



Biobutanol concentration by pervaporation using supported ionic liquid membranes

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ABSTRACT

ABE fermentation uses anaerobic bacteria to produce acetone, butanol and ethanol from carbohydrates. Nowadays, ethanol is used as a petrol additive but butanol, due to its unique properties, can become a future biofuel. To recover *n*-butanol from the fermentation broth, pervaporation can be used. However, separation performance of pervaporation is limited by the polymeric membrane. This problem can be overcome by using an ionic liquid, immobilized in the active layer of the membrane.

This paper investigates the performance of supported ionic liquid membranes (SILMs) employed for the pervaporative concentration of *n*-butanol. In the study, two ionic liquids (ILs), i.e. trihexyl(tetradecyl)phosphoniumtetracyanoborate ($P_{6,6,6,14}tcb$) and 1-hexyl-3-methylimidazolium hexafluorophosphate ($Im_6,1hfp$), were used. The ILs were immobilized with the help of polyether block amide (PEBA). To prevent the ionic liquids from leaching out, additional polymeric coating was necessary. For this purpose, an additional amount of PEBA was applied directly on the IL-PEBA layer. The pervaporation process was carried out at 29, 37 and 50 °C. The aqueous feed solution contained three organic components, i.e. acetone, butanol and ethanol in a 3:6:1 mass ratio. The concentration of butanol in the feed was 1.5, 3 and 5 wt%. It was found that the permeation fluxes as well as selectivity of the SILMs could be influenced by different ILs. The highest permeation flux, equal to 6,5 kg/(m² h), was observed for the membrane without an ionic liquid due to a higher water flux. However, the highest concentration of butanol in the permeate was achieved with the $P_{6,6,6,14}tcb$ membrane and the enrichment factor was found to be 14.93 while the selectivity for butanol in relation to water was equal to 8.34.

1. Introduction

The exploitation of fossil fuels such as coal, crude oil and natural gas brings many threats and leads to environmental pollution and degradation. The chemical industry faces the challenge of modifying the production of chemicals and fuels in order to keep the environment in good condition [1].

In recent years, the biological production of fuels has gained considerable importance [2]. Biofuels, such as bioethanol, biobutanol and biodiesel [3], pose an attractive alternative to conventional fuels due to the growing demand for energy, limited supply of fossil fuels and need to reduce global greenhouse gas (GHG) emissions. Table 1 shows a comparison of biofuels with gasoline and diesel fuel [4].

Considerable attention has been drawn to biobutanol, which can potentially become one of the future fuels thanks to its attractive physicochemical properties. Its combustion properties are similar to the properties of gasoline [5,6]. Biobutanol is most commonly produced through the fermentation of sugar, glycerol or lignocellulose feedstocks

[7–9], mainly by *Clostridium* bacteria [10]. *Clostridium acetobutylicum* and *Clostridium beijerinckii* have been the most widely studied strains [11].

Unfortunately, butanol exerts a dominant inhibitory influence on the bacteria, leading to low productivity and its low final concentration in the broth [12]. Technical studies propose genetic modification of the microorganisms in order to increase the amount of products [13,14]. Nevertheless, the concentrations of ABE in the broth still remain relatively low, thus efficient separation methods are desired. Therefore, to improve the efficiency of production, butanol should be continuously removed from the broth, which can be accomplished through the integration of a proper separation method into the fermentation process [15].

According to existing research, several unit operations such as distillation, gas-stripping, adsorption or liquid-liquid extraction can be utilized to separate biobutanol from the broth [16,17]. However, pervaporation is considered one of the most promising techniques. Pervaporation is used in many fields due to its high selectivity and energy

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Table 1
Comparison of properties of selected fuels.

Fuel	Calorificvalue (MJ/L)	RON	MON	Air-fuel ratio	Boiling point [°C]	Freezing point [°C]
Butanol	29.2	96	78	11.2	117.7	–88.6
Ethanol	21.2	129	102	9.0	78.4	–114.3
Gasoline	32.5	91–99	81–89	14.7	27–225	–40.0
Diesel	32.5	–	–	14.6	188–343	–40 to –34

consumption lower than that of conventional separation techniques. Huang et al. [18] compared pervaporation with other separation processes and concluded that pervaporation, solvent extraction and adsorption were the most energy-efficient approaches to the removal of butanol from ABE fermentation broths. The most important advantages of pervaporation include low energy demand and the possibility to separate azeotropic mixtures [19]. Pervaporation is able to efficiently recover alcohols [20,21] from fermentation broths [22,23]. The application of pervaporation to the recovery of butanol is possible if an appropriate membrane is used [15,24–30].

In 1975, Hwang and Kammermeyer [31] defined a membrane as a solid phase dividing another two phases. The membrane can be considered the “heart” of the pervaporation process as it selectively transfers components from the feed to the other, permeate side. The membrane selectivity $\alpha_{i,j}$ for component “i” in relation to another component “j” is most commonly calculated using the concentration of the preferentially permeating component compared with the concentration of the component that is blocked by the membrane – Eq. (1):

$$\alpha_{i,j} = \frac{w_{iP} w_{jF}}{w_{iF} w_{jP}} \quad (1)$$

The enrichment factor E_i can be calculated using Eq. (2):

$$E_i = \frac{w_{iP}}{w_{iF}} \quad (2)$$

where:

w_{iP}, w_{iF} – mass fraction of component i – in the permeate P and the feed F, respectively [–]

w_{jP}, w_{jF} – mass fraction of component j – in the permeate P and the feed F, respectively [–]

The efficiency of pervaporation with regard to butanol can be assessed by calculating the total permeation flux, enrichment factor and selectivity.

Selecting the correct material is important for the preparation of pervaporation membranes [32]. The fundamental criteria are:

- high chemical and mechanical resistance to guarantee long life and stability of the membrane,
- excellent sorption capacity and permeability,
- preferential transfer of the target compound to ensure high performance,
- stability at high temperatures.

The separation process is controlled mainly by the thin active layer; therefore, selecting a suitable material forming the active layer of the membrane becomes a crucial issue. For this reason, new approaches to membrane modification are being sought, including the immobilization of ionic liquids in the membrane to improve the efficiency of the polymer [33]. The immobilization of ILs allows producing membranes with different properties. It also gives an opportunity to create highly selective membranes offering high permeability in comparison with classical ones.

Ionic liquids are organic salts with melting points lower than 100 °C. Room temperature ionic liquids (RTILs) are liquid at room temperature.

Unlike traditional solvents, which can be described as molecular liquids, ionic liquids are composed of ions [34,35].

Recently, ionic liquids have received considerable attention due to their interesting and unique physicochemical properties, negligible vapour pressure, stability over wide temperature ranges, ability to dissolve organic and inorganic compounds and their hydrophobic or hydrophilic nature [36]. These properties have made them an environmentally friendly alternative to traditional organic solvents. Moreover, the possible number of obtainable ionic liquids possessing different properties is very large [37]. Current findings in membrane science indicate that applying appropriate ionic liquids with the intention of recovering butanol increases the selectivity of pervaporation membranes [38].

Membranes with an immobilized ionic liquid are known as supported ionic liquid membranes (SILMs) [39]. Available research papers inform of several methods of membrane modification that can be employed to improve the separation of biobutanol via pervaporation [40–42]. One of the most promising, however, is combining extraction with pervaporation, which relies on the immobilization of an ionic liquid in the membrane [43,44].

This paper concentrates on the pervaporation process, in which the components of the feed solution were selectively separated by the active layer of the membrane. The main purpose of the study was to confirm that the immobilization of ionic liquids in polymeric pervaporation membranes would improve their separation abilities. Double layer membranes with an IL immobilized in the active layer were produced and investigated. The pervaporation process was conducted at 29, 37 and 50 °C using a four-component feed solution containing acetone, butanol, ethanol and water. The feed concentration of *n*-butanol was equal to 1.5, 3 and 5 wt%.

2. Experimental

2.1. Materials

The experiments were performed with membranes containing an immobilized ionic liquid. The selection of ionic liquids was based on the liquid-liquid extraction (LLE) results given in [45–47] and their affinity for butanol. Table 2 shows the recorded differences in the distribution coefficient and selectivity of the selected ionic liquids, achieved with regard to butanol extracted from aqueous solutions. It should be noted that the ionic liquids provide either a high distribution ratio and low selectivity or a low distribution ratio and high selectivity. On the other hand, Garcia-Chavez and co-workers used tetraoctylammonium 2-methyl-1-naphthoate (TOAMNaph) to separate BuOH from water and achieved much higher distribution coefficient accompanied by good selectivity, which makes TOAMNaph worth investigating in future research on pervaporation.

The chemical structures of the ionic liquids that were selected for their high selectivity and used in the membrane preparation process are presented in Fig. 1.

- trihexyl(tetradecyl)phosphoniumtetracyanoborate ($P_{6,6,6,14}tcB$), provided by Merck KGaA,
- 1-hexyl-3-methylimidazolium hexafluorophosphate ($Im_{6,1} hfp$), provided by IoLiTec GmbH.

Table 2
Distribution coefficient and selectivity of the selected ionic liquids towards butanol in liquid-liquid extraction [45–48].

Ionic liquid	$Im_{6,1}tcB$	$P_{6,6,6,14}tcB$	$Im_{6,1}hfp$	TOAMNaph
Distribution coefficient [–]	3.2	2	2.5	21
Selectivity [–]	100	500	72	274

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