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DEHYDRATION PERVAPORATION OF ETHYL ACETATE-WATER MIXTURE VIA SAGO/PVA COMPOSITE MEMBRANES USING RESPONSE SURFACE METHODOLOGY

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Abstract. In the present study hydrophilic sago/polyvinyl alcohol (PVA) blend membranes were used for pervaporation of ethyl acetate-water mixture. The effects of feed concentration, temperature and permeate pressure on the separation factor and permeation flux were studied by using response surface methodology (RSM). The central composite design (CCD) was used to design the experiment and analyze pervaporation performance of homogenous sago/PVA membranes and also to obtain process optimum conditions. It was observed that the permeation flux and selectivity were changed by feed temperature and concentration more than the permeate pressure. The validity of the model was confirmed by the experiments.

Keywords: sago starch, pervaporation, ethyl acetate, polyvinyl alcohol, membrane, response surface methodology.

1. Introduction

Potential industrial applications include the recovery of ethanol from the fermentation process and then the esterification of ethanol and acetic acid to produce the ethyl acetate which attracts more attention due to its low toxicity [1, 2]. Ethyl acetate is a moderately polar solvent that has the advantages of being volatile, relatively non-toxic, and non-hygroscopic. It is a weak hydrogen bond acceptor, and is not a donor due to the lack of an acidic proton [3]. Ethyl acetate can dissolve up to 3 % water and has a solubility of 8 % in water at room temperature. It is unstable in the presence of strong aqueous bases and acids, soluble in most organic solvents, such as alcohol, acetone, ether and chloroform [4]. Furthermore, from 2001 to 2013 the demand of ethyl acetate has increased to 300 % due to its increasing usage in the chemical and pharmaceutical industry. In future, the demand for ethyl acetate will constantly increase [5].

Saving energy is the main purpose in the whole world due to its high cost. In chemical and pharmaceutical industries, the separation process using high feed temperature is the main challenge to reduce the cost of the separation [6-10]. Membrane separation by pervaporation (PV) is an energy saving and environment friendly process [11-13]. Number of factors in the pervaporation process such as separation factor, degree of swelling and permeation flux is affected by a membrane structure [14-16]. Moreover, operation conditions such as permeate pressure, flow rate, feed concentration and feed temperature have side effects on the separation of alcohol–water mixture or organic–organic mixture. As a result, it is necessary to find the operating variables at which the separation factor and permeate flux reach their maximum values [17, 18]. Many studies of alcohol-water pervaporation examine the separation by using "one factor at time" approach, such as permeate pressure being varied while keeping the concentration and temperature constant. However, the effects of temperature, concentration and flow rate may be dependent on each other and it is necessary to consider their interactions [19].

Many researches of pervaporation of alcohol-water mixture or organic-organic mixture demand changing in one parameter while other parameters are constant [20, 21]. The good solution for this is to apply response surface methodology (RSM); it is a statistical tool to design the experiment (DOE). DOE requires less runs compared with other design, and it can save the time of designing the data and materials that will be used for experiments. In a pervaporation process DOE is a very good idea to optimize the separation factor and permeation flux in terms of operating condition.

Ethyl acetate recovering from water by pervaporation has been studied by many researches. Separation factor and permeation flux do not depend only on the operation condition but also the membrane material [22]. A lot of membrane materials have been used for separation of ethyl acetate from water such as chitosan, polyvinyl alcohol/ceramic, polyvinyl alcohol/poly(acryl-onitrile) [2, 3, 23]. However, there is no research on ethyl acetate separation from water by pervaporation using sago starch. Sago is a copolymer material formed from sago starch; it is cheap and available and can be used in this area to reach high separation factor and also high permeation flux by using RSM.

This study is a part of development of sago copolymer membrane for pervaporation of alcohol–water mixture. In this work, the objective is to design the experimental data by using a central composite design (CCR) of response surface methodology. CCR is used for design, analysis and optimizing the effect of permeate pressure, feed concentration and feed temperature using two different types of membranes; the first one is a normal membrane and the second one is a chemical cross-linked membrane. The effectiveness of sago/PVA membrane by the pervaporation process in breaking the azeotropic mixture of ethyl acetate–water mixture is also investigated.

2. Experimental

2.1. Materials

The sago starch used in this study was obtained from Malaysia; hydrolyzed polyvinyl alcohol (86,000 MWt) of 99–100 % purity, ethyl acetate (99 % purity) and glutaraldehyde were purchased from New Jersey USA. The sulfuric acid (99 % purity) was obtained from Thailand, while acetone was purchased from Taman Industry Rawang Selangor Malaysia. Water was deionized in the lab before usage.

2.2. Membrane Preparation

The porous polysulfone substrate was prepared by a solution containing 12 wt% of polysulfone, 11 % of methyl cellosolve (ethylene glycol monomethyl ether), and 77 % of N,N-dimethylformamide (DMF). The casting solution was poured onto glass plates and casted by a casting knife; the thickness of the membrane was 60 μm. The casting film was immediately immersed into a gel bath consisting of 50 wt% dimethlyformamide in distilled water at room temperature for 15 min. The resulted porous membrane was then again immersed in distilled water for 24 h and being left to dry at room temperature for another 24 h. The preparation of sago membrane started by dissolving 3 and 10 wt % of sago and PVA, respectively, in hot water for 4 h at 363 K. Then the solutions were filtered to remove non-dissolved impurities. Sago and PVA were mixed by 50 wt % of each one and stirred for 24 h at 343 K. After that the solution was kept in the oven for another 24 h at 343 K before casting onto polysulfone substrate membrane. The membranes were cross-linked chemically: the sago composite membrane were immersed into solution containing 0.5 wt % of sulfuric acid (H_2SO_4), 2.5 wt% of glutaraldehyde, 48 wt % of acetone and deionized water for 30 min. After that the membranes were dried using vacuum oven for 24 h at 308 K.

2.3. Experimental Setup and Analysis

Fig. 1 shows the pervaporation equipment that we used to separate ethyl acetate from water. The ethyl acetate–water mixture was placed into the feed tank and heated by circling the hot water inside the cover jacket. The water was separated by using sago/PVA membrane, which was placed in the membrane cell with the area of 0.0078 m^2. In the downstream of the membrane the vacuum pump was used. The permeation flux and separation factor data were calculated from the following equations, respectively:

$$J = \frac{w}{A \cdot t} \tag{1}$$

$$a = \frac{\frac{Y_i}{Y_j}}{\frac{X_i}{X_j}} \tag{2}$$

where J is the total permeation flux, g/m^2·h; a is a separation factor; w is the weight of the permeate, g; A is the membrane area; t is the time, h; Y_i and Y_j are the weights of the components i and j in the permeate, g; X_i and X_j are the weights of the components i and j in the feed, g.

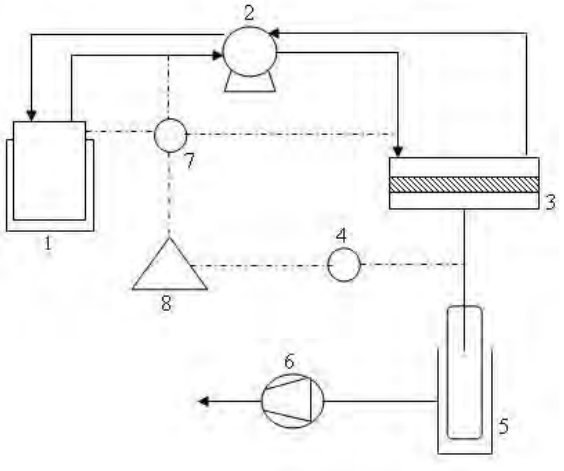


Fig. 1. Schematic diagram of pervaporation process: feed tank (1); circulation pump (2); membrane cell (3); pressure probe (4) cold trap with Dewar flask (5); vacuum pump (6); temperature controleer (7) and control panel (8)

2.4. Design of the Experiment

The response surface methodology designing experimental data is a structured and organized way of experimentation in which all factors are varied simultaneously over a set of experimental runs [24]. In this work, the response surface methodology was used to study the effect of some important parameters of water separation from ethyl acetate–water system and the water in the range of 1–4 wt % by using the pervaporation process. RSM is useful for the modeling and analysis of programs in which a response of interest is influenced by several variables and the objective is to optimize this response [25]. The major goal of RSM is to find the approximating function for predicting future responses and to find out the factor values that could optimize the response function. The central composite design (CCD) is used to design the data for ethyl acetate-water mixture pervaporation. The first step of RSM is to find the relationship between response and independent variables. Generally, the quadratic model is applied as present in the following equation [25]:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum\sum_{j>1} b_{ij} x_i x_j + e \quad (3)$$

where Y is the measured response; b_o is the intercept term; b_i, b_{ii} and b_{ij} are the measures of the effect of variables $x_i, x_i x_j$ and x_i^2, respectively. The variable $x_i x_j$ represents the first order interaction between x_i and x_j ($i < j$) and e is the residual error.

The purpose of variance analysis (ANOVA) is to establish its significance. A second-order model can be constructed efficiently with CCD [26]. CCD is the first-order (2N) designs augmented by additional centre and axial points to allow estimation of the tuning parameters of a second-order model. The axial points are located at (α, 0, 0), (0, α, 0) and (0, 0, α) where is the distance of the axial point from the center and makes the design rotatable. In this study, the value of for this CCD is fixed at 1. In the pervaporation process, the important factors affecting the separation by sago/PVA membranes are feed concentration, permeate pressure, feed temperature, flow rate and the type of membrane. In this work we study the effect of permeate pressure, feed temperature and feed concentration. 14 full factorial experimental designs with three variables where each with two levels namely low (−1) and high (+1) were employed. Table 1 shows the range of the conducted process. In separation of ethyl acetate–water mixture the responses to be monitored in this study are separation factor and permeation flux. The RSM analysis was used to analyze the data after the experimental work. The pervaporation unit used in this work is shown in Fig. 1.

Table 1

Experimental independent variables

Variables	Factor code	Unit	Level and range (coded)		
			-1	0	1
Temperature	A	K	303	323	343
Concentration	B	g/g	1	2.5	4
Permeate pressure	C	kPa	4.7	6.25	8.7

Table 2

Experiment runs and response of pervaporation of ethyl acetate–water mixture

	Run factor			Response 1 Permeation flux, g/m^2·h	Response 2 Selectivity
	A	B	C		
1	323.00000	5.022689	6.7	700	5455
2	323.00000	2.500000	6.7	201.33	8099
3	343.00000	1.000000	4.7	411.01	7821.11
4	323.00000	2.500000	3.3364	256.45	6098
5	303.00000	1.000000	8.7000	131.89	17923
6	356.63586	2.500000	6.7000	490.11	5023
7	303.00000	1.000000	4.7000	167.76	19077
8	343.00000	4.000000	8.7000	809	4098
9	343.00000	4.000000	4.7000	970	3091
10	343.00000	1.000000	8.7000	330.81	11034
11	323.00000	3.000000	6.7000	371.18	6098
12	303.00000	4.000000	8.7000	380.58	7349
13	323.00000	2.500000	6.7000	199.11	8163
14	303.00000	4.000000	4.7000	397.11	7445

Table 3

Analysis of variance (ANOVA) for 2^3 full CCD for permeation flux of sago/PVA membrane

Source	Sum of squares	DF	Mean square	F-value	Prob>F
Model	0.7514	9	0.08439	4.92	0.07
A	0.314827	1	314827.1	19.59301	0.011454
A^2	0.009786	1	9786.5	0.60905	0.478746
B	0.439191	1	439191.2	27.33271	0.006392
B^2	0.070359	1	70358.9	4.37873	0.104530
C	0.017069	1	17068.9	1.06227	0.360938
C^2	0.009126	1	9126.2	0.56796	0.493001
AB	0.03908	1	39079.7	2.43209	0.193885
AC	0.004456	1	4455.7	0.27730	0.626329
BC	0.000472	1	472.2	0.02939	0.872215
Residual	0.064273	4	16068.3		
Pure error	0.000002	1	0.000002		
Lack of fit	0.6427	3	0.021424	8693.9	0.007884
Total SS	0.819333	13			

3. Results and Discussion

The effect of feed concentration, feed temperature and permeate pressure on the separation factor and flux for separation of ethyl acetate-water mixture *via* pervaporation dehydration process were investigated by using CCRD as shown in Table 2. The separation factor and permeation flux in this work vary from 3091 to 19077 and from 131 to 970 g/m^2·h, respectively.

3.1. Effect of Operating Variables on Permeation Flux

Table 3 presents ANOVA for 2^3 full CCD of the permeation flux. Eq. (4) represents quadratic model for permeation flux in terms of coded factors. A positive sign in front of the terms indicates a synergistic effect, while a negative sign indicates the antagonistic effect.

$$\text{Permeation flux (g/m}^2\text{·h)} = 421.83 + 303.38A + + 67.61A^2 + 150.787B + 26.5065B^2 - 71.52C + +72.74\,C^2 + 46.86AB - 42.44AC - 5.15CB \quad (4)$$

As it is noted in Table 3, the "Model F–value" of 19.59 implies the model significance under 95 % level of confidence. The model is significant, when the value of "Prob > F" is less than 0.05. The "lack of fit–value" of 0.00788 implies the lack of fit is insignificant relative to pure error. Consequently, the suggested model for permeation flux in Eq.(4) is valid for this study.

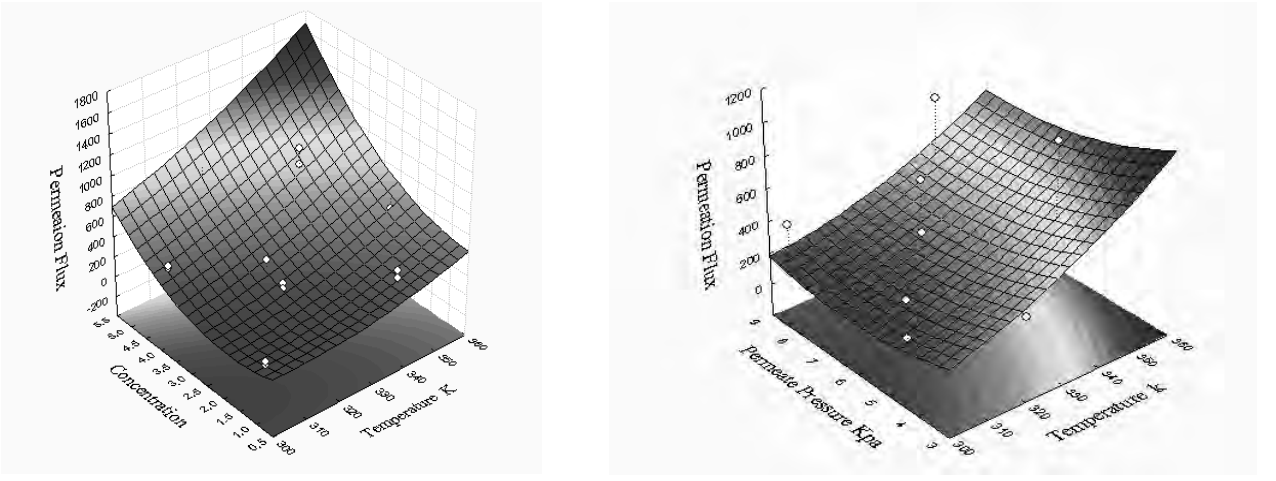
To confirm that the model is reliable, the response should be predicted with reasonable accuracy by the model and compared with data of experiments. From the comparison it was established that the value of correlation coefficient R2 was 0.9171, and this confirms the accuracy of the model. Fig. 2 indicates three-dimensional display of the response surface plot for permeation flux from interaction between feed temperature and feed concentration (Fig. 2a) and feed temperature and permeates pressure (Fig. 2b). As we can see from Fig. 2a, the high permeation flux is obtained at high feed temperature and low feed concentration, while Fig. 2b shows that the permeation flux increases with increasing the feed temperature and low permeates pressure.

3.2. Effect of Operating Variables on Selectivity

Table 4 represents ANOVA for 14 full CCD of the selectivity. The quadratic regression equation describing the effect of the process variables on the selectivity in terms of coded factors is presented as Eq. (5):

$$\text{Selectivity} = 5176.16 - 2945.9A + 1476.56A^2 - 1068.64B + + 395.24B^2 + 1115.23C - 884.34C^2 + 883.31AB + + 1229.36AC - 96.20BC \quad (5)$$

As we can see from Table 4, it is noted that the "Model F-value" of 67.20 implies the model significance under 95% level of confidence. The terms A, B, C, A^2, B^2, AB and AC in this case are significant model terms. The "lack of fit" of 311.32 implies the lack of fit is not significant relative to the pure error. Consequently, the suggested model for selectivity (Eq.(5)) is valid for this study. The experimental value of selectivity is compared with its predicted model value, and showed that the value of correlation coefficient R^2 is 0.9934, which confirmed the accuracy of the model. Fig. 3 represents three-dimensional display of the response surface plot for selectivity from the interaction between feed temperature and feed concentration (Fig. 3a), feed temperature, and permeates pressure (Fig. 3b). It is clear from Fig. 3 that the highest selectivity is observed at low feed temperature and then decreases with the increase in temperature. However, the increase in the feed concentration increases the selectivity proportionally. Fig. 3b illustrates the high selectivity obtained at low feed temperature and high permeates pressure.



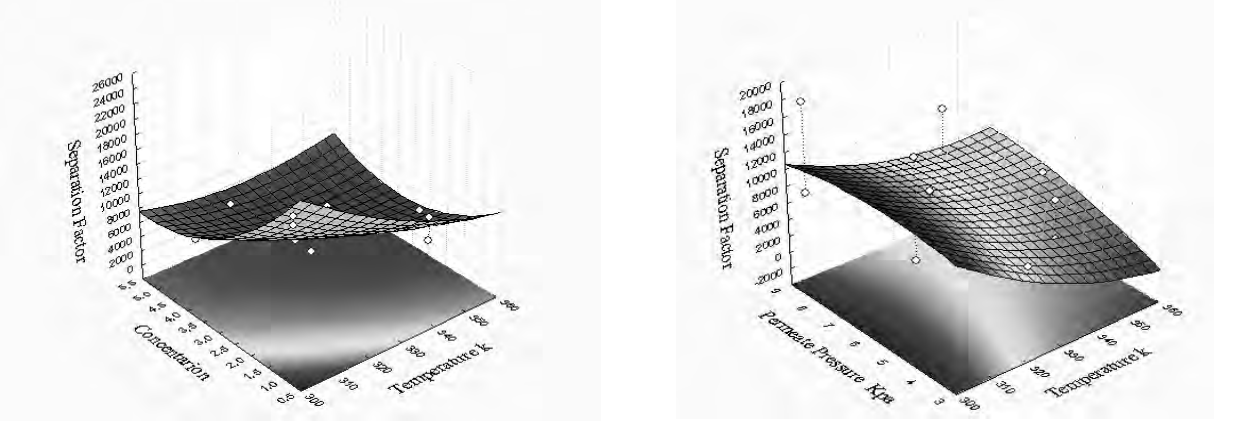
a) b)

Fig. 2. Effect of feed temperature and concentration on the permeation flux at permeate pressure of 6.4 kPa (a); feed temperature and permeate pressure on the permeation flux at 2.7 wt % of water in the feed concentration (b)

Table 4

Analysis of variance (ANOVA) for 2^3 full CCD for selectivity of sago/PVA membrane

Source	Sum of squares	DF	Mean square	F-value	Prob > F
Model	289527050	9	32169672	67.20	0.001
A	29298439	1	29298439	61.20	0.001
B	22084917	1	22084917	8.63	0.04
C	4198879	1	4198879	46.14	0.002
A2	4130256	1	4130256	32.24	0.004
B2	15431281	1	15431281	8.77	0.04
C2	1481533	1	1481533	3.09	0.15
AB	13886160	1	13886160	29.01	0.005
AC	3739962	1	3739962	7.81	0.04
BC	164706	1	164706	0.344	0.59
Residual	1914800	4	478700		
Lack of fit	1912752	3	637584	311.32	0.041633
Pure error	2048	1	2048		
Total SS	291441850	13			



a) b)

Fig. 3. Effect of feed temperature and concentration on the separation factor at permeate pressure of 6.4 kPa (a); feed temperature and permeate pressure on the selectivity at 2.7 wt % of water in the feed concentration (b)

3.3. Optimal Condition and Verification of the Model

Obtaining the optimal condition is the last step of RSM for removal water from ethyl acetate by sago/PVA membrane *via* pervaporation. An optimum pervaporation dehydration process is the process that exhibits the maximum achievable flux of water through the membrane. The optimal conditions were found: feed temperature 343 K, initial feed concentration of water 4.23wt % and permeate pressure 4.1 kPa. Pervaporation of ethyl acetate–water mixture proceeds under the conditions close to the optimal: feed temperature 343 K, feed concentration of water 4 wt % and permeate pressure 4.7 kPa. The permeation flux was found to be 957 g/m^2·h in the range predicted by Eq. (4) – 942.17 g/m^2·h.

4. Conclusions

This study presents research focused on the recovery of ethyl acetate from water mixture using sago/PVA blend membrane *via* pervaporation. The effect of pervaporation operating values on the permeation flux and selectivity was successfully investigated using a statistical design of the experiment. The sago/PVA blend membrane was able to separate ethyl acetate from water under different operating conditions. Moreover, RSM was demonstrated to be effective and reliable in a proposing model fitting the experimental data, predicting and finding the optimal conditions for the pervaporation process. Feed temperature and concentration were found to have large effects on the permeation flux through sago/PVA membrane. The optimal conditions established by RSM were: feed temperature 343 K, feed concentration of water 4.23 wt % and permeate pressure 4.1 kPa. The results of this study prove the sago membrane to be used for separation of alcohol-water mixture by pervaporation. In addition in this research the flow rate and thickness of the membrane were not included in the study and to establish the maximum permeation flux and selectivity these factors should be included. RSM can also make it possible to predict these responses. Finally, this study can be applied if the flow rate and thickness are constant.

Acknowledgments

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ДЕГІДРАТАЦІЙНЕ ДИФУЗІЙНЕ ВИПАРОВУВАННЯ ЕТИЛАЦЕТАТ-ВОДНОЇ СУМІШІ ЗА УЧАСТЮ САГО/ПВС КОМПОЗИТНИХ МЕМБРАН З ВИКОРИСТАННЯМ МЕТОДУ БОКСА-ВІЛСОНА

Анотація. *Показано можливість використання гідрофільних саго/ПВС (полівініловий спирт) мембран для дифузійного випаровування етилацетат-водної суміші. Досліджено вплив концентрації та температури вихідного потоку і тиску розчиненої речовини на коефіцієнт розділення і проникаючу здатність потоку з використанням методу крутого сходження (метод Бокса-Вілсона). З використанням методу центрального композиційного дизайну розроблено дизайн експерименту, проаналізовано ефективність дифузійного випаровування гомогенних саго/ПВС мембран, а також знайдено оптимальні умови процесу. Встановлено, що проникаюча здатність потоку і селективність залежать від температури подачі та концентрації більше, ніж тиску проникнення. Експериментальним шляхом підтверджено адекватність моделі.*

Ключові слова: *саго крохмалю, дифузійне випаровування, етилацетат, полівініловий спирт, мембрана, метод Бокса-Вілсона.*