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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1002/cjce.20468>

Canadian Journal of Chemical Engineering, 89, 5, pp. 1255-1265, 2011-10-01

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PROCESS ENERGY EFFICIENCY IN PERVAPORATIVE AND VACUUM MEMBRANE DISTILLATION SEPARATION OF 2,3-BUTANEDIOL[†]

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This work focused on the energy aspects of the pervaporative separation of 1-butanol/2,3-butanediol. A numeric model was developed to simulate the mass and energy balance of the pervaporation process. It was found that the distribution of evaporation heat requirement over the membrane area is asymmetric, and more than 85% of the heat was consumed in the 60% of the membrane area. It was also revealed that recycling the permeate having higher than 5% w/w 2,3-butanediol can improve the recovery of 2,3-butanediol, and thus enhance the process energy efficiency. Two recycling strategies (the single or multiple point admission of permeate to the retentate flow) were explored. The specific energy requirement (the heat required by generating 1 kg 99.5% w/w 2,3-butanediol as product) was proposed to evaluate the process energy efficiency of both the pervaporation and vacuum membrane distillation, and it was shown that pervaporation can bring about nearly four times energy savings over the vacuum membrane distillation.

Ce travail était axé sur les aspects énergétiques de la séparation pervaporative de 1-butanol/2,3-butanediol. Un modèle numérique a été créé pour simuler le bilan massique et énergétique du processus de pervaporation. On a découvert que la distribution de la consommation calorifique de l'évaporation sur la surface de la membrane est asymétrique et plus de 85% de la chaleur était consommée dans les 60% de la surface de la membrane. On a également révélé que le recyclage du perméat supérieur à 5% p/p 2,3-butanediol peut améliorer la récupération de 2,3-butanediol et ainsi accroître l'efficacité énergétique du processus. Deux stratégies de recyclage (l'admission unique ou multiple du perméat au flux de rétentat) ont été explorées. Le besoin énergétique particulier (la chaleur requise par la production de 1 kg 99,5% p/p 2,3-butanediol comme produit) a été proposé pour évaluer l'efficacité énergétique du processus à la fois de la pervaporation et de la distillation de membrane sous vide et il a été démontré que la pervaporation peut occasionner presque quatre fois les économies d'énergie par rapport à la distillation de membrane sous vide.

Keywords: pervaporation, vacuum membrane distillation, process energy efficiency, numerical model, product recovery, permeate recycling

INTRODUCTION

As a fermentation product, 2,3-butanediol has long been produced by distillation (Larson and Stormer, 1973; Magee and Kosaric, 1987; Garg and Jain, 1995; Lee, 1999; Jansen and Tsao, 2007). Because of the low concentration of 2,3-butanediol in the fermentation broth, and the stronger hydrogen bonding interaction between water molecules, recovery of 2,3-butanediol by distillation is a very energy-intensive process (Neel and Huang, 1991; Shao and Huang, 2007). As an attempt, an integrated process comprising of solvent extraction and pervaporation (PV) has been proposed to deal with this recovery. In the integrated process, 2,3-butanediol in the fermentation broth was first extracted using 1-butanol, and the extracted 2,3-butanediol was further enriched by a PV membrane process. We recently

investigated the PV separation of 1-butanol/2,3-butanediol using polydimethylsiloxane (PDMS) and PDMS filled with ZSM-5 zeolite membranes, the results showed that the ZSM-5-filled PDMS membrane appears very promising for the separation (Shao and Kumar, 2009a,b, 2010). As a continued effort, this current work is dedicated to the energy aspects of the PV process, with the

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Can. J. Chem. Eng. 9999:1–11, 2011

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DOI 10.1002/cjce.20468

Published online in Wiley Online Library

(wileyonlinelibrary.com).

emphasis given to demonstrating that for conducting recovery of 2,3-butanediol the proposed PV (the integrated process) is better than the energy-intensive distillation.

Compared with the traditional column-tray distillation, membrane distillation (MD) exhibits some advantages, including lower capital investment, flexible processing capability, more vapor-liquid contact area in per unit volume of the separator, and less energy-intensiveness (reflux is generally not considered in MD). According to literature (Qureshi et al., 1994; Izquierdo-Gil et al., 1999, 2000; Huang et al., 2002; El-Bourawi et al., 2006; Cerneaux et al., 2009), the mass transport driving force for MD can be created either by maintaining a temperature difference across the porous membrane, or by using a sweeping gas stream or using a vacuum operation to remove all the transporting species on the downstream face of the membrane. A brief theoretical analysis reminds that the vacuum MD tends to give the highest process selectivity because of easy availability of the low permeate pressure. Therefore in this work the vacuum MD process was selected as the reference framework for evaluating the energy efficiency of the proposed PV process.

To compare the energy efficiency of the two processes, the energy balance of the PV and vacuum MD were modelled. Some important parameters, which characterise the process heat transfer (e.g., distribution of heat transfer over the membrane area, and total heat flow needed for PV separations) were investigated. It is found that permeate-recycling is an efficient approach for increasing the product recovery, and the permeate-recycling improves the energy efficiency of PV though it increases the total energy requirement. The process energy efficiency is evaluated in terms of the specific energy requirement, which is defined as the total evaporation heat needed for producing one kilogram of 99.5% w/w 2,3-butanediol. Results showed that the process energy efficiency of PV is much better than that of vacuum MD as it is directly used for recovering 2,3-butanediol from the fermentation broth.

THEORETICAL

A Numerical Model for Evaluating Mass and Energy Balance of PV

According to Fick's first law, the mass transfer through the membrane results from diffusion of a transporting species in the membrane, therefore the membrane flux of a transporting species can be expressed as:

$$\frac{dF}{dA} = -D \frac{dC_m}{d\ell} \quad (1)$$

where F is the mass flow rate of the feed component (1-butanol or 2,3-butanediol), A is the membrane area, D is the diffusion coefficient, C_m is the concentration in the membrane phase, and ℓ is the location variable.

Based on the solution-diffusion theory (Neel and Huang, 1991), the concentration of a transporting species in the upstream membrane surface is in equilibrium with its feed concentration, namely: $C_m/C_f = K$, where K is the partition coefficient. Since the concentration of the transporting species at the downstream membrane face can be neglected in PV due to the vacuum operation. Equation (1) can be rewritten as Equations (2) and (3):

$$\frac{dF}{dA} = \frac{DK}{\ell} C_f \quad (2)$$

Figure 1. The mass transport and balance across a typical membrane sector for illustrating the numerical simulation of the pervaporation process.

$$\frac{dF_i}{dA} = -\frac{P_i(X)}{\ell} \cdot \frac{F_i}{\sum_{i=1}^2 (F_i/\rho_i)} \quad (3)$$

where $P(X) = DK$, the permeability of the membrane for the feed component, which is usually dependent upon the feed composition, X is the feed mass fraction of 1-butanol, and ρ is the specific density of the component. Based on Figure 1, transforming Equation (3) into a difference equation gives:

$$\frac{F_i^{(k)} - F_i^{(k-1)}}{A^{(k)}} = -\frac{P_i(X^{(k-1)})}{\ell} \cdot \frac{F_i^{(k-1)}}{\sum_{i=1}^2 (F_i^{(k-1)}/\rho_i)} \quad (4)$$

The mass fraction of 1-butanol in the feed coming into the membrane sector (k) from the previous one is determined by:

$$X^{(k-1)} = \frac{F_{1\text{-butanol}}^{(k-1)}}{\sum_{i=1}^2 F_i^{(k-1)}} \quad (5)$$

Based on mass balance, the mass fraction of component i in permeate of the membrane sector (k) is achieved by:

$$Y_i^{(k)} = \frac{F_i^{(k-1)} - F_i^{(k)}}{\sum_{i=1}^2 (F_i^{(k-1)} - F_i^{(k)})} \quad (6)$$

The boundary conditions ($F_i^{(0)}$, $X^{(0)}$) of Equation (4) are known, therefore all the process quantities including $F_i^{(k)}$, $X^{(k)}$, and $Y_i^{(k)}$ ($1 \leq k \leq K$) can be obtained by selecting an appropriate membrane area $A^{(k)}$ for each of the membrane sectors. The criterion for selecting the membrane area for the membrane sector is such that the stage cut for each of the components never exceeds 3%. The total membrane area needed for the separation is dependent upon the objective purity ($1 - X$) of the product, as the targeted purity is reached, the total membrane area can be estimated by:

$$A^{\text{total}} = \sum_{k=1}^K A^{(k)} \quad (7)$$

The percentage of membrane area $A(L)$ from membrane sector 1 through L is defined as:

$$A(L) = \frac{1}{A^{\text{total}}} \sum_{k=1}^L A^{(k)} \cdot 100\% \quad (8)$$

In case permeate of membrane sectors (from L to L' and $1 \leq L < L' \leq K$) is gathered for recycling, the mean mass fraction of

Table 1. Physical properties of liquids used in process simulation

Feed components	Molecular weight (Da)	Boiling point (°C)	Vapor pressure ^a (mm Hg ^b)	Evaporation enthalpy ^c (kJ/mol)	Specific evaporation heat (kJ/g)	Permeability ^a (cm ² /s)
1-Butanol	74	117	33.3	52.2	0.71	1.10E-8exp(1.93X)
2,3-Butanediol	90	180	1.31	66.6	0.74	2.68E-10exp(4.23X)
Water	18	100	92.6	45.5	2.53	—

^a The value of the permeability at 50°C.

^b 1 mm Hg $\cong$ 133.3 Pa.

^c Data from Eusebio et al. (2003); Sharma et al. (1996); and Gilani et al. (2006).

component i in the accumulated permeate is obtained by:

$$\bar{Y}_i = \frac{F_i^L - F_i^{L'}}{\sum_1^2 (F_i^L - F_i^{L'})} \quad (9)$$

The recovery R of 2,3-butanediol (denoted as diol in the sub-script) is defined as:

$$R = \frac{F_{\text{diol}}^{(K)}}{F_{\text{diol}}^{(0)}} \quad (10)$$

The heat flow rate needed for evaporating component i in membrane sector k is obtained by:

$$Q_i^k = -(F_i^k - F_i^{k-1}) \cdot \Delta H_i^{\text{evaporation}} \quad (11)$$

where ΔH is the evaporation enthalpy. The heat transferred over membrane sector k is:

$$E(k) = \sum_{i=1}^2 Q_i^k \quad (12)$$

The cumulative heat transferred over membrane sectors (from 1 to L) can be written as:

$$E^{\text{cumulative}}(L) = \sum_{i=1}^2 \sum_{k=1}^L Q_i^k \quad (13)$$

When $L=K$, the cumulative heat is equal to the total heat Q^{total} transferred throughout the membrane separator. Considering the fact that vapor permeate in PV needs to be condensed.

Figure 2. The dependence of permeate and retentate 2,3-butanediol mass fraction upon the percentage of membrane area. The initial feed mass flow rate is 360 kg/h, and the initial mass fraction of 2,3-butanediol is 0.05.

Theoretically this portion of energy consumption equals the total evaporation heat, therefore the total energy consumption of the PV process is:

$$Q^{PV} = 2 \cdot Q^{total} \quad (14)$$

The process energy efficiency is characterised by the energy needed for producing 1 kg of 2,3-butanediol having the objective purity (99.5% w/w), and it can be written as:

$$Eff.^{PV} = \frac{Q^{PV}}{R \cdot F_{diol}^{(0)}} = \frac{Q^{PV}}{F_{diol}^{(K)}} \quad (15)$$

Since both the apparent heat and the mixing heat, and the vacuum operation cost involved in the separation is much less than the evaporation heat that is needed to drive the separation, all these minor energy components are not considered in this modelling.

An Analytical Model Describing Mass Balance and Energy Consumption of Vacuum MD Process for Direct Recovery of 2,3-Butanediol From Its Fermentation Broth

Consider a fermentation broth stream consisting of water and 2,3-butanediol, and the flow rate of the components are m and n , respectively. Assume that the liquid and the vapor are always in equilibrium throughout evaporation across the membrane area (refer to Fig. 1, where the membrane is non-porous). Suppose that

dm of water and dn of 2,3-butanediol are locally evaporated, and that mass transport through the porous distillation membrane is predominated by the viscous flow regime, thus the mole fraction of water in the permeate phase is determined by:

$$y = \frac{dm/m}{dm/M + dn/N} \quad (16)$$

where M , and N represent the molecular weight of water and 2,3-butanediol, respectively. By neglecting the small losses of dm and dn , the mole fraction of water in feed is:

$$x = \frac{m/M}{m/M + n/N} \quad (17)$$

Assuming the feed is an ideal solution, based on the vapor-liquid equilibrium, the mole fraction of water at the vapor-liquid interface is:

$$y = \frac{x \cdot p^{water}}{x \cdot p^{water} + (1-x) \cdot p^{diol}} \quad (18)$$

where p^{water} and p^{diol} are the saturated vapor pressure of water and 2,3-butanediol, respectively. Recalling the viscous flow assumption, the mole fraction of water in permeate should be equal to that at the vapor-liquid interface, therefore inserting Equations

Figure 3. The plot of the percentage of feed component passing through the pervaporation membrane versus the percentage of membrane area.

(16) and (17) into Equation (18) yields:

$$\frac{dm/M}{dm/M + dn/N} = \frac{(m/M) \cdot p^{\text{water}}}{(m/M) \cdot p^{\text{water}} + (n/N) \cdot p^{\text{diol}}} \quad (19)$$

Rearranging Equation (19) gives:

$$\frac{dm}{m} = \frac{dn}{n} \left(\frac{p^{\text{water}}}{p^{\text{diol}}} \right) \quad (20)$$

Integrating Equation (20) from the initial feed quantities (M_0 , n_0) to a random intermediate state (m , n) gives Equations (21) and (22):

$$\int_{m_0}^m \frac{dm}{m} = \beta \int_{n_0}^n \frac{dn}{n} \quad (21)$$

$$\frac{m}{m_0} = \left(\frac{n}{n_0} \right)^\beta \quad (22)$$

where $\beta = p^{\text{water}}/p^{\text{diol}}$, the relative volatility, which is a constant at a temperature. Note m and n in the mixture can be correlated with the mass fraction (X) of 1-butanol by:

$$\frac{m}{n} = \frac{X}{1-X} \quad (23)$$

Eliminating “ m ” between Equations (22) and (23) gives:

$$n = n_0 \left(\frac{n_0}{m_0} \cdot \frac{X}{1-X} \right)^{1/\beta-1} \quad (24)$$

With a set objective purity ($1 - X$) of 2,3-butanediol, the mass flow rate (m and n) in the product stream can be estimated, and the recovery ($R(X)$) of 2,3-butanediol of the vacuum MD process can be obtained as:

$$R(X) = \frac{n}{n_0} \cdot 100\% = \left(\frac{n_0}{m_0} \cdot \frac{X}{1-X} \right)^{1/\beta-1} \cdot 100\% \quad (25)$$

Again, considering the vapor condensation, the total energy required by the vacuum MD process can be evaluated by:

$$Q^{\text{MD}} = 2 \cdot [(m_0 - m) \cdot \Delta H_{\text{water}} + (n_0 - n) \cdot \Delta H_{\text{diol}}] \quad (26)$$

Note in Equation (26), the energy consumed for condensing vapor permeate is also considered. Similarly, the process energy efficiency is characterised by the specific energy demand by:

$$\text{Eff.}^{\text{MD}} = \frac{Q^{\text{MD}}}{R(0.995) \cdot n_0} \quad (27)$$

Using Equations (15) and (27), the process energy efficiency of PV and vacuum MD can be calculated and compared.

Figure 4. The distributions of evaporation heat over membrane area. The initial flow rate is 360 kg/h, and the initial mass fraction of 2,3-butanediol is 0.05.

RESULTS AND DISCUSSION

Simulation Conditions and Membrane Performance

Fermentation is generally a product-inhibiting process; the economical concentrations of 2,3-butanediol in the fermentation broth are in the range of 4–6% w/w (Shao and Kumar, 2009b). A mean value of 5% w/w was considered as the initial concentration of 2,3-butanediol in the broth when MD was employed to enrich 2,3-butanediol directly from the fermentation broth. In the case of an integrated solvent extraction and PV process as a substitute for the MD, according to our earlier work (Shao and Kumar, 2009a), as the initial concentration of 2,3-butanediol in the fermentation broth is 5% w/w, the concentration of 2,3-butanediol in the extract phase is very close to 5% w/w as 1-butanol is employed as the solvent, and this value was used as the initial feed concentration of 2,3-butanediol for PV separation.

The experimentally obtained permeability and some important thermodynamic data for estimating the energy demand of both PV and MD are summarised in Table 1. Since the process energy efficiency is theoretically independent of the feed flow rate, only one feed flow rate (360 kg/h) is considered in the simulation. In order to determine the permeation rate (P/ℓ) of a composite membrane for 1-butanol and 2,3-butanediol, a representative value of $5\ \mu\text{m}$ is assigned to the thickness of the supported thin film. The target purity of 2,3-butanediol is set at 99.5% w/w, all the process parameters (such as product recovery and energy efficiency) for both PV and MD were evaluated with respect to this purity.

Distribution of Mass Transfer Over Membrane Area

The total membrane area needed for enriching 2,3-butanediol from the initial concentration of 5% w/w to the anticipated purity

of 99.5% w/w was $123.7\ \text{m}^2$. In order to have an overview of the mass transfer occurring over the entire membrane area, the mass fractions of 2,3-butanediol in both permeate and retentate streams were plotted against the percentage of membrane area in Figure 2. Clearly the total membrane area can be divided into two distinct sections. Membrane in Section I (0–60%) removes essentially pure 1-butanol from the retentate because of the semi-permeable property of the membrane and more importantly the dilute retentate concentration of 2,3-butanediol. Membrane in Section I is thus responsible for pre-concentrating 2,3-butanediol. By contrast membrane in the Section II (60–100%) deals with higher concentrations of 2,3-butanediol, and the permeate concentration of 2,3-butanediol starts getting increasingly higher as the separation progresses. This portion of the membrane serves to refine 2,3-butanediol to the targeted product purity.

It can be conceived that due to the permeability difference between the components, the permeate flux should change from one place to another across the membrane in a PV separator. The dependence of 1-butanol and 2,3-butanediol (in percentage) passing through membrane upon the percentage of total membrane area used is illustrated in Figure 3, and the local mass transport intensity (LMTI) of the membrane for each of the components can be obtained as the slope of the curves shown in Figure 3.

$$\text{LMTI} = \left[\frac{d(\text{Mass}(\%))}{d(\text{Area}(\%))} \right] \quad (28)$$

Clearly LMTI is an index measuring the quantity of a component transporting over 1% of the total membrane area. Evidently,

Figure 5. The mass fraction of 2,3-butanediol in permeate and the accumulated permeate versus the mass fraction of 2,3-butanediol in retentate at 50°C .

Figure 6. The flowchart of pervaporation without (A) and with (B) 1-point-permeate-recycling at 50°C, the initial feed flow rate is 360 kg/h, and the initial mass fraction of 2,3-butanediol is 0.05.

the membrane at the feed inlet has the highest LMTI. It can also be found that the LMTI decreases slowly before the percentage of membrane area reaches 60%, and this mild LMTI decline in Section I is replaced with a sharp decrease in Section II, where the quantity of the remaining 1-butanol in the retentate is quite limited, particularly when the percentage of membrane area is higher than 80%. Clearly, the lowest LMTI is at the retentate outlet, and the majority of mass transport takes place in Section I.

Distribution of Heat Transfer Across Membrane Area

A phase change from liquid to vapor is involved in PV separation. As discussed previously, the LMTI varies from one location to another, it is thus practically important to know how much evaporation heat should be offered to each unit membrane area at different locations of the separator. This information allows us to design an efficient PV process by providing the right amount of evaporation heat at different locations so that the separation can be operated properly. The heat demand of each of the membrane sectors and the cumulative heat demand were depicted in Figure 4. As expected, a good large part (85%) of the evaporation heat is consumed by the membrane in Section I (0–60% membrane area), where according to the LMTI, the majority of 1-butanol is removed. Suggesting that in practical operation more powerful heat exchangers should be deployed in Section I to enable the separation.

Permeate-Recycling for Improved Product Recovery and Process Energy Efficiency

The interdependence of the permeate and retentate concentration of 2,3-butanediol is plotted in Figure 5. It is shown that the mass fraction of 2,3-butanediol in permeate ranges from 0.00 to 0.82. Apparently recycling the permeate containing higher concentrations of 2,3-butanediol is a feasible approach to improve its recovery. The recycling is conducted in such a way that all the permeate having a 2,3-butanediol mass fraction higher than 0.05 (i.e., the initial mass fraction) is accumulated, and the accumulated permeate is admitted to the retentate stream at a point, where the composition is theoretically the same as that of the accumulated permeate, while all the other permeate (<0.05 in mass fraction) is collected and sent back as solvent to extract 2,3-butanediol. The flow rate, and composition of the recycled permeate are obtained by iteration, and the detailed data are specified on the flowchart shown in Figure 6, which are 18.2 kg/h and 11.4% w/w, respectively. As shown in Figure 7A, with the permeate recycling, the final product recovery is enhanced from 64.6% to 74.7%. It is also noted that due to the increased processing duty with the permeate recycling the total membrane area for the processing is increased from 123.7 to 135.8 m². Considering the tremendous long-term energy savings by elevating the concentration of 2,3-butanediol from 5 to 11.4% w/w in the retentate, the extra capital investment in membrane area appears insignificant.

Figure 7. The dependence between the product purity and product recovery of the pervaporation process with and without considering the 1-point permeate recycling (A), comparison between 1-point and 3-point permeate recycling (B) at 50°C.

According to thermodynamics, the benefit of permeate-recycling can be further enhanced by recycling permeate at multiple points in the PV process. The disadvantage of single point recycling is that 2,3-butanediol in a higher concentration of permeate has to mix with that of a low concentration of permeate. Obviously this kind of mixing wastes the energy required for getting them separated, a multi-point permeate-recycling strategy tends to reduce this type of energy waste. Here a 3-point-recycling was attempted, and the three permeate streams are obtained by collecting the permeate in three different ranges of 2,3-butanediol concentration: the stream I took all the permeate in the range of

(5–10% w/w), stream II (10–60% w/w), and stream III (60–82% w/w) (Fig. 8). The composition and the flow rate of these three streams are summarised in Table 2. Just like the 1-point-recycling, the compositions of the retentate at the three points are exactly the same as those of the permeate streams I, II, and III. According to Figure 7B, the resulting improvement in recovery relative to the 1-point-recycling is not so significant. This could be due to the fact that the flow rates of higher concentration permeates (e.g., permeate streams II and III) are too small to bring a big effect. And 1-point-recycling is therefore adequate for improving the process performance of PV (Fig. 6).

Figure 8. The flowchart of pervaporation separation process considering the 3-point-permeate-recycling at 50°C. The initial flow rate is 360 kg/h, and the initial mass fraction of 2,3-butanediol is 0.05.

Table 2. The flow rate and composition of the recycled permeate in the three permeate streams

Permeate stream	Permeate flow rate (kg/h)	Conc. of 2,3-butanediol (% w/w)
Stream I	11.1	6.7
Stream II	5.6	21.4
Stream III	0.7	70.6

Comparison of PV With MD in Process Energy Consumption and Process Energy Efficiency

Distillation remains so far the key industrial means for separating 2,3-butanediol from its aqueous fermentation broth. Some researchers also attempted the vacuum MD as a substitute (El-Bourawi et al., 2006). Phase change occurs in both PV and MD, but the key permeate in PV and MD is 1-butanol, and water, respectively. According to the thermodynamic data summarised in Table 1, the specific evaporation heat of water is over three times higher than that of 1-butanol, implying that the direct MD is a more energy-intensive process than PV. The heat flow required

Figure 9. The heat flow needed for enriching the feed from the initial mass fraction of 2,3-butanediol to a higher mass fraction by pervaporation or vacuum membrane distillation.

Figure 10. The specific energy needed for enriching the feed from the initial mass fraction of 2,3-butanediol to a higher mass fraction by pervaporation and vacuum membrane distillation.

for enriching 2,3-butanediol from the initial feed composition to a higher purity by both PV and the MD is illustrated in Figure 9. The total heat flow needed for enriching 2,3-butanediol from 0.05 to 0.995 by PV is nearly four times lower than that by MD. Therefore recovering 2,3-butanediol by the proposed integrated process can save a lot of energy.

In order to compare the process energy efficiency, the specific energy demand for producing 1 kg of 2,3-butanediol of a higher purity are described in Figure 10, and once again it is indicated that PV excels the MD. At the targeted product purity of 0.995, the energy demand for PV and MD are 38 and 148 MJ/kg, respectively. Meaning that if MD is employed for processing the fermentation broth directly the process energy efficiency would be nearly four times less than PV. In addition, Figure 10 showed that the impact of permeate-recycling on enhancing the energy efficiency of PV is quite remarkable. Permeate-recycling is thus an attractive measure for improving both the product recovery and process economics for PV.

CONCLUSIONS

Mathematical models (the numerical and analytical one) for describing both mass and energy balances between the feed and permeate side of PV and MD were developed. The process simulation showed that the distributions of mass and heat transport over the membrane area are asymmetrical, and the majority of mass and heat transfer was taking place in the 60% of the membrane area from the feed inlet. Therefore more powerful heat exchangers should be deployed for this energy-intensive membrane section. It was shown that the strategies of both 1- and 3-point permeate-recycling enhanced the product recovery and reduced the specific

energy demand of the PV process. Further results showed that 1-point-recycling was adequate for enhancing product recovery and process energy efficiency. Comparison of PV and MD revealed that PV was a more energy-efficient process for enriching the 2,3-butanediol product. It was possible to save nearly four times of the specific energy demand by using PV in place of the vacuum MD.

NOMENCLATURE

A	membrane area (m^2)
E	energy distribution
Eff.	energy efficiency of the process (MJ/kg)
F	mass flow rate of the feed component (g/s)
ΔH	evaporation enthalpy (kJ/mol)
i	subscript representing the feed component i
k	superscript representing the number of the numbered membrane sector
K	number of the membrane sectors
ℓ	thickness of the active thin film of the composite membrane (cm)
L	random number of the numbered membrane sector
m	mass flow rate of water in MD (g/s)
M	molecular weight of water (Da)
LMTI	local mass transfer intensity
n	mass flow rate of 2,3-butanediol in the MD (g/s)
N	molecular weight of 2,3-butanediol (Da)
P	membrane permeability (cm^2/s)
Q	evaporation energy flow (kJ/h)
R	product recovery (%)
x	mass fraction of 1-butanol in the feed for PV

X	mole fraction of water in the feed for MD
Y	mass fraction of 1-butanol in permeate of PV
Y	mole fraction of water in the permeate of MD
β	relative volatility of water to 2,3-butanediol
ρ	density of the feed component (g/cm^3)

ACKNOWLEDGEMENTS

The financial supports of AAFC's Agriculture Bioproducts Innovation Program and NRC's National Bioproducts Program are gratefully acknowledged.

REFERENCES

- Cerneaux, S., I. Struzynska, W. M. Kujawski, M. Persin and A. Larbot, "Comparison of Various Membrane Distillation Methods for Desalination Using Hydrophobic Ceramic Membranes," *J. Membr. Sci.* **337**, 55–60 (2009).
- El-Bourawi, M. S., Z. Ding, R. Ma and M. Mhayet, "A Framework for Better Understanding Membrane Distillation Separation Process," *J. Membr. Sci.* **285**, 4–10 (2006).
- Eusebio, M. E., A. J. L. Jesus, M. S. C. Cruz, M. L. P. Leitao and J. S. Redinha, "Enthalpy of Vaporation of Butanediol Isomers," *J. Chem. Thermodyn.* **35**, 123–129 (2003).
- Garg, S. K. and A. Jain, "Fermentative Production of 2,3-Butanediol: A Review," *Bioresour. Technol.* **51**, 103–109 (1995).
- Gilani, H. G., G. Khiati and A. K. Haghi, "Liquid-Liquid Equilibrium of (Water, 2,3-Butanediol, 2-Ethyl-1-Hexanol) at Several Temperatures," *Fluid Phase Equilib.* **247**, 199–204 (2006).
- Huang, R. Y. M., P. Shao, X. Feng and W. Anderson, "Separation of Ethylene Glycol Aqueous Solutions Using Sulfonated Poly(ether ether ketone) (SPEEK) Pervaporation Membranes: Membrane Relaxation and Separation Performance Analysis," *Ind. Eng. Chem. Res.* **41**, 2957–2965 (2002).
- Izquierdo-Gil, M. A., M. C. Garcia-Payo and C. Fernandez-Pineda, "Air Gap Membrane Distillation of Sucrose Aqueous Solutions," *J. Membr. Sci.* **155**, 291–297 (1999).
- Izquierdo-Gil, M. A., M. C. Garcia-Payo and C. Fernandez-Pineda, "Air Gap Membrane Distillation of Aqueous Alcohol Solutions," *J. Membr. Sci.* **169**, 61–69 (2000).
- Jansen, N. and G. T. Tsao, "Bioconversion of Pentoses to 2,3-Butanediol by *Klebsiella Pneumonia* Laboratory of Renewable Resources Engineering (Online Book Chapter)," Purdue University, West Lafayette, IN, USA (2007), pp. 85–98.
- Larson, S. H. and C. F. Stormer, "Diacetyl (Acetoin) Reductase From *Aerobacter Aerogenes*-Kinetic Mechanism and Regulation by Acetate of the Reversible Reduction of Acetoin to 2,3-Butanediol," *Eur. J. Biochem.* **34**, 100–106 (1973).
- Lee, J., "The Conversion of 2,3-Butandiol to Methyl Ethyl Ketone Over Zeolites, PhD Thesis," Purdue University, USA (1999).
- Magee, R. J. and N. Kosaric, "The Microbial Production of 2,3-Butanediol," *Adv. Appl. Microbiol.* **32**, 89–91 (1987).
- Neel, J. and R. Y. M. Huang, Eds., "Introduction to Pervaporation, Pervaporation Membrane Separation Processes," Elsevier, Amsterdam (1991).
- Qureshi, N., M. M. Meagher and R. W. Hutjins, "Recovery of 2,3-Butanediol by Vacuum Membrane Distillation," *Sep. Sci. Technol.* **291**, 1733–1748 (1994).
- Shao, P. and R. Y. M. Huang, "(Review) Polymeric Membrane Pervaporation," *J. Membr. Sci.* **287**, 169–172 (2007).
- Shao, P. and A. Kumar, "Recovery of 2,3-Butanediol From Water by a Solvent Extraction and Pervaporation Separation Scheme," *J. Membr. Sci.* **28**(1–2), 160–168 (2009a).
- Shao, P. and A. Kumar, "Separation of 1-Butanol/2,3-Butanediol Using ZSM-5 Zeolite-Filled Polydimethylsiloxane Membranes," *J. Membr. Sci.* **339**, 143–150 (2009b).
- Shao, P. and A. Kumar, "Pervaporative Enrichment of 2,3-Butanediol From 1-Butanol and 2,3-Butanediol Using a Polydimethylsiloxane and ZSM-5 Mixed Matrix Membrane: Effect of Ethanol as an Impurity," *Sent to Chem. Eng. Process.* (2010).
- Sharma, S., G. Pandey, T. Chakrarti and P. Khanna, "Liquid-Liquid Equilibrium for Water, 2,3-Butanediol, 3-Methyl-1-Butanol With Sodium Sulfate and Sodium Carbonate at 303.15K," *J. Chem. Eng. Data* **41**, 306–309 (1996).

Manuscript received July 22, 2010; revised manuscript received September 24, 2010; accepted for publication September 27, 2010.