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Separation of acetone–butanol–ethanol (ABE) from dilute aqueous solutions by pervaporation

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Abstract

In acetone–butanol–ethanol (ABE) fermentation, which is a potential process of producing feed stock chemicals and liquid fuels from renewable biomass, product inhibition is a severe problem affecting the bioconversion. This study is concerned with the separation of acetone–butanol–ethanol (ABE) from dilute aqueous solutions by pervaporation. Poly(ether block amide) (PEBA 2533) membranes were used. The separation of binary acetone–water, *n*-butanol–water and ethanol–water mixtures by the membranes was initially carried out using a relatively thick (100 μm) membrane to evaluate the membrane permselecivity, which was found to be in the order of *n*-butanol > acetone > ethanol. The effects of feed composition, operating temperature and membrane thickness on the membrane performance were studied. It was shown that the boundary layer effect became significant when a thinner membrane (30 μm) was used, especially for *n*-butanol separation. In addition, the separation of quaternary acetone–*n*-butanol–ethanol–water mixtures was also studied, and the potential of the membrane for ABE extraction from dilute aqueous solutions was demonstrated. From an application point of view, the recovery of butanol from the fermentation broth could be a niche application for the membrane.

Keywords: Pervaporation; Membrane; Poly(ether block amide); Acetone–butanol–ethanol

1. Introduction

Fermentation is an attractive process for producing feed stock chemicals from renewable biomass. The production of butanol by acetone–butanol–ethanol (ABE) fermentation used to be one of the largest bioprocesses until the 1950s, but later it was replaced by the less expensive petroleum-based chemical synthesis. In recent years, interest in bio-based butanol has been revived primarily due to concerns with fossil fuel depletion, and microbial production of butanol is considered to be a potential source of liquid fuels. There is a relatively wide range of substrates suitable for ABE fermentation [1], but the process suffers from severe product inhibition, which is one of the primary reasons that the traditional batch process of ABE fermentation is not economically viable. The low concentration of the fermentative products (<5 wt%, depending on the fermentation process) means not only a cost intensive product separation but also a large volume for downstream processing and waste water treatment [2]. Since butanol is less volatile than water, the separation of butanol from dilute aqueous solutions by distillation is unfavorable; it is estimated that at a butanol concentration of <5%, the energy consumption required for butanol purification will exceed the energy content of the butanol recovered [1].

As a result, in order to make the fermentation process economically attractive, more efficient butanol recovery processes are needed. Several methods (including gas stripping, adsorption, extraction, membrane distillation, perstraction, and pervaporation) (see, for example [3]) have been investigated during last decade in order to improve the recovery of ABE from the fermentation broth. Among these methods, pervaporation appears to be particularly promising. It is based

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Table 1
Membranes used for butanol separation pertinent to ABE fermentation

Membranes	Operation mode	References
PDMS	Vacuum pervaporation	[5,6,13,15,20]
	Sweep gas pervaporation	[10,11,17,19]
PDMS filled with silicalite	Vacuum pervaporation	[5,6,9,12–14]
EPDR	Vacuum pervaporation	[5]
SBR	Vacuum pervaporation	[5]
PMS	Vacuum pervaporation	[20]
PTMSP	Vacuum pervaporation	[7,16,18,20]
Porous PP (pore size 0.2 μm)	Sweep gas pervaporation	[1,3]
Porous PTFE (pore size 0.1–0.45 μm)	Sweep gas pervaporation	[8]

PDMS: poly(dimethyl siloxane); SBR: styrene butadiene rubber; EPDR: ethylene propylene diene rubber; PTMSP: poly[-1-(trimethylsilyl)-1-propyne]; PP: propylene; PTFE: polytetrafluoroethylene and PMS: poly(methoxy siloxane).

on the selective permeation of the ABE components through a membrane in preference to water. Pervaporation can be coupled with fermentation so that the inhibitory products from the fermentation broth can be removed continuously as soon as they are formed, thereby enhancing the process productivity. Only the membrane permeated components undergo liquid–vapor phase change during pervaporation, and from an energy consumption point of view, butanol recovery by pervaporation is more economical than distillation. Unlike perstraction, a membrane process that requires an additional separation step for product recovery from the extractants, pervaporation does not involve external mass separating agent, and thus there is no harmful effect on the microorganisms in the fermentation broth. In addition, pervaporation membranes are generally non-porous; in the case of asymmetric composite membranes where a dense skin layer is supported by a microporous substrate, it is the non-porous skin that is in contact with the feed solution. Consequently, the fermentation medium can be retained by the membrane without clogging the pores of asymmetric membranes.

Pervaporation separation of ABE components from a fermentation broth derives from selective permeation of ABE through the membrane in preference to water, and organophilic membranes are generally required [4]. However, very few polymer membranes are available for this application. Polydimethylsiloxane (PDMS) is so far the most widely used organophilic membrane material, as illustrated in Table 1, which summarizes the membranes used in recent studies on ABE removal from model butanol solutions or fermentation broths. Silicalite has been used as a filler in the PDMS membranes to improve the membrane selectivity. In addition to the PDMS-based membranes, other rubbery polymer membranes such as poly(methyhoxy siloxane), styrene butadiene rubber, and ethylene propylene diene rubber [5,20] have also been investigated for pervaporation related to ABE separation. Further, membranes prepared from poly[-1-(trimethylsilyl)-1-propyne], which is a glassy polymer with a large free volume, were also found to be selective to organic compound permeation [7,16,18,20]. Although microporous membranes made from hydrophobic polypropylene [1,3] and polytetrafluoroethylene [8] have been used, they generally do not exhibit a high selectivity as the separation is based on the flow of the ABE and water vapors through the pores of the membrane. It is essentially a membrane striping process where the hydrophobic membrane primarily functions as a barrier that prevents the aqueous solution from entering the membrane pores [21]. In contrast to the nonporous membranes in pervaporation, the porous membranes used in the stripping process rarely govern the separation.

Poly(ether block amide) (PEBA) is a group of copolymers comprising of flexible polyether segments and rigid polyamide segments. Depending on the nature and the relative content of the two segments, certain PEBA polymers have attracted great interest as a promising membrane material. PEBA membranes have shown excellent selectivity for the extraction of aroma compounds from water by pervaporation, especially for the enrichment of esters from dilute aqueous solutions [22,23]. Boddeker et al. [24], who carried out an comparative study on pervaporation of four isomeric butanols through a PEBA 40 membrane, showed that the permeation flux of the PEBA membrane was higher than the PDMS and polyether-based polyurethane membranes. Moreover, PEBA membranes were also reported to be effective for the removal of phenol from phenolic resin wastewater streams [25,26].

In this study, PEBA 2533 was chosen as the membrane material for ABE separation. It contains 80 wt% organophilic poly(tetramethylene glycol) soft segments and 20 wt% nylon 12 hard segments. This material has a considerably high affinity to butanol, and as a mater of fact, butanol can dissolve PEBA 2533 at elevated temperatures [27]. Consequently, it was expected that the membranes would yield a good flux and selectivity in consideration of its favorable solubility properties to butanol, the component to be separated from aqueous solutions. In spite of some research on PEBA membranes for organic separation from water by pervaporation, a literature search showed that there has not been any study on using PEBA membranes for ABE extraction from dilute aqueous solutions. The objective of this study is to explore the applicability of utilizing PEBA 2533 membranes for the separation of acetone–butanol–ethanol from dilute aqueous solution, pertinent to ABE removal from fermentation broths. Pervaporation is a rate controlled process, and for a given membrane material, a high permeation flux can be achieved by using thin membranes. We have recently developed a new method of preparing ultrathin PEBA 2533 membranes (as thin as 0.3 μm) [27]. However, considering that the boundary layer effect (i.e. concentration polarization) will be more significant with thinner membranes, it was decided to use relatively thick membranes in the present study for the sake of evaluating the permselectivity of the PEBA 2533 mem-