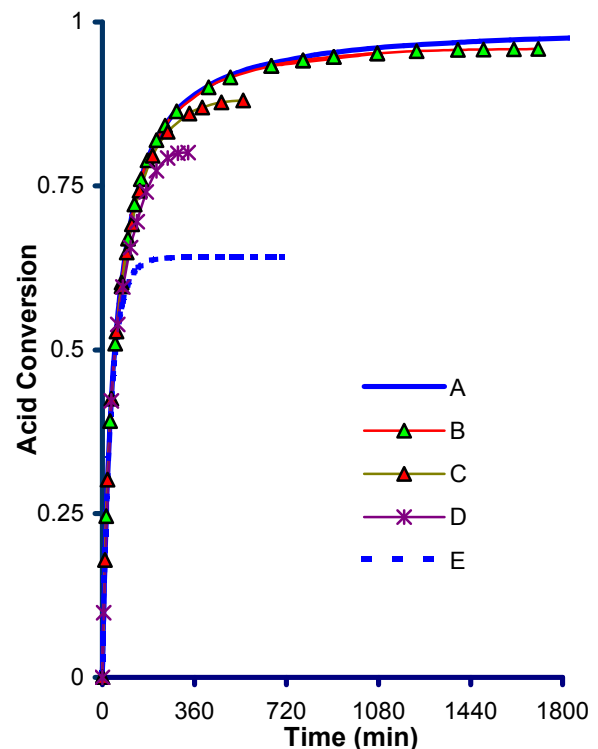Figure 5. The effect of membrane selectivity on the performance of a membrane reactor (membrane flux: 2.15 $kg/m^2.h$, area: 3.5 m^2, alcohol to acid feed ratio (molar): 1, membrane selectivity: A: 10000, B: 1000, C: 100; D: 25, E: conventional batch reactor).

acetic acid and the amount of ethyl acetate formed at two different reaction times (1 h and 4 h) are presented in Table 1. The conversion and ester yield in batch and PVMR with a membrane flux of 0.5 kg/m^2.h. are almost similar when the reaction time is 1 h. This may be due to the combined effect of the following two reasons: (1) initially the rate of water generation is fast and the membrane flux is unable to remove the water completely as it is formed and (2) the reaction rate is limited by the rate constant (kinetic regime). The acid conversion and ester yield in membrane reactor is considerably higher (up to approximately 30 %) than that in the batch reactor when the reaction period is 4 h. Here the reaction is in the intermediate regime where the rate of water generation decreases and the beneficial effect of its removal by the membrane becomes prominent. The table shows that there is an increase in ester yield with increase in membrane flux due to the rapid removal of water generated during the reaction. Although the effect of selectivity on ester yield is negligible at lower conversions, it becomes pronounced as the reaction approaches 100 % conversion (higher reaction time). This is because at higher conversions, the alcohol loss through the membrane with low selectivity will limit the maximum acid conversion/ester yield that can be realized.

Table 1. Effect of membrane characteristics (selectivity and flux) on acid conversion and ester yield (alcohol to acid feed molar ratio: 1:1, acid initial conc.: 8.33 $kmol.m^{-3}$, initial reactor volume: 0.12 m^3, membrane area: 3.5 m^2)

Membrane Flux ($kg / m^2. h$)	Membrane Selectivity	Reaction Time = 1 h		Reaction Time = 4 h	
		% Acid Conversion	Ester Yield (kg)	% Acid Conversion	Ester Yield (kg)
0.5	25	53.1	46.7	67.9	59.8
	100	53.3	46.9	69.5	61.2
	1000	53.3	46.9	70.1	61.6
	10000	53.4	47.0	70.2	61.6
2.15	25	53.9	47.4	78.7	69.3
	100	54.8	48.2	82.5	72.4
	1000	55.2	48.5	83.9	73.0
	10000	55.2	48.6	84.1	73.0
Batch Reactor		52.8	46.5	64.1	56.4

In general, the beneficial effect of membrane flux is more noticeable in the intermediate regime and that of selectivity in the equilibrium regime. Therefore it may be possible to improve the performance of a PVMR with a specific membrane by proper selection of the operating regime.

3.3   Optimization of reactor performance

The conversion profile of acid in membrane reactor can be divided into three regimes, (1) where the membrane reactor behaves almost like a batch reactor (kinetic regime), (2) where the performance deviates and becomes better than that of the batch reactor (intermediate regime), and (3) where the conversion profile of acid in membrane reactor progresses asymptotically towards the final value that is much higher than that in a conventional batch reactor (equilibrium regime). In PVMR, the point at which the deviation from batch reactor conversion occurs depends upon factors like membrane flux, area, reaction rate constant etc. The effect of membrane flux and area on the conversions in a membrane reactor is presented in Fig. 6. A higher flux results in higher increment in conversion in the intermediate regime till the conversion approaches the asymptotic value and the efficiency of byproduct removal decides the enhancement in conversion. Doubling the area of the membrane with flux of 0.5 kg/m^2.h results in a conversion profile similar to that of the membrane with higher flux 2.15 kg/m^2.h and lower area of 3.5 m^2. It

indicates that the overall performance of low flux membranes may be improved by increasing its area. Also it may be economic to optimize the membrane flux and area for a specific reaction based on the kinetics.

The effect of feed composition and membrane selectivity on the conversion profile of membrane reactors is presented in Fig. 7. The final conversion of acetic acid in a membrane reactor with high selectivity membrane (graph D) is higher than that in a similar reactor with a low selectivity membrane (graph E), when stoichiometric ratio of reactants is used. This happens due to the relatively high loss of alcohol by pervaporation through the membrane of low selectivity. This can be compensated by the use of a higher feed ratio of alcohol to acid. Graphs A, B and C show that as the alcohol/acid ratio increases, the conversion becomes higher than that of D (membrane with high selectivity). At very high alcohol to acid ratios (A and B in Fig. 7), the acid conversion reaches 100% within short reaction times. However the difference between the conversion profiles by changing the feed ratio from 5 to 20 is marginal, indicating the need to use the optimum feed ratio based on the membrane characteristics. Further, as the feed ratio increases the acid conversion profiles for the batch and the membrane reactor become closer. Although it is not practicable to use such a diluted feed, the presented case signifies the limitation of influence of feed ratio on the reactor performance. This figure also shows that increasing the amount of alcohol in feed transforms batch reactor's performance to that of membrane reactor. Hence it may be economic to optimize the feed ratio for a reaction based on the knowledge of membrane selectivity, flux and area.
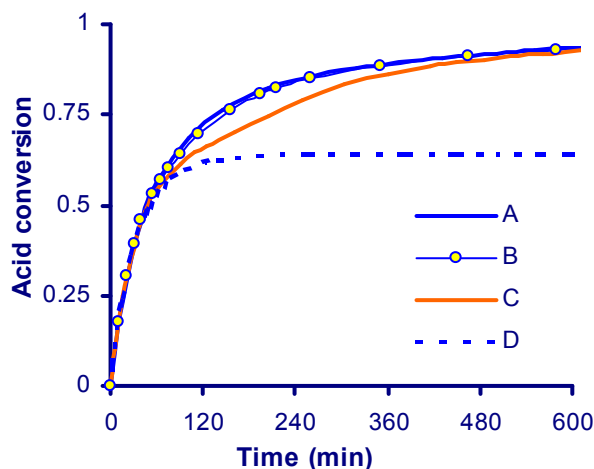

Figure 6. The combined effect of membrane area and membrane flux on the performance of membrane reactor (membrane selectivity: 10000, acid to alcohol feed ratio (molar): 1:1; A: area = 3.5 m², flux = 2.15 kg/m².h; B: area = 7.0 m², flux = 0.5 kg/m².h; C: area = 3.5 m², flux = 0.5 kg/m².h; D: batch reactor, no membrane)
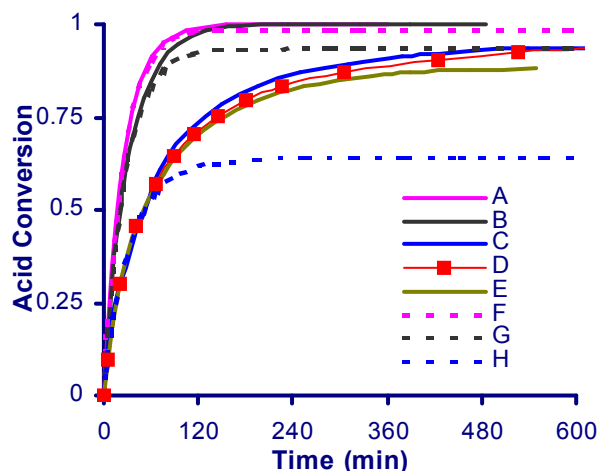
Figure 7. The combined effect of feed composition and membrane selectivity on the performance of a membrane reactor (membrane flux: 2.15 kg/m².h, area: 3.5 m²; A: selectivity = 100, alcohol/acid = 20; B: selectivity = 100, alcohol/acid = 5; C: selectivity = 100, alcohol/acid = 1; D: selectivity = 10000, alcohol/acid = 1; E: selectivity = 100, alcohol/acid = 1; and conventional batch reactor, no membrane, F: alcohol/acid = 20; G: alcohol/acid = 5; H: alcohol/acid = 1)

The influence of membrane selectivity and feed ratio on the acid conversion and ester yield in membrane reactors with different membrane flux and area at two different reaction times compared with corresponding conversion and yield in a batch reactor is presented in Table 2. The table shows that the ester yield and acid conversion in the membrane reactors with different membrane characteristics are similar to those in a batch reactor under similar conditions, when these are operated in the kinetic regime. This is mainly because at this reaction time, both the batch and the membrane reactor are operating in the kinetic regime of the reaction. The advantage of using the membrane reactor becomes pronounced as the reaction approaches equilibrium as can be seen from the results when the reaction time is 4 h. At this reaction time, for a feed mole ratio of one, the high selectivity, high flux, high area membrane gives higher conversion and yield. For this membrane doubling the area results in only a marginal increase in the conversion and ester yield. Again there is only a marginal difference between the highly selective membrane and a membrane with low selectivity and high flux. In fact the low selectivity high flux membrane's performance in terms of the conversion and yield are superior to that of the low flux high selectivity membrane even

at higher surface area. There is an increase in acid conversion with increase in the alcohol to acid mole ratio in the feed. However, the ester yield decreases at higher feed ratios in the case of both batch and membrane reactors. This is because at high feed ratios, the yield is limited by the amount of the limiting reactant (acid, in this case), which keeps on reducing with increase in the feed ratio. A maximum feed ratio of 20 has been considered out of academic curiosity to see the relative performance between the batch and the membrane reactor. At this feed ratio there is no benefit in using the membrane reactor in place of the batch reactor.

Table 2. The influence of membrane characteristics (membrane flux and selectivity) and operating parameters (membrane area and alcohol to acid molar feed ratio) on acid conversion and eater yield in kinetic and transition regime.

Membrane Characteristics		Area (m^2)	Alcohol / Acid in Feed (mol / mol)	Reaction Time = 1 h		Reaction Time = 4 h	
Selectivity	Flux			Acid Conversion (%)	Ester Yield (kg)	Acid Conversion (%)	Ester Yield (kg)
10000	2.15	3.5	1.0	55.2	48.6	84.1	73.0
		7.0		57.2	50.3	84.6	74.4
	0.5	3.5		53.4	47.0	70.2	61.6
		7.0		53.9	47.4	77.9	68.4
100	2.15	3.5	1.0	54.8	48.2	82.5	72.4
			1.1	57.4	48.1	86.4	72.4
			5	85.3	25.3	99.9	29.6
			20	91.5	7.8	99.9	8.4
25	2.15	3.5	1.0	53.9	47.4	78.7	69.3
			1.1	56.5	47.4	83.0	69.6
			5	84.8	25.1	99.9	29.6
			20	91.5	7.8	99.9	8.5
Batch Reactor		-	1.0	52.8	46.5	64.0	56.4
			1.1	55.3	46.4	66.9	56.4
			5	83.0	24.6	93.3	27.6
			20	90.6	7.7	98.4	8.4

Table 2 shows a 28% increase in the ester yield for a reaction time of 4 h when the reaction is carried out in a membrane reactor (flux: 2.15 kg/m^{2}h, area: 3.5 m^2, time: 4 h, selectivity: 100) compared to that of the batch reactor. This can translate into an equivalent advantage in production cost, more when the associated decrease in separation cost is also taken into account. The increase in ester yield corresponding to a membrane selectivity of 10000 (all the other conditions the same) is 29.4% which is marginally higher than that of a membrane reactor having membrane selectivity 100.

4. SUMMARY AND CONCLUSION:

In this paper we have modeled a pervaporation membrane reactor based on the underlying reaction and separation phenomenon using the esterification of ethanol with acetic acid as the model reaction. The simple spreadsheet based approach used for the analysis was able to successfully predict the literature data (Tanaka et. al., 2001). Of the different possible sequences in which the reaction and mass transfer can occur in the reactor (e.g. parallel, series, series-parallel), the one that considers the reaction and separation occurring in series best fitted the experimental results and was used for the analysis. Using this model, it is possible to predict the membrane characteristics that will give the best performance for specific reaction kinetics.

Two intrinsic characteristics that decide the performance of the membrane are the flux and the selectivity. The membrane flux dictates the rate of removal of the byproduct, water, in the model reaction whereas the selectivity decides the amount of the reactant (alcohol) carried away along with water. Our analysis shows that while selectivity up to a certain minimum value contributes to the membrane reactor performance, higher values do not have any profound influence on membrane reactor performance. The membrane reactor performance is more sensitive to the product of flux and membrane area. In shell and tube type membrane reactors this parameter will decide the number of tubes to be used for specific membrane flux. The performance of a membrane reactor can be enhanced by proper selection of the membrane area in relation to its flux such that the byproduct removal rate matches with its generation by reaction (kinetics). The disadvantages of using a membrane with low selectivity can be overcome by slight tuning of the feed ratio to compensate for the reactant loss.

The analysis also shows that the reaction time in a batch membrane reactor can be divided into three regimes, the kinetic regime, the equilibrium regime and the intermediate regime. The batch reactor and membrane reactor exhibit similar performance when the reaction is in the kinetic regime. In this regime the membrane just permeates the byproduct, which is to be removed. As the reaction nears equilibrium, the difference between the performance of the batch and membrane reactors becomes prominent. This is because the disturbance in the reaction equilibrium caused by the removal of the byproduct water results in driving the reaction further and an enhancement in the acid conversion and ester yield.

The analysis further indicates that if tubular membrane reactors are operated in the kinetic regime, there may not be any difference in the conversion and product yield as compared to a simple plug-flow reactor under similar reaction conditions. When the residence time in a tubular membrane reactor is selected such that the reaction is in the intermediate/equilibrium regime, in addition to product/byproduct separation, considerable enhancement in conversion and yield compared to the conventional flow reactor can be obtained. To make the best utilization of membrane reactor capabilities, it is suggested that it may be operated in these regimes.

ACKNOWLEDGEMENTS

NOTATION

N	amount of the component, kmol
X	conversion of limiting component, %
t	time for one cycle, min
A_m	permeation area of the membrane, m^{-2}

Greek Letters

Φ	membrane flux, $kg\ m^{-2}\ h^{-1}$
α	membrane selectivity (weight ratio of water to alcohol in permeate over that in organic)

Subscripts

A, Al, W, E	acid, alcohol, water, ester, before and after the reaction
a, al, w, e	acid, alcohol, water, ester, during the reaction, in the reactor
i	the iteration number
f	final, at the end of the reaction time

Superscripts

$'$	component leaving reactor component of the cycle
$''$	component leaving separator component of the cycle
$*$	component permeated through the membrane, Permeate

F   component entering into the batch reactor before start of the reaction, Feed
P   component coming out of the batch reactor after final conversion, Product

REFERENCES

Krishna, R., "Reactive Separations: More Ways to Skin a Cat", Chem. Eng. Sci., Vol. 57, 1491-1504 (2002).

Saracco, G., Neomagus. H.W.J.P., Versteeg, G.F., Swaaij, W.P.M. van, "High Temperature Membrane Reactors: Potential and Problems", Chem. Eng. Sci., Vol. 54, 1997-2017 (1999).

Sirkar, K.K., Shanbhag, P.V., Kovvali, A.S., "Membrane in a Reaction: A Functional Perspective", Ind. Eng. Chem. Res., Vol. 38, 3715-3737 (1999).

Julbe, A., Farrusseng, D., Guizard, C., "Porous Ceramic Membranes for Catalytic Reactors - Overview and New Ideas", J. of Memb. Sci., Vol. 181, 3-20 (2001).

Wőltinger, J., Drauz, K., Bommarius, A.S., "The Membrane Reactor in the Fine Chemical Industry", Applied Catalysis A: General,Vol. 221, 171-185 (2001).

Dixon, A.G., "Recent Research in Catalytic Inorganic Membrane Reactors", Int. J. of Chem. Reactor Eng., Vol. 1, 1-35 (2003).

Lim, S.Y., Park, B., Hung, F., Sahimi, M., Tsotsis, T.T., "Design Issues of Pervaporation Membrane Reactors for Esterification", Chem. Eng. Sci., Vol. 57, 4933-4946 (2002).

Zhu, Y., Minet, R.G., Tsotsis, T.T., "A Continuous Pervaporation Membrane Reactor for the Study of Esterification Reactions using a Composite Polymeric/Ceramic Membrane", Chem. Eng. Sci., Vol. 51, No. 17, 4103-4113 (1996).

Molinari, R., Grande, C., Drioli, E., Palmisano, L., Schiavello, M., "Photocatalytic Membrane Reactors for Degradation of Organic Pollutants in Water", Catalysis Today, Vol. 67, 273-279 (2001).

Sundmacher, K., Hoffmann, U., "Design and Operation of Electrochemical Gas Purification", Chem. Eng. Sci., Vol. 54, 2937-2945 (1999).

Sundmacher, K, Schultz, T., "Electrochemical Chlorine Absorption in Cyclone Membrane Reactor: Analysis of Reaction Mechanism and Transport Phenomena", Chem. Eng. J., Vol. 82, 117-129 (2001).

Tanaka, K., Yoshikawa, R., Ying, C., Kita, H., Okamoto, K., "Application of Zeolite Membranes to Esterification Reactions", Catalysis Today, Vol. 67, 121-125 (2001).

Beers, A.E.W., Spruijt, R.A., Nijhuis, T.A., Kapteijn, F., Moulijn J.A., "Esterification in a Structured Catalytic Reactor With Counter-Current Water Removal", Catalysis Today, Vol. 66, 175-181 (2001).

Keurentjes, J.T.F., Janssen, G.H.R., Gorissen, J.J., "The Esterification of Tartaric Acid With Ethanol: Kinetics and Shifting the Equilibrium by Means of Pervaporation", Chem. Eng. Sci., Vol. 49, No. 29A, 4081-4089 (1994).

Krupiczka, R., Koszorz, Z., "Activity-Based Model of the Hybrid Process of an Esterification Reaction Coupled with Pervaporation", Separation and Purification Technology, Vol. 16, 55-59 (1999).

Nemec D., Gemert, R. van, " Performing Esterification Reactions by Combining Heterogeneous Catalysis and Pervaporation in a Batch Process", Ind. Eng. Chem. Res., Vol. 44, 9718-9726 (2005).

Tanna, N.P., Mayadevi, S., "Performance Analysis of a Membrane Reactor for Reversible Reactions", Indian Chem. Engr., Section B, Vol. 47, No. 3, (2005).