



Thermopervaporation concept for biobutanol recovery: The effect of process parameters



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ABSTRACT

This work addresses the development of energy-saving (low-cost) pervaporation approach for the recovery of biobutanol from the ABE fermentation broth. To achieve this goal, thermopervaporation (TPV) separation of dilute aqueous solutions of 1-butanol through the hydrophobic poly(1-trimethylsilyl-1-propyne) (PTMSP) membranes in the plate-and-frame module with an air gap was investigated. The TPV approach allows separation at atmospheric pressure and in the presence of noncondensing gases of ABE fermentation (carbon dioxide and hydrogen). Different process parameters such as the air gap width, the temperature of the feed mixture, the permeate condensation temperature, and the membrane thickness were studied. The width of the air gap between the membrane and the condensation surface (the cooling plate) should not be lower than 2.5 mm. The TPV mode of separation of water/butanol mixture using self-supported PTMSP dense membranes makes it possible to achieve the following process performance: the permeate flux exceeds 0.5 kg/(m² h) (membrane thickness is 16 μm) and the separation factor for the butanol/water mixture is about 120 (membrane thickness is 115 μm) at the atmospheric pressure and at a condensation temperature of 10 °C.

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1. Introduction

Butanol is an important feedstock chemical and second-generation alcohol fuel that can be produced by fermentation using renewable resources as substrates. As compared to ethanol which is a traditional fuel additive, butanol can be easily mixed with gasoline and diesel fuel, it has a lower vapor pressure but is less miscible with water. Taking into account these advantages, butanol seems to be a far more superior alternative fuel. Moreover, butanol is currently used as an extractant in food and flavor industry. Because of its potential for carcinogen carry-over, the use of petroleum-derived butanol is not desirable. All of these markets are steadily growing [1,2].

On the other hand, acetone–butanol–ethanol (ABE) fermentation has its long history and is credited as a successful commercial fermentation process, even though the average final solvent concentration is low and varies between 10 and 18 g/L. However, after the World War II, the fermentation-derived butanol (biobutanol) process has declined because biobutanol failed to compete with petrochemically produced butanol due to the progress in petrochemical industries [2,3].

In recent years, the interest from industry to biobutanol has been resumed [1,2,4,5]. Special attention has been focused on the improvement of the traditional batch fermentation process and on the development of some novel fermentation technologies. A superior culture has been developed but the process engineering can still be applied to the ABE fermentation to make it economically viable. One approach involves recycling of the fermenter effluent to the fermenter and conversion of the residual sugar to the final product. However, recycling is successful only when this process is coupled to the technology of the effective product recovery and removal of inhibitory products [1,6,7]. Several techniques have been used for the recovery of ABE from the fermentation effluents. These techniques include adsorption, liquid–liquid extraction, perstraction, gas stripping, membrane distillation, pervaporation, and salt induced phase separation [1,8,9]. However, combined optimization of the fermentation process and product recovery mode has not been tested yet on an industrial scale due to the high costs of product recovery [2].

Hydrophobic pervaporation is known to be the membrane technique which provides selective separation of organics from water by evaporation through hydrophobic membranes, and this approach is considered to be the most promising separation technology for the recovery and partial concentration of butanol, acetone, and ethanol from the ABE fermentation broth [10]. Both

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performance and conversion rate can be markedly improved when, as an alternative to the conventional batch processes, pervaporation-bioreactor hybrid processes (pervaporation membrane bioreactor) are used.

Unfortunately, all existing commercial membranes based on poly(dimethylsiloxane) fail to demonstrate high separation factors for the butanol/water mixtures. Separation factors for the aqueous mixture containing 0.01 mol fraction of butanol are equal to 9, 31, and 9 for Pervatech, Pervap 4060 and PolyAn, respectively [11]. Highly permeable glassy poly (1-trimethylsilyl-1-propyne) (PTMSP) and its blends are credited as promising membrane materials for the recovery of biobutanol from the ABE fermentation broths [12–14]. Thus, the addition of hydrophobic silica increases the permeate flux up to 10 kg/(m² h), however, the alcohol/water selectivity is compromised [13]. At the same time, introduction of only 1.2 wt% of an elastomeric filler, poly(dimethylsiloxane) (PDMSM), to the host PTMSP matrix made it possible to increase both the permeate flux up to 75% and the separation factor up to 67% [14].

Nowadays, the commercial pervaporation process is performed using vacuum for the creation and maintenance of the process driving force (vacuum pervaporation) [15]. For biobutanol production, this approach seems to be energetically unfavorable because not only ABE but also non-condensable gases (e.g. carbon dioxide and hydrogen) are produced and present in marked concentrations in the ABE fermentation media. In this case, separation costs appear to be high.

To overcome the drawbacks of vacuum pervaporation, since 2009 we were engaged in the development of the thermopervaporation (TPV) approach for the removal of biobutanol from the fermentation broths [16–18]. It should be pointed out that the TPV is the least investigated mode of pervaporation when permeate is condensed against the cooling surface within the membrane module at the atmospheric pressure. For the first time, this approach has been advanced by Aptel et al. in [19] where the authors studied the TPV separation of positive azeotropic liquid systems using hydrophilic poly(tetrafluoroethylene)-based membranes with the N-vinylpyrrolidone-modified surface. For the separation of the dioxane/water azeotrope, the TPV process was shown to be characterized by the following parameters: the permeate flux was higher than 100 kg/m² per day, and water/dioxane selectivity exceeded 10. Noteworthy is that these parameters correspond to the performance of vacuum pervaporation.

Hence, in the TPV process, the difference in partial pressures between the feed (upstream) and permeate (downstream) sides is provided by the temperature gradient across a membrane and a membrane module. This system is supported by a condenser (a cooling plate) on the permeate side of the membrane module with an air gap between a membrane and a cooling plate.

Noteworthy is that, since 1976 [19], only few publications on TPV are available [17–24].

In this connection the basic objective of this research addresses the study of the factors controlling the TPV process upon the recovery of butanol from the model fermentation mixtures using the PTMSP membranes. The effect of the air gap width, membrane thickness, feed and condensation temperatures on the process of thermopervaporation separation was investigated.

2. Experimental

2.1. Membranes

PTMSP was synthesized by polymerization of 1-trimethylsilyl-1-propyne on the NbCl₅ catalyst [25]. Molecular weight (MW) of PTMSP was $M_w = 200$ kg/mol.

The PTMSP membranes were prepared by casting polymer solutions in chloroform onto a cellophane support; then, the solvent was evaporated for 100–200 h under ambient conditions. The membrane thickness was varied from 16 to 115 μm. Prior to the pervaporation measurements, all membranes were soaked in 1-butanol and dried until their constant weight was attained. In this work, these membranes are referred to as “initial membranes”. Then, the *initial membranes* were pre-conditioned upon thermopervaporation separation of 2% aqueous solution of butanol (the feed temperature is 60 °C) until the steady-state performance was attained (3–5 weeks depending on the membrane thickness). In general, all experiments were performed for the pre-conditioned membranes, unless the type of the used membrane is deliberately specified.

2.2. Thermopervaporation

Thermopervaporation experiments were conducted on the setup shown in Fig. 1. The TPV module included liquid-carrying contours with different temperatures. In the first contour, a cooling agent thermostated with a thermostatic coolant was circulated. The second contour consists of the vessel containing the to-be-separated mixture, which was heated to a desired temperature with a heat exchanger, and a peristaltic pump. The accuracy of the maintained temperature was ±0.2 °C. The temperatures of the feed mixture and the cooling agent at the upstream and downstream sides of the TPV module were measured using the temperature detectors.

The module consisted of two mirror-symmetric flow chambers separated by a membrane and a cooling plate spaced by an air gap. The permeate was condensed against the cooling plate and removed from the module under the action of the force of gravity into a collector.

The working membrane area was 48 cm². Thermopervaporation process was conducted at a feed temperature of 40–70 °C (±0.2 °C), and the downstream pressure was equal to the atmospheric pressure. The condensation temperature of the permeate was varied from 0 to 20 °C.

Flux was estimated by weighting the collected permeate. Total permeate flux J [kg/m² h] was calculated as $J = m/(st)$ where m is the weight of the permeate [kg] passed through the membrane with area s [m²] within time t [h]. Separation factor for the binary mixture is calculated as

$$\alpha = \frac{Y/(1-Y)}{X/(1-X)},$$

where Y and X stand for the weight fractions of the target component (butanol) in the permeate and feed mixtures, respectively. Then, mass fluxes of butanol and water in the permeate are $J_b = J \cdot Y$ and $J_w = J - J_b$.

Composition of the feed and permeate mixtures was analyzed by the method of gas chromatography on a Crystallux 4000 M gas chromatograph equipped with a TCD detector; the working parameters were the following: the injection temperature was 220 °C, the column temperature was 180 °C, and the detector temperature was 220 °C. The probes were analyzed on a Porapak Q packed column. The water-butanol permeate (which is a two-phase system) was examined by adding water to homogenize the sample.

The efficacy of the pervaporation process was characterized by the pervaporation separation index ($PSI = J \cdot (\alpha - 1)$), which depends on the joint action of the two factors – permeate flux and separation factor.

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