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Multiresponse optimization based on the desirability function for a pervaporation process for producing anhydrous ethanol

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Abstract−A pervaporation process for producing anhydrous ethanol from industrial ethyl alcohol (95% v/v) was performed with a commercial PVA/PAN membrane. A central composite rotatable experimental design together with response surface methodology was implemented for studying and modeling the influence of operating conditions in terms of the temperature and the flow rate of the feed on the pervaporation performance, namely, the permeate flux and the separation factor. To obtain a trade-off between the permeate flux and the separation factor, a method for simultaneous optimization of multiple responses based on an overall desirability function was used. The optimization resulted in a feed temperature of 66 °C and a feed flow rate of 42 L/h. These operating conditions are expected to respond with a permeate flux of 0.107 kg/m^2 h and a separation factor of 40, which correspond to a satisfactory overall desirability.

Key words: Multiresponse Optimization, Overall Desirability Function, Central Composite Rotatable Design, Response Surface Methodology, Pervaporation

INTRODUCTION

Pervaporation (PV) is a membrane separation process in which the feed mixture is placed in contact with one side of a non-porous or dense membrane, and the permeate is removed in the vapor state from the opposite side by vacuum. Therefore, the permeate undergoes a phase change from liquid to vapor during its transport through the membrane [1]. A typical PV system is shown in Fig. 1.

Ethanol forms an azeotrope with water once it reaches 95.5 wt% at 78.2 °C under atmospheric pressure [2]. Anhydrous ethanol (over 99.5% v/v) is often produced by azeotropic distillation which uses an entrainer such as benzene. Pervaporation is a high potential industrial application for producing anhydrous ethanol. This method is not limited by vapor-liquid equilibrium, does not require use of toxic substances, and is a promising alternative to energy-consuming conventional techniques for separating ethanol mixtures [3-6]. Generally, pervaporation is expected to consume only 13% of energy as compared with azeotropic distillation [7].

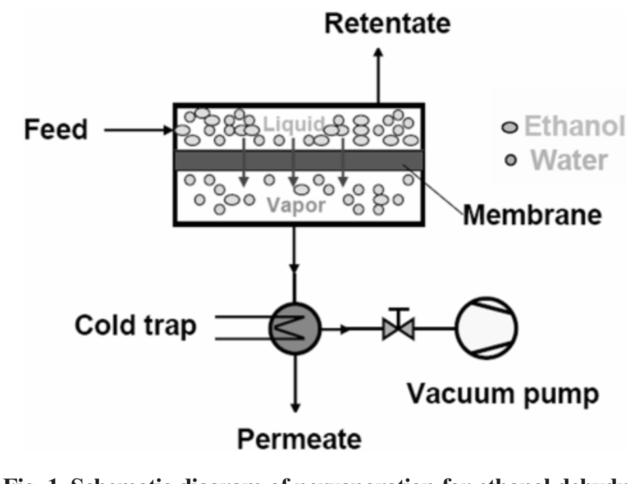

Fig. 1. Schematic diagram of pervaporation for ethanol dehydration.

For dehydration purposes, hydrophilic polymer membranes are often employed. Among them, the cross-linked polyvinyl alcohol (PVA) membranes have been widely used in PV because these membranes have hydroxyl groups that give strong interactions with water molecules through hydrogen bonds [8,9]. In 1982 Gesellschaft für Trenntechnik (GFT) mbH of Germany (now Sulzer Chemtech) commercialized a composite membrane with a cross-linked PVA active layer on a polyacrylonitrile (PAN) support layer for strengthening the membrane [10]. The membrane separation performance is determined by the competition between solution and diffusion of permeates when they transport through the membrane [11]. Generally, according to the solution-diffusion theory [12,13], the permeation process consists of three consecutive steps: (i) sorption of the permeant from the feed liquid to the membrane; (ii) diffusion of the permeant in the membrane; (iii) desorption of the permeant to the vapor phase on the downstream side of the membrane. Therefore, the membrane material plays an important role in successful separation [14]. On the other hand, the performance of PV is not only dependent on the characteristics of membranes, but also on the operating conditions [5].

In this research, the PV of industrial ethanol using a commercial PVA/PAN membrane was investigated. Experimental design, modeling, and optimization were carried out by central composite rotatable design (CCRD) [15], response surface methodology (RSM) [15], and a desirability function approach (DFA) [15,16] in order to find optimal operating conditions for achieving a high permeate flux and a high separation factor at the same time.

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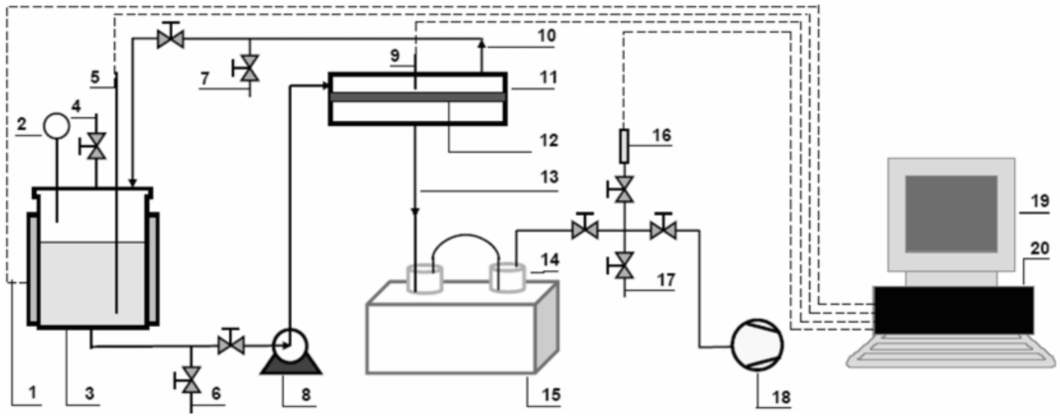

Fig. 2. Schematic diagram of the pervaporation equipment.

1. Heating jacket-temperature controller (T/C)
2. Pressure gauge
3. Feed tank
4. Vent
5. Thermo-couple
6. Drain
7. Sample valve
8. Metering pump
9. Thermocouple
10. Retentate
11. Membrane module
12. Membrane
13. Permeate
14. Glass tube
15. Electric cold trap
16. Digital vacuum gauge
17. Vent
18. Vacuum pump
19. Computer control system
20. Process controller

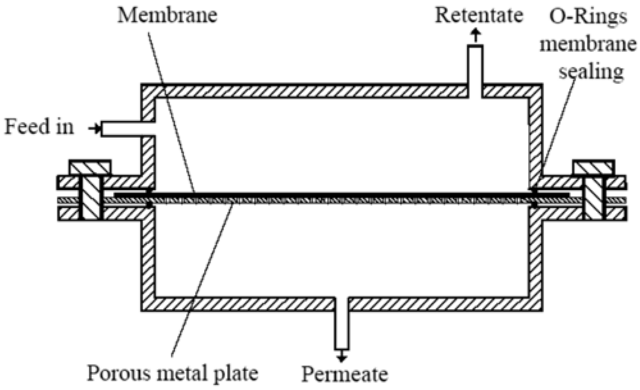

Fig. 3. Configuration of the pervaporation module.

EXPERIMENTAL

1. Materials

The experiments were performed with industrial ethyl alcohol 95% v/v (93.7 wt%) manufactured by Samchun Pure Chemical Co., LTD through a GFT cross-linked PVA/PAN membrane provided by Sulzer Chemtech. The membrane can be used at temperatures up to 100 °C for dehydration of organic solvents such as ethanol.

2. Apparatus

The pervaporation system and the cell used in this study are illustrated in Figs. 2 and 3, respectively. An effective membrane area of 0.014 m^2 was placed on a porous metal plate support in the module. The feed solution was kept at a constant temperature in a stainless steel container by an electric heating jacket and a temperature controller. From the feed tank, the feed mixture with a volume of 2 L was circulated by a pump through the membrane module and returned back to the tank.

During the experiments, the downstream pressure was maintained as low as 0.5 torr with a vacuum pump, and measured by a Shim gauge. At a given temperature, the experiment was run for 2 h. The vacuum pressure and process temperatures of tank cover, feed solution, and inside module were monitored by a computer control system.

The permeate was condensed in an electric cold trap, cooled with pure ethanol at −40 °C, collected at predetermined time intervals, and then it was thawed and weighted. The total permeate flux was calculated directly by measuring the weight of the collected permeate and the time. The feed and permeate concentrations were measured by a refractometer.

3. Software

The experimental design, data analysis, and desirability function optimization to find the optimum conditions were performed by using a statistical program JMP (SAS Institute Inc., Carry, NC) [17].

METHODOLOGY

1. Performance Parameters (Responses or Objective Functions)

The separation performance of the membranes can be evaluated on the basis of the total permeation flux J ($kg/m^2\,h$) and the separation factor α [12].

$$J = \frac{1}{A}\frac{\Delta W}{\Delta t} \tag{1}$$

$$\alpha = \frac{y_{water}/y_{ethanol}}{x_{water}/x_{ethanol}} \tag{2}$$

where ΔW (kg) is the collected amount of permeate during the experimental time interval Δt (h), A (m^2) is the effective membrane area, and x, y are the weight fraction of either water or ethanol in the permeate and the feed, respectively.

2. Design of Experiments

A CCRD method [15] was used to design the experiments with two design variables k=2, feed temperature T (°C) and feed flow rate F (L/h). The design consisted of a two-level fractional factorial (or core) and two other kinds of points, the center point and axial (or star) points as illustrated in Fig. 4. The axial points are located

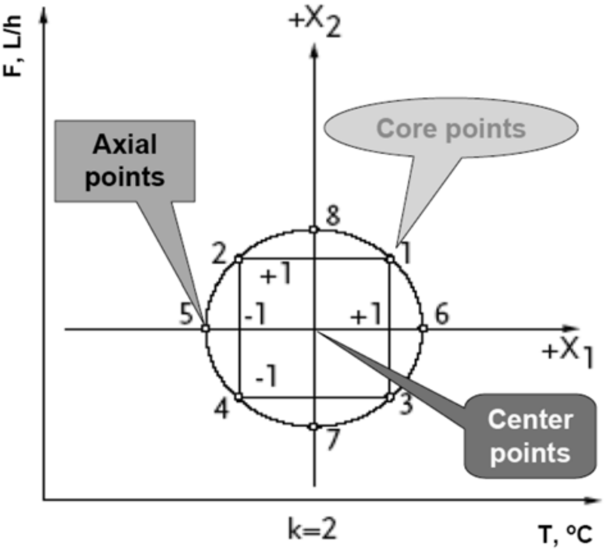

Fig. 4. Distribution of rotatable design points.

Table 1. Variable levels for a central composite rotatable experimental design

Design variables	Variation levels					Variation intervals
	$-\theta$	$-$	0	$+$	θ	
Temperature, T (°C)	46	50	60	70	74	10
Flow rate, F (L/h)	32	40	60	80	88	20

Table 2. CCRD with coded and actual design variables and experimental results

Trial no.	Levels of coded variables		Values of actual variables		Response functions (Observed)	
	X_1	X_2	T (°C)	F (L/h)	$J\times10^3$ (kg/m^2 h)	α
1	+	+	70	80	131.4	35.45
2	−	+	50	80	75.14	41.49
3	+	−	70	40	52.45	60.41
4	−	−	50	40	80.40	43.00
5	$-\theta$	0	46	60	86.93	46.28
6	θ	0	74	60	68.78	50.84
7	0	$-\theta$	60	32	55.17	52.52
8	0	θ	60	88	92.74	33.78
9	0	0	60	60	118.9	38.22
10	0	0	60	60	172.6	32.40

on the coordinate axes at a distance from the experimental center, taking into account the rotatability condition $\theta=2^{k/4}=1.414$. The variables and their levels are shown in Table 1. The experiment matrix is summarized in Table 2 with the total number of experimental points $N=2^k+2k+n_c=2^2+2\times2+2=10$, which includes $2^k=4$ core points (trial nos. 1-4), 2k=4 star points (trial nos. 5-8), and $n_c=2$ center points (trial nos. 9-10). The relationships between the coded and actual variables were defined as follows.

$$X_1=\frac{(T-60)}{\Delta T} \tag{3}$$

$$X_2=\frac{(F-60)}{\Delta F} \tag{4}$$

where ΔT and ΔF are variation intervals of the feed temperature and the feed flow rate, respectively as shown in Table 1.

3. Modeling

The correlation of the operating conditions and pervaporation performance was quantified by RSM, which is a collection of statistical and mathematical methods useful for modeling and analyzing engineering problems. A second-order polynomial equation to fit responses to variables based on this method can be expressed as follows [15].

$$Y_i=\beta_0+\beta_1X_1+\beta_2X_2+\beta_{12}X_1X_2+\beta_{11}X_1^2+\beta_{22}X_2^2+\varepsilon_i \tag{5}$$

where Y_i is the response, i=1, 2, …; m is the number of individual responses, in this work m=2; β_0, β_1, β_2, β_{12}, β_{11}, and β_{22} are the intercept, linear, interaction, and quadratic coefficients, respectively. These regression coefficients are determined by the least squares method with the residual error ε_i defined by the difference between the predicted and the observed values.

4. Optimization

A DFA was used to obtain two optimum responses (J and α) based on the fitted quadratic response surface models constructed by RSM. This approach was introduced Harrington (1965) introduced this approach and Derringer and Suich (1980) further developed it [15]. It is based on transforming the measured property of each response to a dimensionless desirability scale, d_i, defined as a partial desirability function whose value varies from zero, undesirable response, to one, desirable response. This enables the combination of results from properties measured on different scales.

Depending on whether a particular response is to be maximized, minimized, or assigned a target value, different desirability functions can be used. In this research, a one-sided linear desirability function was chosen to maximize each response as follows [16].

$$d_i=\frac{Y_i-Y_{i\text{-}min}}{Y_{i\text{-}max}-Y_{i\text{-}min}} \tag{6}$$

where $Y_{i\text{-}min}$ and $Y_{i\text{-}max}$ are the minimum and the maximum values of response i, which are obtained from the mathematical model Eq. (5). This transformation results in a continuous function on whose value is between 0 and 1.

Once these individual d_i functions are defined for all responses, they are combined into one objective function D, representing the overall desirability, which is calculated as the geometrical average of partial desirability functions [16].

$$D=\left[\prod_{i=1}^{m}d_i\right]^{1/m} \tag{7}$$

The overall desirability function D also varies from 0 to 1. If any d_i fails to meet the target requirements, the D will have a value of 0. On the other hand, if all responses are acceptable, the value of D will fall in the interval [0, 1] and will increase with increasing individual desirability values.

RESULTS AND DISCUSSION

1. Regression Models

From the experimental results shown in Table 2, mathematical models based on Eq. (5) were obtained as follows.

The permeate flux model

$$Y_1=77.93181+37.19192X_1+4.323737X_2 -0.2775X_1X_2+15.58574X_1^2+4.009206X_2^2 \quad (8)$$

The separation factor model

$$Y_2=42.22461-8.7X_1-2.77147X_2-0.2725X_1X_2 +2.392936X_1^2-0.85962X_2^2 \quad (9)$$

Figs. 5a and 5b illustrate the comparison of the actual values of responses obtained experimentally and the predicted values computed by the model Eqs. (8) and (9). As shown in these figures, these models are acceptable as the square of the correlations between the actual and predicted responses are 0.97 and 0.95 for permeate flux and for separation factor, respectively.

2. Sensitivity Analysis

The effects of the variables on the responses are as shown in Figs. 6a and 6b. When feed temperature increases, the permeation flux increases, but the separation factor decreases. According to the solution-diffusion mechanism, the mass transfer in the liquid and the sorption into the membrane increase with the feed temperature. Additionally, at higher temperatures, the polymer chains become more flexible, causing an increase in the free volume that enhances the diffusion of the permeants in the polymer matrix [5].

The increase in feed flow rate causes an increase in the driving force to transport across the membrane and an increase of membrane swelling at low ethanol concentrations. Thus, the total flux is increased, and the separation factor is reduced. However, at high concentrations, the influence of feed flow rate on the dehydration process was not significant in comparison with other factors, because the free volume and swelling of the hydrophilic composite membranes decreased significantly with the water content in the feed [18,19].

3. Simultaneous Optimization of Multiple Responses

Summaries of the effects of the design variables on the responses and the overall desirability as the prediction profiles are shown in Fig. 7. The dotted red lines show the current variable settings and response values, and the blue curves represent the 95% confidence

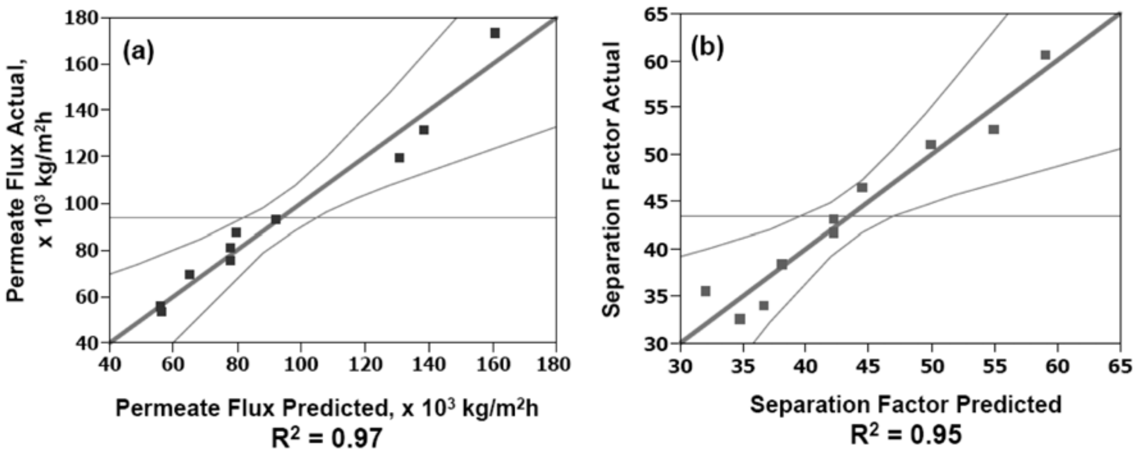

Fig. 5. Correlations between the actual and predicted response values of (a) permeate flux and (b) separation factor.

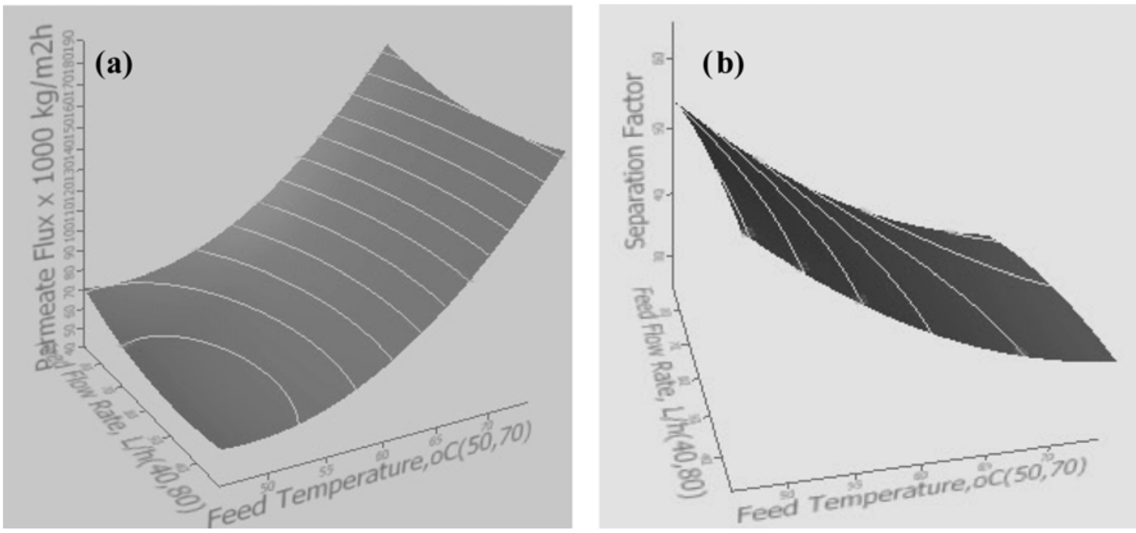

Fig. 6. The effect of feed temperature and feed flow rate on (a) permeate flux and (b) separation factor.

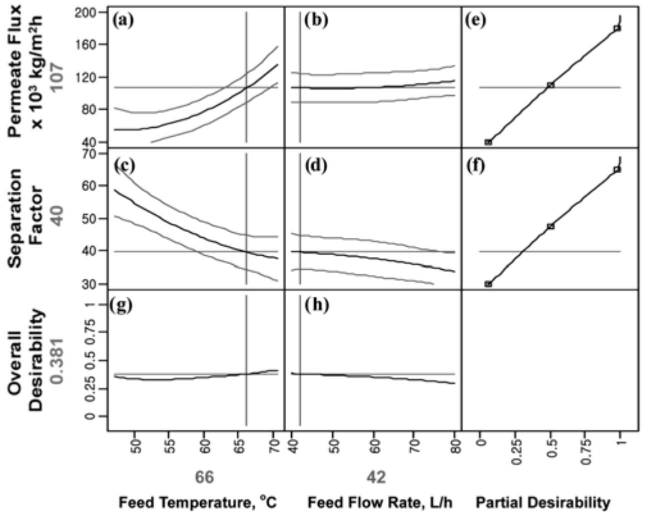

Fig. 7. The graphs of predicted (a, b, c, d), individual desirability (e, f) and overall desirability (g, h) profiles for permeate flux and separation factor.

intervals for each profile. Note that a trade-off is necessary between the permeate flux and the separation factor. In order to simultaneously optimize these two objective functions, the overall desirability function optimization method was implemented as follows.

First, the minimum and maximum values of the two responses $Y_{i\text{-}min}$ and $Y_{i\text{-}max}$ are determined by solution of the following problems.

$$\begin{gathered}\min Y_i\\ \text{subject to } -1.414 \le X_j \le 1.414,\ j=1, 2\\ \max Y_i\\ \text{subject to } -1.414 \le X_j \le 1.414,\ j=1, 2\end{gathered}$$

The solutions are $Y_{1\text{-}min}$=54.3927, $Y_{1\text{-}max}$=161.6833, $Y_{2\text{-}min}$=33.5072, and $Y_{2\text{-}max}$=58.5031. Substituting these values into Eq. (6) results in the individual desirabilities as follows.

$$\begin{aligned}d_1=&0.219395+0.346647X_1+0.040299X_2\\ &-0.00259X_1X_2+0.145267X_1^2+0.037368X_2^2\end{aligned} \tag{10}$$

$$\begin{aligned}d_2=&0.348984-0.348X_1-0.11086X_2\\ &-0.0109X_1X_2+0.095717X_1^2-0.03438X_2^2\end{aligned} \tag{11}$$

Second, the individual desirability functions are combined into the overall desirability function by Eq. (7), which gives the following equation.

$$\begin{aligned}D=&(0.219395+0.346647X_1+0.040299X_2\\ &-0.00259X_1X_2+0.145267X_1^2+0.037368X_2^2)^{1/2}\\ &\times(0.348984-0.348X_1-0.11086X_2-0.0109X_1X_2\\ &+0.095717X_1^2-0.03438X_2^2)^{1/2}\end{aligned} \tag{12}$$

This function should be maximized by choosing the best conditions of the operating parameters (temperature and flow rate) or the coded variables (X_1 and X_2).

Finally, in order to make both responses reach maximal values, the trade-off between the objective functions J and α is carried out through the maximization of the overall desirability function D.

The optimal result was obtained at X_1=0.6 and X_2=−0.9, which correspond to T=66 °C and F=42 L/h. At this operating condition, it is predicted that the permeate flux J=0.107 kg/m^2 h and the separation factor α=40. These values were obtained by the trade-off between J and α at the individual desirabilities d_1=0.487 and d_2=0.296, hence the overall desirability D=0.381, which belongs to a satisfactory range 0.37-0.63 [15].

In addition, the optimization results are also illustrated with the combination of surface contour plots of the two responses in Fig. 8. The overlay indicates that the region of optimal performance for the two responses 0.0975 kg/m^2 h<J<0.1255 kg/m^2 h and 39<α<40 corresponds to the intervals from 65 °C to 68 °C and from 40 L/h to

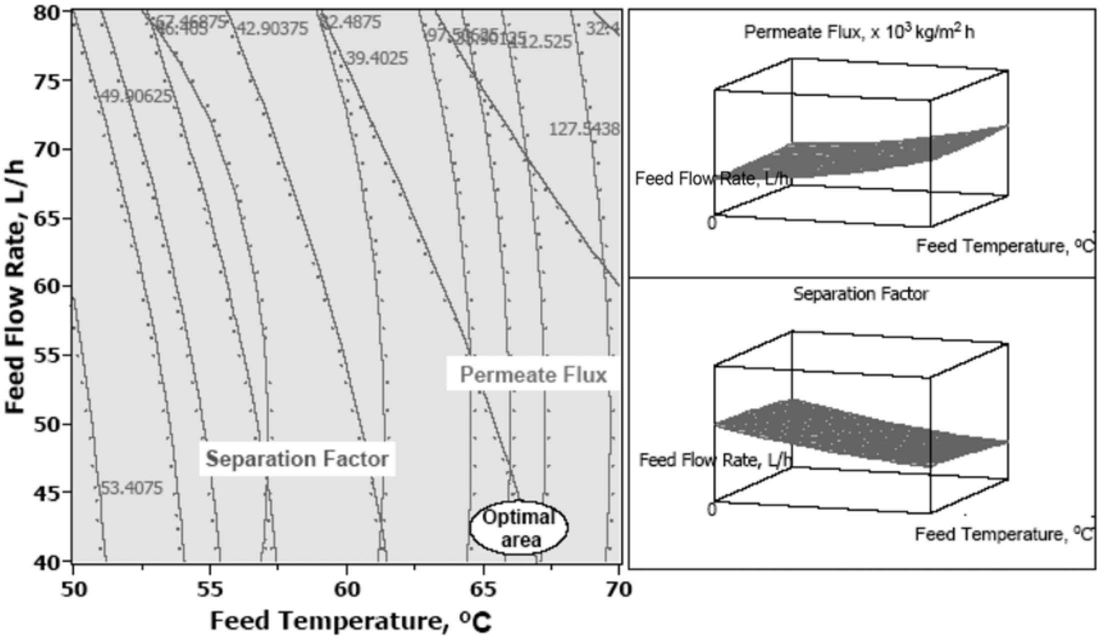

Fig. 8. Overlay of surface response contour plots of permeate flux and separation factor.

43 L/h for feed temperature and feed flow rate, respectively. It indicates that the above trade-off values of the two responses are in the optimal region.

CONCLUSIONS

A pervaporation process for ethanol dehydration using a GFT cross-linked PVA/PAN membrane was investigated in this study. The design variables are the feed temperature and flow rate, and the responses are the permeate flux and the separation factor. A CCRD method was used for experimental design, and RSM was used to obtain regression models for the responses from the experimental data.

A satisfactory trade-off between the permeate flux and the separation factor was obtained by application of simultaneous optimization of multiple responses based on an overall desirability function, which gave optimal operating conditions for the feed temperature and flow rate. It is expected that the methodology used in this work can be applied to various processes with more design variables.

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