Optimization of operating conditions of a pervaporation process for production of anhydrous ethanol

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1. Introduction

Recently, pervaporation (PV) is considered as a great potential industrial process for the separation of azeotropic, close–boiling, or aqueous organic mixtures since this technique is less power–consuming than azeotropic and conventional distillations [1]. The dehydration of aqueous ethanol solution for production of anhydrous ethanol is the best–developed area of the PV applications in industry. In addition, ethanol forms an azeotrope with water once it reaches 95.5 wt.% at 78.2 ^{o}C under atmospheric pressure [2] hence this mixture is very hard to be separated by using normal distillation.

Design of experiments has been done by central composite rotatable design (CCRD) [3] to obtain mathematical models for expression of the PV performance (flux and selectivity) as functions of operating conditions (temperature, concentration, and flow rate). The main purposes of this study are optimization and trade–off PV performance based on the experimental mathematical models to achieve high flux and separation factor simultaneously, as well as determining a good factor setting to separate azeotropic ethanol by statistical processing using of computer program (JMP) [4]. It is a statistical analysis application by SAS (statistical analysis system) Institute, Inc.

2. Experimental

2.1. Materials

For all experiments, GFT cross–linked PVA/PAN membrane provided by Sulzer Chemtech was used. A binary mixture of 93–98 wt.% ethanol was prepared from anhydrous industrial ethyl alcohol (assay by GC analysis 99.9+%) manufactured by SK Chemicals.

2.2. Pervaporation experiments

The pervaporation apparatus used in this study is illustrated in Fig. 1. The effective membrane area of 138 x 10^{-4} 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 using over resistance heater and a temperature controller. From the feed tank, the feed mixture (a volume of 2 L) was circulated with a pump through the membrane module and returned back to the tank.

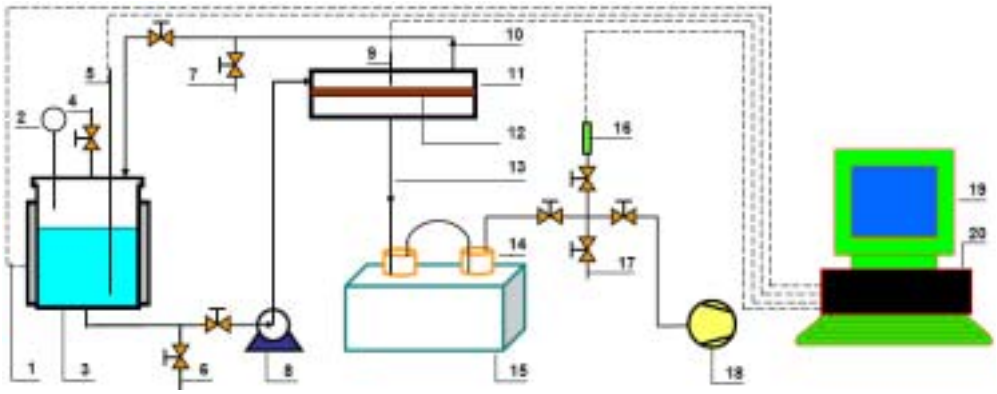


Fig. 1. Schematic diagram of the pervaporation equipment: (1) over temperature–temperature controller (T/C), (2) pressure gauge, (3) feed tank, (4) vent, (5) thermo–couple, (6) drain, (7) sample valve, (8) metering pump, (9) thermo–couple, (10) retentate, (11) membrane module, (12) membrane, (13) permeate, (14) glass tube, (15) electric cold trap, (16) digital vacuum gauge, (17) vent, (18) vacuum pump, (19) computer control, and (20) process controller.

During the experiments, the downstream pressure was maintained at 0.5 torr using a vacuum pump and measured by a Shim gauge. To reach a steady–state at a given temperature, the experiment was run for 1 h. The vacuum pressure and process temperatures (over, feed solution, and inside module) are monitored by a computer control.

The permeate was condensed in an electric cold traps cooled with pure ethanol (–40 ^{o}C) and collected at determined time intervals, then it was thawed and weight. The feed and permeate compositions were determined by a refractometer.

According to CCRD design, conditions of factors variations is given in Table 1.

Table 1 Factor variation intervals [3]

Feed factors	**Variation levels**					**Variation intervals**
	–1.682	**–**	**0**	**+**	**1.682**	**x**
x_1–Temperature (^{o}C)	43	50	60	70	77	10
x_2–Concentration (wt. % EtOH)	93	94	95.5	97	98	1.5
x_3–Flow rate (L/h)	26	40	60	80	94	20

From the experimental data, separation performance of the membranes can be evaluated on the basis of total permeation flux, J (g/m^2 h) and separation factor, α.

$$J = \frac{\mathrm{W}}{\mathrm{A\ x\ t}} \quad (1) \qquad \text{and} \quad \alpha = \frac{y_{\mathrm{water}} / y_{\mathrm{ethanol}}}{x_{\mathrm{water}} / x_{\mathrm{ethanol}}} \quad (2)$$

Where W (g) is the total amount of the permeate during the experimental time interval t (h) at a steady state and A (m^2) is the effective membrane area, and y, x are the weight fraction of either water or ethanol in the permeate and feed, respectively.

3. Results and discussion

3.1. Experiment–mathematical modeling

The following mathematical models in the form of second–order equation polynomials were formed with the regression coefficients have been obtained by JMP from experimental outcomes.

$$\hat{J} = 51.420913 + 23.454242X_1 - 16.74443X_2 + 5.0986639X_3 + 0.325X_1X_2 - 6.85X_1X_3 - 7.225X_2X_3 + 9.3137701X_1^2 + 2.3841236X_2^2 + 2.4548343X_3^2 \quad (3)$$

$$\hat{\alpha} = 103.4836 - 18.24347X_1 + 17.10654X_2 - 3.524334X_3 - 8.625X_1X_2 - 1.725X_1X_3 - 0.825X_2X_3 + 4.1967715X_1^2 + 5.2220763X_2^2 + 0.7319482X_3^2 \quad (4)$$

where $\hat{J}$ and $\hat{\alpha}$ are predicted–calculated permeate flux (g/m^2 h) and separation factor response values, respectively, and X_i is the coded value of the i–th factor, with basic level and variation intervals has been determined as follows: $X_1 = \frac{x_1 - 60}{10}$; $X_2 = \frac{x_2 - 95.5}{1.5}$; $X_3 = \frac{x_3 - 60}{20}$

After checking of statistical significance of regression coefficients, the models are satisfied with 95% confidence.

3.2. Comparison of experimental and calculated data

A comparison between the actual values of responses obtained experimentally and the predicted values computed by the specified models is illustrated in Fig. 2.

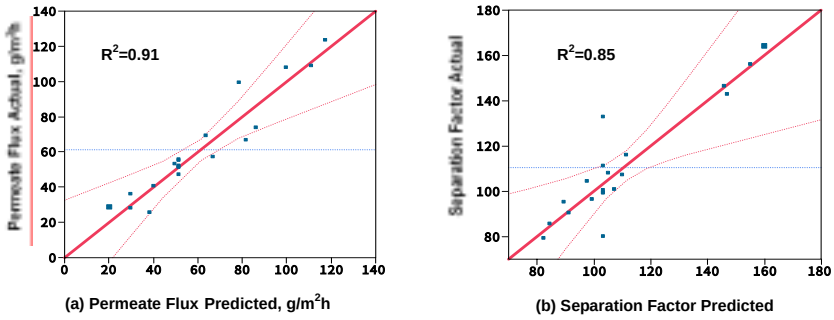


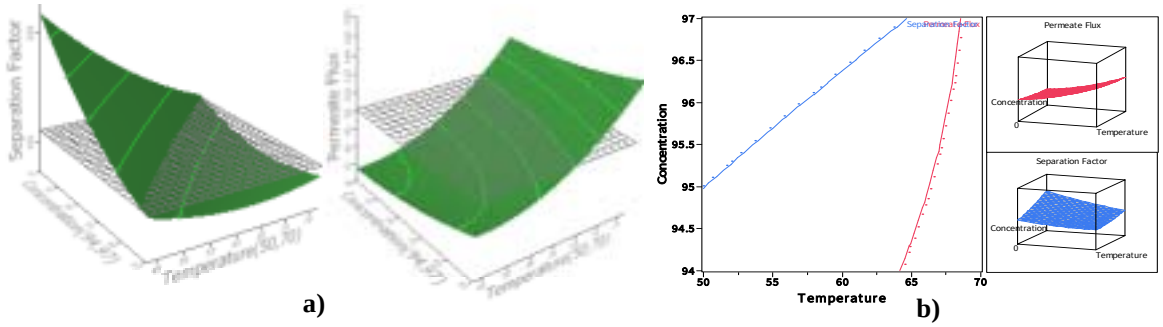
Fig. 2. Illustration of the actual vs the predicted response values of permeate flux (a) and separation factor (b).

3.3. The effect's significance of the factors on the responses

When feed temperature was increased, the permeation flux increased, but the separation factor decreased. The opposite effect of temperature, the total flux decreased and the separation factor increased with increasing feed concentration (wt.% ethanol). The effect of feed flow rate is similar to the influence of temperature but less significant than others on the performance.

3. 4. Simultaneous optimization of two–objective functions

To obtain optimums for all responses, the overall desirability (D) has been applied which is a geometrical average of partial desirability. Fig. 3 shows the contour–surface for the responses by concentration and temperature (holding flow rate constant). When the geometric mean of the desirability measures is at a maximum (D=0.48), the operating conditions are values of 70 ^{o}C, 97 wt.%, and 40 L/h corresponding to the flux and separation factor are at 81.6 g/m^2 h and 110, respectively.

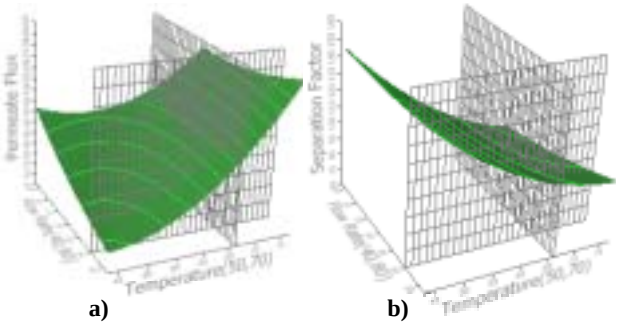


a) **b)**

Fig. 3. Shows (a) the surface and (b) contour profilers for permeate flux and separation factor.

3.5. Conditions for breaking the water–ethanol azeotrope

The optimized trade–off has been implemented with the overall desirability function to find a good factor setting and desirable responses for breaking the azeotropic mixture. The surface profilers show three–dimensional surface plot of the responses are also displayed in Fig. 4. The grids that cut across flow rate and temperature at 66 ^{o}C and 40 L/h to obtain the trade–off values between permeate flux and separation factor of 70.3 g/m^2 h and 99.3, respectively, and the overall desirability can reach at D=0.38.



a) **b)**

Fig. 4. The surface profiles for (a) the permeate flux and (b) the separation factor.

4. Conclusions

The set of regression equations for description of PV performance was determined from experimental data. The influence of operating conditions on PV process has been studied, showing that the effect of feed flow rate is less significant than other factors. The reasonable performance was obtained when optimizing two response functions simultaneously of 81.6 g/m^2 h and separation factor of 110. A set of experimental conditions to break the azeotropic ethanol also was found at 66 ^{o}C, and 40 L/h with flux of 70.3 g/m^2 h and selectivity of 99.3.

5. References

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[4] JMP Introductory Guide, Release 7, Copyright © 2007, SAS Institute Inc., Cary, NC, USA.