Effect of Process Factors on Pervaporation Dehydration of Isopropanol

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The paper aimed at studying the performances of pervaporation separation of isopropanol-water system using a Pervatech ceramic membrane at various values of feed mixture flow rate (F=1000 kg/hr), feed water mass fraction (x_F=0.1-0.2), operation temperature (t=60-90 °C), permeate pressure (p_P=1000-9000 Pa) and water separation degree (s_W=0.9, 0.95). Membrane total flux and separation factor were predicted applying a second order response surface model with 3 factors, i.e., x_F, t and p_P. An algorithm for estimating the membrane surface area was presented. Membrane area increased with s_W and x_F and its lowest values (A=13 m^2 for x_F=0.1 and A=24 m^2 for x_F=0.2) were attained for t=60 °C and p_P=9000 Pa. These findings could be applied for optimizing the process of isopropanol dehydration by pervaporation.

Keywords: isopropanol dehydration, permeate flux, pervaporation, separation factor, statistical model

Isopropanol (IPA) is an important chemical intermediate as well as a common cleaning solvent in semiconductor and electronic industries [1-6]. It is mainly produced by propene hydration but also by fermentation process [5,7]. Accordingly, the selection of a suitable separation technique of IPA, which forms an azeotrope with water (12.3-12.6 wt.% water at atmospheric pressure), is an essential issue in its production and applications. Due to a high separation efficiency, low operational costs, ability to break the azeotrope, process control simplicity, process design and integration flexibility, pervaporation (PV) is a promising solution [4-6,8-13].

Process performances, commonly evaluated in terms of membrane total flux (J_t) and water/IPA separation factor (α), mainly depend on the membrane type, feed water mass fraction (x_F), operation temperature (t) and permeate pressure (p_P). Irrespective of the membrane type, for PV separation of IPA-water system ($x_F \le 0.3$), J_t generally increases with x_F and t, whereas á has an opposite trend [1,2,4,10-12]. Various polymeric [1-3,5,6,9,10,12,13], inorganic [4,9] and organic-inorganic hybrid [1,8,9,11] membranes have been extensively tested for PV dehydration of IPA-water system under various operation conditions. Polymeric membranes are widely used due to their relatively low cost, diversity, easy fabrication and scale up [5,11-13]. However, they can have low thermal stability and exhibit a significant swelling at higher values of feed water concentration, resulting in high values of permeate flux and low membrane selectivity. Several physical and/or chemical modifications, *e.g.*, thermal rearrangement, crosslinking by chemical reagents, polymer blends, fabrication of polymer-inorganic hybrid membranes, are commonly used to reduce the membrane swelling and enhance its water selectivity [1-3,5,6,8,9,11-13]. Inorganic membranes are often expensive but they have good thermal stability and are free of swelling. Accordingly, they can be operated at higher temperatures and lead to more constant performances [4,9].

This paper aimed at establishing the influence of process factors on performances of PV separation of IPA-water system using an inorganic membrane module. A statistical model was applied to predict the permeate flux and separation factor depending on feed water concentration, operation temperature and permeate pressure. Membrane surface area was further estimated based on partial and total mass balance in the membrane module and regression equations obtained by statistical analysis.

Modelling of PV separation of IPA-water system

The physical model associated to PV separation of IPA-water system is shown in figure 1, where *F, R, P* represent mass flow rates of feed mixture, retentate, permeate and x_F, x, y are corresponding water mass fractions. The permeate and retentate in the working spaces of PV equipment were assumed as perfectly mixed.

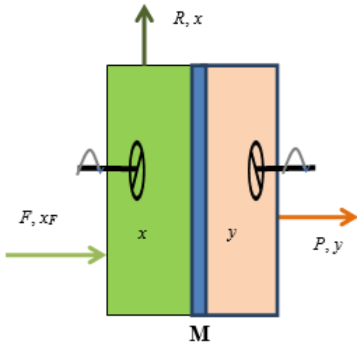

Fig. 1. Physical model of PV separation of IPA-water system in a membrane (M) module.

The process performance in terms of membrane total flux (J_t), selectivity (α) and surface area (A), were estimated according to the following algorithm:

(i)select the appropriate membrane type needed for separating the mixture IPA-water;

(ii)determine the correlations between J_t and α and the manipulated input parameters (factors) of PV process, *i.e.*, feed water concentration (x_F), operation temperature (t) and permeate pressure (p_P), using a second order response surface (SORS) model [14] based on experimental data;

(iii)select a value for each process factor in the fields considered in the factorial experiment as well as a value for fixed process parameters, *i.e.*, feed mixture flow rate (F) and water separation degree (s_W);

(iv)calculate the flow rates and concentrations of permeate and retentate (P, R, y and x) by solving eqs. (1)-(4);

$$F = R + P \quad (1)$$

$$Fx_F = Rx + Py \quad (2)$$

$$\alpha(x_F, t, p_P) = \frac{y/(1-y)}{x/(1-x)} \quad (3)$$

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$$s_W = \frac{Py}{Fx_F} \quad (4)$$

v)if the values of *P*, *R*, *y* and *x* are inappropriate, repeat the calculations for another s_W value;

(vi)calculate *A* using eq. (5).

$$A = \frac{P}{J_t(x_F, t, p_P)} \quad (5)$$

Results and discussions

The dependencies $J_t(x_F, t, p_P)$ and $\alpha(x_F, t, p_P)$ were obtained based on experimental data reported in the related literature [4] for PV dehydration of IPA using a Pervatech ceramic tubular membrane (amorphous silica coated on the inner part of an alumina support tube), 7 mm inner diameter, 10 mm outer diameter, 250 mm length (Pervatech BV, The Netherlands).

Minimal, central (0) and maximal (max) levels of process factors are summarized in table 1, where the dimensionless (coded) values of process factors were determined by eqs. (6)-(8). Table 2 contains the experimentation matrix (rows 1-15) corresponding to a SORS model, where the values of X'_j were calculated using eq. (9), as well as process responses for 3 additional experiments within the centre of experimental plan (rows 16-18). Regression coefficients of SORS statistical models given by eqs. (10) and (11) were determined by eqs. (12)-(15).

The reproducibility variance of PV experiments was obtained based on rows 15-18 in table 2 and was further applied to determine the significance level of regression coefficients by Student test [15-17]. Correlations (16) and (17), expressing the effect of coded factors (X_1, X_2 and X_3) and their interactions on process responses, were

$$X_1 = \frac{x_F - x_{F0}}{x_{F,max} - x_{F0}} = \frac{x_F - 0.1}{0.08} \quad (6)$$

$$X_2 = \frac{t - t_0}{t_{max} - t_0} = \frac{t - 75}{10} \quad (7)$$

$$X_3 = \frac{p_P - p_{P0}}{p_{P,max} - p_{P0}} = \frac{p_P - 4000}{2000} \quad (8)$$

$$X'_j = X_j^2 - \frac{\sum_{i=1}^{15} X_{ji}^2}{15} = X_j^2 - \overline{X_j^2}, j=1\ldots3 \quad (9)$$

$$y_1 = J_t(X_1, X_2, X_3) = \beta_{0,1} + \sum_{j=1}^{3}\beta_{j,1}X_j + \sum_{j=1}^{3}\sum_{\substack{l=1\\l>j}}^{3}\beta_{jl,1}X_jX_l + \sum_{j=1}^{3}\beta_{jj,1}X_j^2 \quad (10)$$

$$y_2 = \alpha(X_1, X_2, X_3) = \beta_{0,2} + \sum_{j=1}^{3}\beta_{j,2}X_j + \sum_{j=1}^{3}\sum_{\substack{l=1\\l>j}}^{3}\beta_{jl,2}X_jX_l + \sum_{j=1}^{3}\beta_{jj,2}X_j^2 \quad (11)$$

$$\beta_{0,k} = \frac{\sum_{i=1}^{15} y_{ki}}{15}, k=1, 2 \quad (12)$$

$$\beta_{j,k} = \frac{\sum_{i=1}^{15} X_{ji} y_{ki}}{\sum_{i=1}^{15} X_{ji}^2}, j=1\ldots3 \text{ and } k=1, 2 \quad (13)$$

$$\beta_{jj,k} = \frac{\sum_{i=1}^{15} X'_{ji} y_{ki}}{\sum_{i=1}^{15} (X'_{ji})^2}, j=1\ldots3 \text{ and } k=1, 2 \quad (14)$$

$$\beta_{jl,k} = \frac{\sum_{i=1}^{15} X_{ji}X_{li} y_{ki}}{\sum_{i=1}^{15} (X_{ji}X_{li})^2}, j, l=1\ldots3, j<l, \text{ and } k=1, 2 \quad (15)$$

Table 1
LEVELS OF PROCESS FACTORS FOR PV DEHYDRATION OF IPA USING A PERVATECH CERAMIC MEMBRANE

Level	Natural factors			Coded factors		
	x_F (kg/kg)	t (°C)	p_P (Pa)	X_1	X_2	X_3
Minimal	0.02	65	2000	-1	-1	-1
Central	0.10	75	4000	0	0	0
Maximal	0.18	85	6000	+1	+1	+1

Table 2
EXPERIMENTATION MATRIX FOR PV DEHYDRATION OF IPA USING A SORS MODEL (ADAPTATION FROM [4])

No.	X_1	X_2	X_3	X'_1	X'_2	X'_3	J_t (kg/(m²·hr))	α
1	-1	+1	+1	0.27	0.27	0.27	1.76	216
2	-1	+1	-1	0.27	0.27	0.27	1.80	990
3	-1	-1	+1	0.27	0.27	0.27	0.95	551
4	+1	+1	+1	0.27	0.27	0.27	7.89	192
5	+1	-1	+1	0.27	0.27	0.27	2.52	220
6	+1	+1	-1	0.27	0.27	0.27	9.55	145
7	-1	-1	-1	0.27	0.27	0.27	0.44	1476
8	+1	-1	-1	0.27	0.27	0.27	2.69	215
9	+1.225	0	0	-0.73	-0.73	-0.73	0.71	740
10	-1.225	0	0	+0.77	-0.73	-0.73	5.36	520
11	0	+1.225	0	+0.77	-0.73	-0.73	6.99	177
12	0	-1.225	0	-0.73	+0.77	-0.73	2.98	133
13	0	0	+1.225	-0.73	+0.77	-0.73	6.14	356
14	0	0	-1.225	-0.73	-0.73	+0.77	3.64	688
15	0	0	0	-0.73	-0.73	+0.77	4.30	405
16	*0*	*0*	*0*	-	-	-	*4.69*	*429*
17	*0*	*0*	*0*	-	-	-	*3.85*	*397*
18	*0*	*0*	*0*	-	-	-	*4.37*	*417*

estimated by neglecting the non-significant coefficients. The effect of natural factors, *i.e.*, x_F=0.02-0.18, t=60-90 °C and p_p=2000-6000 Pa, on membrane total flux (J_t) and separation factor (α) determined by eqs. (16) and (17) is represented in figures 2 and 3.

$$J_t(X_1,X_2,X_3)=3.849+1.427X_1+0.956X_2+1.258X_1X_2-0.288X_1X_3-\\ -0.594\left(X_2^2-0.552\right)+0.98\left(X_3^2-0.552\right) \quad (16)$$

$$\alpha(X_1,X_2,X_3)=468.6-185.5X_1-108.3X_2-118.2X_3+90.4X_1X_2+218X_1X_3+24.2X_2X_3-\\ -88.6\left(X_1^2-0.552\right)+115.8\left(X_2^2-0.552\right)+56.6\left(X_3^2-0.552\right) \quad (17)$$

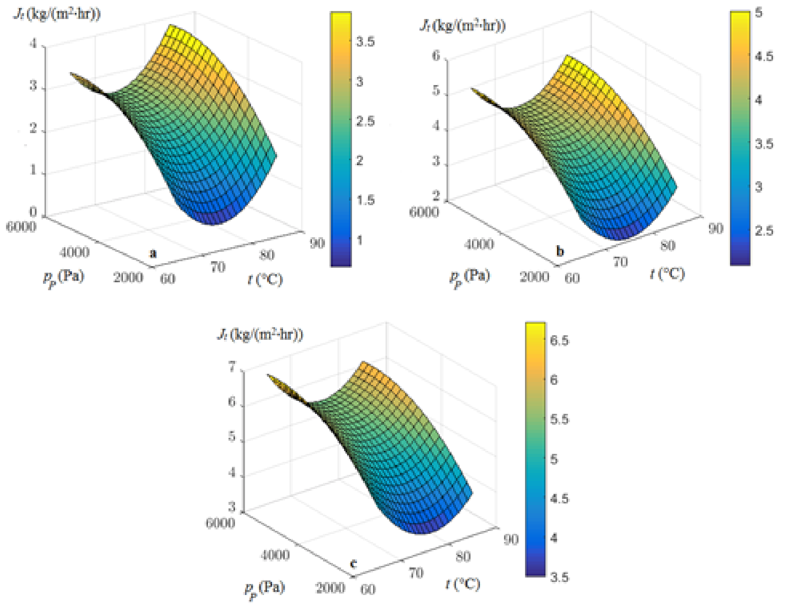

Fig. 2. Variation of membrane total flux (J_t) with permeate pressure (p_p) and operation temperature (t) for different values of feed water mass fraction: (**a**) x_F=0.02; (**b**) x_F=0.10; (**c**) x_F=0.18

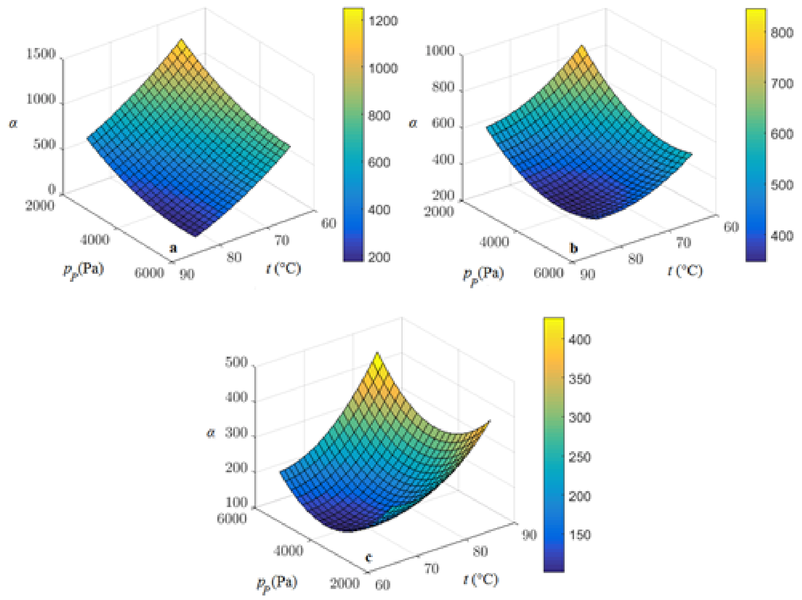

Fig. 3. Variation of separation factor (α) with permeate pressure (p_p) and operation temperature (t) for different values of feed water mass fraction: (**a**) x_F=0.02; (**b**) x_F=0.10; (**c**) x_F=0.18.

By coupling eqs. (1)-(5), (16) and (17), the membrane surface area (A) was calculated for selected values of process parameters, *i.e.*, feed flow rate (F), feed water concentration (x_F), operation temperature (t), permeate pressure (p_p) and water separation degree (s_W).

Tables 3 and 4 contain values of A obtained for PV separation of IPA-water mixture using a Pervatech ceramic membrane under the following conditions: F=1000 kg/hr, x_F=0.1, 0.2, t=60-90 °C, p_p=1000-9000 Pa and s_W=0.90, 0.95. Tabulated data reveal that A increased with s_W and x_F for t=60, 70 °C and its lowest values (A=13 m² for x_F=0.1 and A=24 m² for x_F=0.2) were achieved for t=60 °C and p_P=9000 Pa.

Data summarized in table 5, referring to the effect of s_W and x_F on mass flow rate and composition of permeate and retentate for F=1000 kg/hr, t=60 °C and p_p=9000 Pa, highlight the following issues: (i) P (107.5-221.6 kg/hr) increased with s_W and x_F, whereas R (778.4-892.5 kg/hr) exhibited an opposite trend; (ii) x (0.006-0.025) and y (0.711-0.930) increased with x_F and decreased with an increase in s_W.

Table 3
PERVATECH MEMBRANE SURFACE AREA FOR PV DEHYDRATION OF IPA (x_F=0.1 kg/kg and F=1000 kg/hr)

s_W	0.9				0.95			
p_P (Pa) \ t (°C)	60	70	80	90	60	70	80	90
1000	30	25	28	55	33	28	34	74
3000	65	44	57	292	72	53	74	310
5000	55	42	56	201	62	52	78	580
7000	25	26	49	57	29	36	96	103
9000	13	20	63	40	16	38	88	84

Table 4
PERVATECH MEMBRANE SURFACE AREA FOR PV DEHYDRATION OF IPA (x_F=0.2 kg/kg and F=1000 kg/hr)

s_W	0.9				0.95			
p_P (Pa) \ t (°C)	60	70	80	90	60	70	80	90
1000	60	45	49	78	64	53	59	55
3000	131	79	128	262	138	93	117	104
5000	112	73	83	197	116	86	112	136
7000	49	42	50	66	53	52	81	104
9000	24	24	33	31	26	35	66	55

Table 5
FLOW RATE AND COMPOSITION OF PERMEATE AND RETENTATE FOR PV DEHYDRATION OF IPA USING A PERVATECH MEMBRANE
(F=1000 kg/hr, t=60 °C, p_P=9000 Pa, mean value of A: A_m=16.5 m^2)

s_W	0.90				0.95			
x_F (kg/kg)	P (kg/hr)	R (kg/hr)	x (kg/kg)	y (kg/kg)	P (kg/hr)	R (kg/hr)	x (kg/kg)	y (kg/kg)
0.1	107.5	892.5	0.011	0.837	133.6	866.4	0.006	0.711
0.15	150.4	849.6	0.018	0.897	177.5	822.5	0.009	0.803
0.2	194.5	806.5	0.025	0.930	221.6	778.4	0.013	0.857

Conclusions

Performances of PV dehydration of IPA using a Pervatech ceramic membrane at various values of process parameters, *i.e.*, feed mixture flow rate (F=1000 kg/h), feed water mass fraction (x_F=0.1-0.2), operation temperature (t=60-90 °C), permeate pressure (p_P=1000-9000 Pa) and water separation degree (s_W=0.9, 0.95), have been evaluated. A SORS model with 3 factors (x_F, t and p_P) was applied to predict the membrane total flux (J_t) and separation factor between water and isopropanol (α). Obtained regression equations highlighted an increase in J_t with x_F and t as well as lower values of á for higher levels of all process factors.

The dependencies $J_t(x_F,t,p_P)$ and $\alpha(x_F,t,p_P)$ were further used to calculate the mass flow rates and concentrations of permeate and retentate (P, R, y, x) as well as the membrane surface area (A) for selected levels of process parameters. Membrane surface area increased with s_W and x_F and its lowest values (A=13 m^2 for x_F=0.1 and A=24 m^2 for x_F=0.2) were attained for t=60 °C and p_P=9000 Pa. These findings can facilitate the design, operation and optimization of PV dehydration of IPA-water system.

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References

1. DAS, P., RAY, S.K., KUILA, S.B., SAMANTA, H.S., SINGHA, N.R., Sep. Purif. Technol., **81**, 2011, p. 159.
2. SAJJAN, A.M., PREMAKSHI, H.G., KARIDURAGANAVAR, M.Y., J. Ind. Eng. Chem., **25**, 2015, p. 151.
3. SALEHIAN, P., CHUA, M.L., ASKARI, M., SHI, G.M., CHUNG, T.S., J. Membrane Sci., **493**, 2015, p. 299.
4. WEE, S.L., THIAN, C.T., BATHIA, S., Sep. Purif. Technol., **71**, 2010, p. 192.
5. XU, Y.M., LE, N.L., ZUO, J., CHUNG, T.S., J. Membrane Sci., **499**, 2016, p. 317.
6. ZUO, J., WANG, Y., SUN, S.P., CHUNG, T.S., J. Membrane Sci., **405-406**, 2012, p. 123.
7. JOJIMA, T., INUI, M., YUKAWA, H., Appl. Microbiol. Biotechnol., **77**, 2008, p. 1219.
8. AMIRILARGANI, M., SADATNIA, B., J. Membrane Sci, **469**, 2014, p. 1.
9. CHAPMAN, P.D., OLIVEIRA, T., LIVINGSTON, A.G., LI, K., J. Membrane Sci., **318**, 2008, p. 5.
10. CSEFALVAY, E., SZITKAI, Z., MIZSEY, P., FONYO, Z., Desalination, **229**, 2008, p. 94.
11. HUA, D., ONG, Y.K., WANG, Y., YANG, T., CHUNG, T.S., J. Membrane Sci., **453**, 2014, p. 155.
12. HUA, D., CHUNG, T.S., J. Membrane Sci, **492**, 2015, p. 197.
13. SALEHIAN, P., YONG, W.F., CHUNG, T.S., J. Membrane Sci., **518**, 2016, p. 110.
14. AL JANABI, A.A.A., PARVULESCU, O.C., DOBRE, T., ION, V.A., Rev. Chim. (Bucharest), **67**, no. 1, 2016, p. 150.
15. ARUS, A.V., NISTOR, I.D., PLATON, N., ROSU, A.M., MUNTIANU, G., JINESCU, C., Rev. Chim. (Bucharest), **66**, no. 1, 2015, p. 88.
16. DOBRE, T., STOICA, A., PARVULESCU, O.C., STROESCU, M., IAVORSCHI, G., Rev. Chim. (Bucharest), **59**, no. 5, 2008, p. 191.
17. ION, V.A., PARVULESCU, O.C., DOBRE, T., Appl. Surf. Sci., **335**, 2015, p. 137

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