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Pervaporative Enrichment of 2,3-Butanediol from its Mixture with 1-butanol using a Polydimethylsiloxane and ZSM-5 Mixed Matrix Membrane: Effects of Ethanol as a By-product[§]

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A ZSM-5 filled polydimethylsiloxane membrane with 44.4 wt. % zeolite loading was used in the pervaporative removal of 1-butanol from its mixtures with 1-butanol. A small quantity of ethanol was added to the feed as a by-product to test the response of the membrane. It was found that the permeation behavior of other feed components was changed and membrane selectivity decreased. This change was attributed to the frequently-observed inter-component coupled transport in multi-component feed systems. The impact of ethanol on recovery of 2,3-butanediol was evaluated using a simulated continuous operation, which enriched 2,3-butanediol to 99.5 wt. % from a feed containing 5 wt. % 2,3-butanediol and less than 1.0 wt. % ethanol. It was observed that membrane selectivity improves as ethanol concentration decreases in the stream due to its preferential removal. The final recovery of 2,3-butanediol was not significantly reduced as the concentration of ethanol was below 1.0 wt. %.

Keywords: Pervaporation, coupled transport, mixed matrix membrane, 2, 3-butandiol, ethanol

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1 INTRODUCTION

2 The importance of 2,3-butanediol as a versatile chemical feedstock has long been identified. It
3 can be easily converted into methyl ethyl ketone, an industrial solvent; into 1, 3-butadiene, a
4 monomer for rubber synthesis; and into various esters as effective plasticizers for thermoplastic
5 polymer processing (Lee, 1999; Syu, 2001; Jansen et al., 2010; Garg et al., 1995). 2,3-butanediol
6 can be produced by chemical synthesis or by biomass conversion through fermentation. Since
7 bioconversion is a green process, and more importantly, in this way many abundantly available
8 cheap resources (e.g., crop residue) and process wastes (e.g., wood waste) can be transformed
9 into valuable product without causing environmental concerns. It is generally believed that the
10 biomass conversion approach represents the future direction in manufacturing this much-needed
11 chemical feedstock.

12 Recovery of the dilute 2,3-butanediol from the fermentation broth is a challenging task (Garg et
13 al., 1995; Magee et al., 1987). The key factors responsible for this challenge are its high boiling
14 point (184 °C), and high affinity with water, which is the major components of the broth. It has
15 been found that no single method is energy-efficient for the recovery of 2,3-butanediol (Maddox,
16 1996). An integrated process (Shao and Kumar., 2009) based on solvent extraction and
17 membrane pervaporation has been proposed. In this process, 1-butanol was employed as the
18 extracting solvent, which demonstrated excellent capability in terms of its high partition
19 coefficient and good selectivity. The dehydrated extract stream containing mainly 2,3-butanediol
20 and 1-butanediol was further treated by pervaporation using polydimethylsiloxane (PDMS)
21 membrane, through which the solvent 1-butanol was removed for recycling, and 2,3-butanediol
22 was enriched in the retentate. Subsequent research effort (Shao and Kumar, 2009) was given to

1 the improvement on the selectivity of PDMS membrane using ZSM-5 zeolite. It was found that
2 with the incorporation of zeolite, the filled membrane showed reduced permeability and
3 increased selectivity. The advantage of the filled membrane over the pure PDMS membrane was
4 demonstrated by a simulation, revealing that recovery of 2,3-butanediol could be enhanced by
5 25.8 %.

6 One noteworthy fact on the study is that the feeds used in experiments are not the real broth but
7 simulated mixtures, which retain merely the key components of the fermentation broth, i.e. water,
8 and 2,3-butanediol. As a matter of fact, a small quantity of byproduct (e.g., ethanol) is usually
9 present in the fermentation stream (Larson, 1973; Mas, et al., 1988; Ui et al., 1986; 1998). It is
10 well known that in membrane separations the presence of small quantities of by-products in feed
11 may drastically change the membrane performance (Vu et al., 2003; Chern et al., 1983; Djoekita,
12 2000; Ratcliffe et al., 1999; Mazur and Chan, 1982; Funk et al., 1986; Shao and Huang, 2007). In
13 order to address this uncertainty, experiments were conducted with ethanol added as a by-
14 product in the feed. The coupled transport (Baranowski, 1991; Kuhn, et al., 2009; Yu et al.,
15 2007), which is frequently encountered in pervaporation, particularly in multi-component feed
16 separation, was observed in this work, and the resulting unusual transport properties of the
17 membrane were thus interpreted in this theory. The variation of ethanol concentration in the
18 retentate stream was studied by simulation, and its impacts on membrane selectivity and final
19 recovery of 2,3-butanediol are also reported in this work.

EXPERIMENTAL

Materials

Solvents 2,3-butanediol (98.0 wt.%, the balance is mainly isomers) and 1-butanol (99.7 wt.%) were purchased from Sigma-Aldrich, Canada, anhydrous ethanol was purchased from Brampton, Canada, and pentane (99.7 wt.%) from Fisher Scientific. Silicone elastomeric base (dimethyl siloxane) and the corresponding curing agent (dimethyl, methylhydrogen siloxane) were obtained from Dow Corning, USA. ZSM-5 zeolite powder (3 μ m, Si/Al ratio 137) was obtained from Zeolyst, USA. Pure water (18.1 M Ω .cm) used was generated with a Milli-Q® water purification system. The pre-purified helium (99.999 %) carrier gas was supplied by BOC Gases, Canada.

Preparation of ZSM-5 Filled PDMS Membranes

The silicone elastomeric base (ten parts) and curing agent (one part) into pentane for preparing 10 wt.% silicone rubber pre-polymer solution, the pre-dried ZSM-5 powder was then added into the solution, with the zeolite loading controlled at 44.4 wt. % as this loading gives the best membrane selectivity (Shao et al., 2009). The ZSM-5 particles were dispersed in the pre-polymer solution using a sonicator (150D, VWR International) for 30 min. A portion of 27 ml of the suspension was used for making each membrane sample in a horizontally set Teflon dish (85 mm in diameter). After evaporation of pentane, the membrane was moved to an oven to perform cross-linking at 90°C for 12 h. The thickness of the membrane was measured with a micrometer at three different locations, and the mean thickness of the membrane was 367 ± 5 microns.

Membrane Characterization by Scanning Electron Microscopy

A selected membrane sample was immersed in liquid nitrogen for 30 seconds and cut into strips. The dried strips were then sputter coated with gold, and the cross-section of the membrane was imaged using a JEOL 840A scanning electron microscope (SEM). The SEM image as shown in Fig. 1 indicates that the uniform dispersion of the ZSM-5 filler, and the good adhesion between the ZSM-5 filler and the surrounding PDMS were achieved.

Pervaporation Performance of the Filled Membrane

The feed used for evaluating membrane performance is the ternary mixtures of 1-butanol/2,3-butanediol/ethanol, which also contains small quantities of water for simulating the real compositions of the dehydrated extract as done in our earlier work (Shao et al., 2009; 2009). The downstream pressure in pervaporation was kept at 2 mmHg (267 Pa) using a vacuum pump. As the membrane permeation reached a steady state, permeate was collected in a glass tube submerged in liquid nitrogen. The mass of permeate was measured with a electronic balance, and the composition of permeate was analyzed using a SRI 8610G gas chromatograph equipped with a HAYESEP D column and a TCD detector. The temperatures of the oven, injector, and detector were all kept at 270°C.

Membrane permeability (P) and selectivity (α) are defined as follows:

$$P_i = \frac{W \cdot Y_i}{A \cdot t} \cdot \frac{\ell}{\Delta C_i} \quad (1)$$

$$\Delta C_i = \frac{X_i}{\sum (X_k / \rho_k)} \quad (2)$$

$$\alpha_j^i = \frac{P_i}{P_j} \quad (3)$$

where W is the mass of the permeate collected in time interval t , A is the effective membrane area for the separation, ℓ is the membrane thickness, C is the concentration of the component in the feed, which acts as the driving force for mass transport as the concentration of permeate in the downstream is ignored, ρ is the density of a feed component, and X and Y represent the mass fraction of a component in the feed and permeate phase, respectively.

RESULTS AND DISCUSSION

Permeation Behaviors of Feed Components

The partial fluxes of the ZSM-5 filled PDMS membrane for components 1-butanol, 2,3-butanediol, ethanol, and water at 50°C are illustrated in Fig. 2. 1-butanol and 2,3-butanediol are the two key components of the feed, in which ethanol was kept essentially in the range of 0.80-0.92 wt.%, and the contents of water 0.38, 0.95, 0.35 and 0.63 wt.%. It was clear that the flux of 1-butanol increased exponentially as its content in the feed increased, suggesting that swelling occurred to the filled PDMS membrane. The swelling of the membrane resulted largely from 1-butanol, which is the major feed component and for which the membrane shows higher affinity. Similar behavior is with ethanol transport through the membrane. For the less permeable 2,3-butanediol, more complicated permeation was observed. As the concentration of 1-butanol increased from 43 to about 65 wt. %, the mass transport driving force for 2, 3-butanediol was actually reduced, the flux of 2,3-butanediol was, however, increased. According to the mass transport equation shown in Eqn (4):

$$Flux = \frac{\bar{D}}{\ell} \Delta C \quad (4)$$

where C and D are the concentration and diffusion coefficient of 2,3-butanediol, respectively. Clearly the increased flux of 2,3-butanediol was mainly due to its enhanced mean diffusivity in the highly swollen membrane because of the higher content of 1-butanol in the feed. This type of transport characteristic of 2,3-butanediol was not observed in our earlier work, where the same membrane was tested with the same feeds but without ethanol (Shao et al., 2009). Obviously, the presence of ethanol at a low concentration contributed to this complex membrane transport. In addition to 1-butanol, PDMS also shows a high affinity for ethanol, and PDMS is thus a typical membrane material selected for removing ethanol from the fermentation broth (Vane et al., 2008; Vane, 2005; Bowen et al., 2007).

Permeability and Selectivity

The permeability of 1-butanol, 2,3-butanediol, ethanol, and water is shown in Fig.3. As discussed previously, the membrane was swollen by the feed, largely by the solvent 1-butanol, the permeability of the component thus became dependent upon the feed concentration of 1-butanol. The exponential concentration-dependence of the permeability is summarized in Table 1. In our previous work (Shao et al., 2009), the filled membrane displayed a higher permeability for 1-butanol than for water. However, a reversed permeability order was observed in this work as shown in Fig. 3. The favored permeation of water in the filled hydrophobic membrane certainly benefits from its small molecular size. Yet in this case, the coupled transport between water and ethanol should be responsible for this reversed order. In multiple components membrane separation, it is generally believed that the strength of component/component and

component/membrane interactions can be measured by the difference in their solubility parameter (Shao et al., 2007). The three components (polar δ^p , dispersion δ^d , and hydrogen bonding interaction δ^h) of the solubility parameter as represented in Fig. 4 were normalized in the following manner:

$$f_i = \frac{(\delta^i)^2}{(\delta^p)^2 + (\delta^d)^2 + (\delta^h)^2} \quad (5)$$

where superscript i stands for p , d , and h , respectively. Obviously, 2,3-butanediol and ethanol are the closest components to water. Since the concentration of 2,3-butanediol is very low in the membrane phase (One of the indicators is the lower membrane flux for 2,3-butanediol), it can be reasonably considered that coupled transport occurred primarily between water and ethanol, and the coupled transport facilitated the mass transfer of water in filled membrane.

Since ZSM-5 is more hydrophobic than PDMS (Shao et al., 2009), the local position of the solubility parameter of the filled membrane should be even farther from the hydrogen bonding pole than that of PDMS as shown in Fig. 4. As a result, the filled PDMS membrane should have shown higher permeability for 1-butanol than ethanol. This prediction is only found valid as the PDMS membrane was used for removing the solute ethanol and 1-butanol from their aqueous solutions (Shao et al., 2009). It is not the case in this multiple components separation, where ethanol is the one of the minor components, and 1-butanol is, however, one of the major components, which act as the solvent. This reversed order in permeability implies that coupled transport had truly occurred to the minor component ethanol. And according to Fig. 4, the dominant coupling component, responsible for this enhanced ethanol transport in the membrane should be 1-butanol.

1 The selectivity of the membrane for the more permeable component over 2,3-butanediol was
2 depicted in Fig. 5. As mentioned previously, due to the favorable coupled transport, both water
3 and ethanol experienced increased permeation, the selectivity of the hydrophobic membrane for
4 water and ethanol exceeds that of 1-butanol. This permeation characteristic ensures that ethanol
5 can be preferentially removed by the membrane, it can thus be anticipated that no serious
6 challenge can be created as the membrane is used for processing the feed stream, in which
7 ethanol exists as a by-product.

8 Fig. 6 shows the demonstrated selectivity of the filled membrane while processing feeds with
9 and without ethanol. Obviously the filled membrane lost some selectivity when dealing with feed
10 containing 0.80-0.92 wt.% ethanol. Fortunately, this loss is not significant. As the separation
11 continues, the ethanol content in the feed would keep decreasing, and the selectivity loss would
12 become even less significant. By extrapolating, it can also be seen in Fig. 6 that the two
13 selectivity lines intersect at a point very close to the zero concentration of 1-butanol (the pure
14 2,3-butanediol feed). Obviously, the membrane demonstrates the highest selectivity as the
15 contents of ethanol and 1-butanol approach zero. On the other hand, it also suggests that the
16 linear regression treated for the selectivity data as shown in Fig. 6 is reasonable.

17 Effects of Temperature

18 The temperature-dependence of the partial flux of 1-butanol, 2,3-butanediol, ethanol and water is
19 plotted in Fig. 7(a). The dependence can be characterized by the Arrhenius relationship except in
20 the case of 2,3-butanediol. Interestingly, for 2,3-butanediol, the Arrhenius relationship still holds
21 true if the temperature range is divided into two sections (30-50°C, and 50-80°C). The specific
22 reasons for this are not quite clear. It is likely that at lower temperatures, the dissolution of 2, 3-

butanol in the membrane is dominated by its interactions with ethanol (according to Fig. 4, 2,3-butanediol shows the highest affinity for ethanol), and the solubility and thus permeation flux of 2,3-butanediol in the membrane could be well enhanced. With the rise of feed temperature, thermodynamically, the concentration of ethanol in the membrane phase would reduce, also the association between ethanol and 2,3-butanediol can no longer be as strong. It could be visualized that “disintegration” would gradually occur to the coupling between 2,3-butanediol and ethanol, and meanwhile the relatively weak interaction between 2,3-butanediol and 1-butanol would turn back to be the dominant interaction, and eventually govern the dissolution of 2,3-butanediol in the membrane phase. In support for this analysis, it is clear from data listed in Table 2, that the permeation activation energy of 2,3-butanediol in the range of 30-50 °C is much smaller than that in the range of 50-80°C. The permeation activation energy of the component was estimated by Eqn. (6) (Shao et al., 2005; Huang et al., 2001; 2002):

$$(Ea_i)^{permeation} = \frac{\partial \ln F_i}{\partial (1/T)} \quad (6)$$

where F is the partial flux, T is the temperature (K). The difference may primarily be due to the change in the dissolution enthalpy of 2,3-butanediol in the altered membrane environment as the feed temperature rises. The temperature-dependence of the selectivity was plotted in Fig. 7(b). Due to this unique transport feature of 2,3-butanediol over the wide range of feed temperatures, the selectivity of the membrane for all the more permeable component (water, ethanol and 1-butanol) at the lower temperature range increases with increasing temperature, and reaches a peak value at a temperature around 50°C. Also in higher temperature range, that type of coupling is significantly suppressed and the typical temperature-dependence of the selectivity is thus restored.

Numerical Simulation of 2,3-Butanediol Enrichment in Continuous Operation

As demonstrated previously, the presence of ethanol in the feed diminishes membrane selectivity. Since ethanol concentration keeps on decreasing during the course of pervaporation, the membrane selectivity would increase as the separation proceeds. In order to evaluate the impact of this reduced yet variable membrane selectivity on the enrichment of 2,3-butanediol, a simulated continuous pervaporation operation was performed based on the laboratory permeability data, for a targeted product purity of 99.5 wt.%. The details on the three feeds considered were summarized in Table 3. The contents of ethanol considered in two of the feeds are 0.5 and 1.0 wt.%, respectively. For calculating the permeation rates of a potential composite membrane for the separation, the thickness of the filled PDMS thin film is assigned a typical value of 5 microns (Shao et al., 2009).

Assuming PV is an isothermal process, and a plug-flow on the retentate side of the membrane. By ignoring the possible diffusion layer resistance in the retentate flow, and neglecting the permeate concentration/vapor pressure on the downstream side of the membrane, the permeation of the feed component i across the membrane can thus be governed by:

$$\frac{dF_i}{dA} = -\frac{P_i(X)}{\ell} \cdot \frac{F_i}{\sum_{i=1}^3 (F_i / \rho_i)} \quad (7)$$

where F is the mass flow rate of the feed component i . Rewriting Eqn. (7) into a difference equation gives:

$$\frac{F_i^{(n+1)} - F_i^{(n)}}{A^{(n)}} = - \frac{P_i(X^{(n)})}{\ell} \cdot \frac{F_i^{(n)}}{\sum_{i=1}^3 (F_i^{(n)} / \rho_i)} \quad (8)$$

The mass fraction of 1-butanol in the feed coming into the divided membrane section ($n+1$) from the previous section (n) is obtained by:

$$X^{(n)} = \frac{F_{1-bu \tan ol}^{(n)}}{\sum_{i=1}^3 F_i^{(n)}} \quad (9)$$

All the boundary conditions ($F_i^{(0)}, X^{(0)}$) of Eqn. (8) are known, $F_i^{(n)}$ and $X^{(n)}$ ($n=1, 2, 3 \dots, N$) can thus be obtained based on Eqns. (8) and (9) by performing iteration. The mass fraction of component i in permeate of sector ($n+1$) can be calculated by:

$$Y_i^{(n+1)} = \frac{P_i(X^{(n)}) \cdot F_i^{(n)}}{\sum_{i=1}^3 P_i(X^{(n)}) \cdot F_i^{(n)}} \quad (10)$$

The percentage of membrane area ($A(M)$) and final recovery (R) of product is defined as follows:

$$A(M) = \frac{\sum_{n=1}^M A^{(n)}}{\sum_{n=1}^N A^{(n)}} \cdot 100\% \quad (11)$$

$$R = \frac{F_{2,3-bu \tan ediol}^{(N)}}{F_{2,3-bu \tan ediol}^{(0)}} \quad (12)$$

where $0 \leq M \leq N$. The final recovery of product equals the ratio of the flux rate of 2,3-butanediol at the membrane inlet and outlet as shown in Eqn. (12).

Ethanol Removal, Product Enrichment and Recovery

The change of mass flow rate of ethanol, 1-butanol and 2,3-butanediol along with the percentage of the membrane area is illustrated in Fig. 8(a). It is known that ethanol is the most permeable components in the feed, as expected, its flow rate drops most rapidly, and the rapidness is indicated by the slope (K) of the curve:

$$K_i = \left(\frac{\partial \ln F_i}{\partial A_p} \right) \approx \frac{\Delta F_i}{F_i} \cdot \frac{1}{\Delta A_p} \quad (13)$$

According to Eqn. (13), this rapidness refers to the relative flow rate drop with respect to the membrane area. It is shown in Fig. 8(a) that about 80% of ethanol can be removed over the first 40% of membrane area, and at this stage 50% of 1-butanol is removed as well, indicating that ethanol is preferentially removed from the feed. The selectivity of the filled membrane during the separation process is shown in Fig. 8(b), it can be seen that due to the preferential permeation of ethanol, the membrane selectivity increases very rapidly at the beginning of the separation, and quickly approaches the “normal” selectivity as the separation goes further. It seems that presence of ethanol in the feed will not cause significant concerns for the processing of 2,3-butanediol.

The mass fraction variation of the three feed components with respect to the percentage of membrane area is depicted in Fig. 8(c), where the preferential removal of ethanol by the membrane is more clearly demonstrated. It appears that over the first 50% of the membrane area, the product gets enriched slowly because of the presence of bulky 1-butanol, and the product enrichment accelerates over the second half of the membrane area. As the purity of the product

reaches the targeted level of 99.5 wt. %, the concentration of ethanol in the feed/product stream can be reduced well below 100 ppm. Therefore ethanol does not pose a challenge for the enrichment of 2,3-butanediol.

The mass fraction of 2,3-butanediol in the product stream versus its recovery is plotted in Fig. 9, where the content of ethanol appears as the variable parameter (0.0, 0.5, and 1.0 wt.%). Since the membrane is more selective when treating the feed containing a lower ethanol content. For achieving the product at the same purity, the feed containing less ethanol gives a higher product recovery. For the targeted product purity at 99.5 wt. %, the achieved product recovery is 58.4, 61.4, and 64.6% when the ethanol content in feed is 0.0, 0.5, and 1.0 wt.% respectively. According to Fig. 9, it appears that the product recovery can be roughly treated as linearly decreasing with the ethanol content. In practice, with proper control, the content of ethanol as a by-product (Yu, et al., 1982) is no more than 1.0 wt. %, e.g., 0.2 wt. %. According to the linear relationship, the loss in the final product recovery is about 1.2%. This is a small loss, and it is clear that by controlling the ethanol concentration in the feed, the efficiency of the separation process is not significantly reduced.

CONCLUSIONS

ZSM-5 filler was uniformly dispersed in the PDMS membrane matrix. The presence of ethanol in the feed changed the permeation behaviors of all the feed components. This permeation behavior could be interpreted with the coupled transport resulting from the component/component interactions. It was shown that due to the presence of ethanol, membrane selectivity was reduced. However, ethanol is preferentially removed from the feed stream, and the selectivity of the membrane was restored. Numerical simulation of a continuous operation

showed that the presence (e.g., 0.2 wt. %) of ethanol reduces the recovery of the product by 1.2%, which was insignificant.

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1 **FIGURES CAPTIONS**

2 Figure 1. SEM image of the cross-section of the ZSM-5 filled polydimethylsiloxane membrane,
3 the ZSM-5 loading is 44.4 wt. %.

4 Figure 2. Partial fluxes of the filled membrane for 1-butanol, 2, 3-butanediol, ethanol, and water
5 at 50°C.

6 Figure 3. Dependence of the membrane permeability (1-butanol, 2, 3-butanol, ethanol, and water)
7 upon the feed concentration of 1-butanol at 50 °C.

8 Figure 4. Three-dimensional representation of the solubility parameters of 1-butanol, 2, 3-
9 butanediol, ethanol, water, and PDMS membrane.

10 Figure 5. Selectivity of the filled membrane for water, ethanol, and 1-butanol over 2, 3-
11 butanediol at 50°C.

12 Figure 6. Comparison of membrane selectivity evaluated in feeds with and without ethanol (0.92
13 wt. %), respectively, at 50°C.

14 Figure 7. Temperature-dependence of membrane flux (a) and selectivity (b) which were
15 characterized with a feed containing 1-butanol (40.88 wt. %), 2, 3-butanediol (57.80 wt. %),
16 ethanol (0.93 wt. %) and water (0.39 wt. %) from 30 to 80 °C.

17 Figure 8. Variation of mass flow rate (a), and mass fraction (c) of 1-butanol, 2, 3-butanediol and
18 ethanol with respect to the percentage of membrane area, and (b) the selectivity the membrane
19 demonstrated in the course of separation at 50°C.

20 Figure 9. Purity versus recovery of 2,3-butanediol in a continuous operation at 50°C.

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Figure 1: The SEM cross -section view of the ZSM-5 filled polydimethylsiloxane membrane, the ZSM-5 loading is 44.4 wt. % .

Figure 2: The partial flux of the filled membrane for 1-butanol, 2, 3-butanediol, ethanol and water at 50°C.

Figure 3: The dependence of the membrane permeability (1-butanol, 2, 3-butanol, ethanol, and water) upon the feed concentration of 1-butanol at 50°C.

Figure 4: The three-dimensional representation of the solubility parameters of 1-butanol, 2, 3-butanediol, ethanol, water, and the PDMS membrane.

Figure 5: The selectivity of the filled membrane for water, ethanol, and 1-butanol over 2, 3-butanediol at 50°C.

Figure 6: The comparison of membrane selectivity evaluated respectively in feeds with and without ethanol (0.80-0.92 wt. %) at 50°C

Figure 7(a): The temperature-dependence of membrane flux characterized with a feed of 1-butanol (40.88 wt. %), 2, 3-butanediol (57.80 wt. %), ethanol (0.93 wt. %) and water (0.39 wt. %) from 30 to 80 °C.

Figure 7(b): The temperature-dependence of membrane selectivity characterized with a feed of 1-butanol (40.88 wt. %), 2, 3-butanediol (57.80 wt. %), ethanol (0.93 wt. %) and water (0.39 wt. %) from 30 to 80 °C.

Figure 8(a): Variation of mass flow rate of 1-butanol, 2, 3-butanediol and ethanol with respect to the percentage of membrane area during the separation at 50°C.

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Figure 8(b): Selectivity of the membrane in the course of separation at 50°C.

Figure 8(c): The variation of mass fraction of 1-butanol, 2, 3-butanediol and ethanol with respect to the percentage of membrane area during the separation at 50°C.

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Figure 9: The plot of 2, 3-butanediol purity in feed versus the recovery of 2,3-butanediol in a continuous operation at 50°C.

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Table 3

The feed compositions and other parameters involved in the simulation

Feeds	Temp.	Flowrate	Ethanol	1-Butanol	2,3-Butanediol	Product
	(°C)	(kg/h)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
I	50	360	0.0	95.0	5.0	99.5
II	50	360	0.5	94.5	5.0	99.5
III	50	360	1.0	94.0	5.0	99.5

Tables

Table 1. 1-Butanol-concentration-dependence of the permeabilities of feed components

Components	Permeability (cm ² /s)
1-Butanol	$P=1.10\text{E-}8*\text{EXP}(1.93X)^a$
2, 3-Butanediol	$P=2.68\text{E-}10*\text{EXP}(4.23X)$
Ethanol	$P=1.39\text{E-}8*\text{EXP}(2.35X)$
Water	$P=4.29\text{E-}8*\text{EXP}(1.57X)$

^a X stands for the mass fraction of 1-butanol in the feed.

Table 2

The permeation activation energy of feed components.

Feed component	Temperature range (°C)	Permeation activation energy ^a (Ea) ^{permeation} (kJ/mol)
Water	30-80	31.8
Ethanol	30-80	42.7
1-Butanol	30-80	33.3
2,3-Butanediol	30-50	36.8
	50-80	67.4

^a $(Ea)^{permeation} = (Ea)^{diffusion} + (\Delta H)^{dissolution}$

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