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Extraction of butanol from aqueous solutions using a membrane contactor and an ionic liquid

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ABSTRACT

The aim of the study was to evaluate the membrane extraction of butanol from aqueous solutions employing hydrophobic and highly selective ionic liquid. In comparison with the typical recovery processes, the membrane extraction provides higher selectivity and lower energy consumption. The extraction was performed using 1-hexyl-3-methylimidazolium tetracyanoborate ionic liquid and the polypropylene hollow fiber membrane contractor. The concentration of butanol in the feed solution was equal to 3 wt% and feed flow rate was equal to 10 dm^3 h^{-1}. Different feed pressures ranging from 0.03 to 0.07 MPa were applied. On the basis of the experimental results, the conditions ensuring an efficient extraction process were established.

Keywords: Biobutanol; Membrane extraction; Membrane contactor; Ionic liquid

1. Introduction

Nowadays, the greatest part of the energy used globally is obtained from conventional resources such as coal, natural gas and oil. The continuous depletion of these fuels increases the demand for renewable resources. Biomass is organic matter produced by plants or animals, and it can also be a waste product from various processes. Biofuels have a high energy potential. Compared with the conventional fuels, biofuels such as bioethanol or biodiesel have a number of beneficial properties as substitutes for petroleum and its derivatives. Some of them have higher energy content and exhibit lower toxicity. Alcoholic fermentation is one of the oldest and most understood biotechnological processes. Materials containing starch (cereal grains, corn) or sucrose (sugar cane, sugar beets) are usually used as substrates for this process. Most of the current studies on biofuels concentrate on bioethanol (produced by fermentation of sugars) and biodiesel (produced by transestrification of oil). Both of them are mainly used as additives to fuels and significantly affect their quality [1,2].

2. Biobutanol

Biobutanol (predominantly n-butanol) is a product of acetone-butanol-ethanol (ABE) fermentation, which commonly involves the use of Clostridium bacteria. Considering the combustion properties, similar to those of gasoline and more favorable than ones of bioethanol, biobutanol can play a key role in the fuel industry, thus in reducing the use of fossil fuels [3].

First of all, n-butanol is less corrosive to the engine components than ethanol, its vapor pressure is lower and it is non-hygroscopic. The calorific value of n-butanol is close to that of gasoline (29.2 MJ dm^{-3} and 32 MJ dm^{-3}, respectively) and higher than that of ethanol (19.6 MJ dm^{-3}). The heat of evaporation of n-butanol is slightly higher than that of gasoline (0.43 MJ dm^{-3} and 0.36 MJ dm^{-3}, respectively). However, it is still much lower than that of ethanol, which is

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equal to 0.92 MJ dm^{-3}. Furthermore, compared with ethanol, n-butanol is also relatively resistant to the uncontrolled spontaneous combustion. According to the current regulations, bioethanol must be added to gasoline (in some EU countries even up to 10%). The consumption of pure gasoline and consumption of gasoline blended with bioethanol are similar (because of the energy content). On the other hand, the addition of ethanol causes the fuel consumption to go up; hence, the emission of greenhouse gases increases [4–7].

At present, the large-scale use of biobutanol is difficult because of its price (984 € m^{-3}, while in case of gasoline, it is equal to 558 € m^{-3}). It is partly caused by the high cost of bioorganic substrate and the cost of butanol recovery from the fermentation broth. The ABE fermentation produces butanol in low concentrations (0.5–3 wt%), which combined with its high boiling point (117.2°C), makes the separation process difficult – traditional distillation is highly demanding in terms of energy and economically unreasonable. Nowadays, alternative and often more effective methods are taken into consideration [3,6–9].

In this work, an ionic liquid (IL) was used as an extrahent. The main advantages of IL application are as follows:

- near-zero vapor pressure,
- significant temperature range of their stability with a negligible vapor pressure,
- dissolution of organic and inorganic compounds,
- hydrophobicity or hydrophilicity.

ILs were identified as non-flammable, non-volatile, nontoxic, thermally and chemically stable, thus suitable for applications in separation processes.

Works of Simoni et al. [10] and Ha et al. [11] suggested that the imidazolium-based ILs displayed favorable properties for butanol recovery. Recently, liquid–liquid extraction of n-butanol has been intensely studied and each year new results and novel ILs become known and available.

3. Materials and methods

3.1. Reagents

In the study, IL, that is, 1-hexyl-3-methylimidazolium tetracyanoborate ([HMIM][TCB]), supplied by Merck KGaA (Germany) of purity >99% was used. The chemical structure of [HMIM][TCB] is shown in Fig. 1. Butanol of 99.5% purity was purchased from Chempur (Poland).

3.2. Membranes

The membrane extraction process was performed in a contactor containing microporous hollow fiber membranes, 3 mm in diameter. The membrane contactor consisted of seven membranes with the total external surface area of 0.013 m^2. The membranes (made of polypropylene) were purchased from Polymem (Poland).

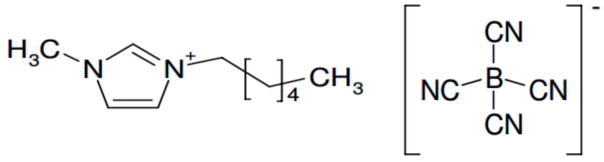

Fig. 1. Chemical structure of 1-hexyl-3-methylimidazolium tetracyanoborate IL.

4. Experimental installation

The experimental setup is shown in Fig. 2.

The aqueous solution containing 3 wt% of butanol was pumped by the gear pump (P) from the thermostated tank (TT) through the capillary membranes located in the membrane contactor (MC). The feed flow rate was equal to 10 dm^3 h^{-1} and the feed pressure, regulated with the precise needle valve (PV), varied from 0.03 to 0.07 MPa. The IL was fed into the shell side of the contactor with the peristaltic pump. Each experiment lasted for 8 h at 25°C. In membrane extraction, butanol and water were permeates transported into the IL (extracting agent). Next, the IL was regenerated for 2 h at 50°C and 10 kPa using the vacuum evaporator. After the evaporation process, the concentrated alcohol solution was subjected to compositional analysis using a gas chromatograph.

The total permeate flux and mass flux of butanol were calculated according to Eq. (1):

$$J_i = \frac{m_i}{A \cdot t} \quad [\frac{g}{m^2 \cdot h}] \tag{1}$$

where J_i is flux of the component [g m^{-2}·h], m_i is mass of the component i [g], A is surface area of the membranes [m^2], and t is time [h].

A mean value of three different measurements was determined and standard deviation was calculated.

5. Results and discussion

Fig. 3 shows how the concentration of butanol in the permeate changed with the feed pressure. In all the experiments,

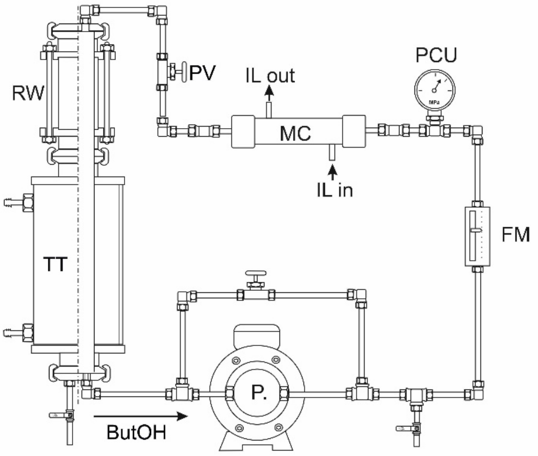

Fig. 2. Schematic diagram of the experimental setup for membrane extraction of butanol from diluted aqueous solutions: TT – thermostated tank, ButOH – flow of the feed solution, P – gear pump, FM – flow meter, PCU – pressure control unit, PV – pressure valve, MC – membrane contactor, RW – revision window, IL in and IL out – inlet and outlet of the ionic liquid.

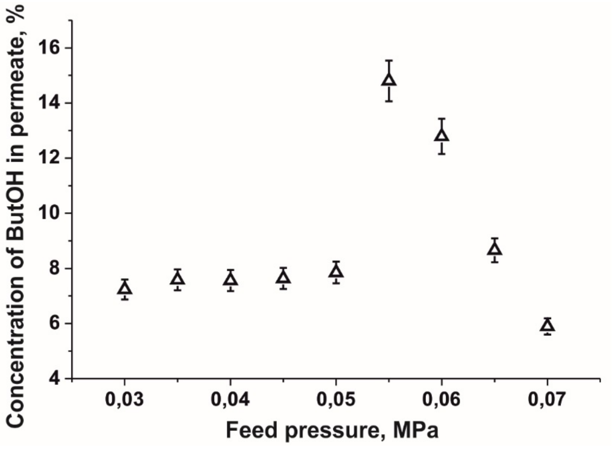

Fig. 3. Concentration of butanol in the permeate in relation to the feed pressure.

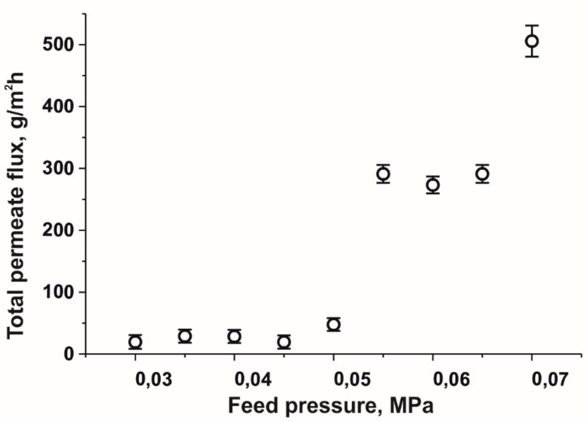

Fig. 4. Total permeate flux at different feed pressures.

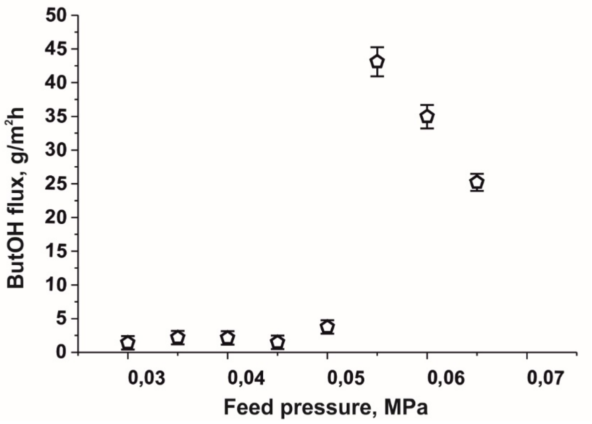

Fig. 5. Butanol flux at different feed pressures.

butanol was successfully separated; however, a small increase in the butanol permeate concentration (up to 8 wt%) was recorded at the feed pressure of 0.05 MPa.

The transmembrane mass transfer at the feed pressures of up to 0.05 MPa was mainly caused by the contact between the IL and the vapors of the water-butanol mixture. The feed pressure of 0.05 MPa was not sufficient to fill the membrane pores with the feed solution. Thus, there was no direct contact between the IL and the feed. At 0.055 MPa, the concentration of butanol in the extract reached 14.8 wt%. The feed penetrated membrane pores and the process of extraction occurred at the liquid–liquid interface. The hydrophobic properties of both, the IL and the membrane promoted the diffusion of butanol into the extract. In Figs. 4 and 5, the permeate and butanol mass fluxes changes related to the feed pressure are presented.

At the feed pressures ranging from 0.03 to 0.05 MPa, low permeate and butanol fluxes were observed – up to 50 g $m^{-2}h^{-1}$ and 3 g $m^{-2}h^{-1}$, respectively. At the same time, the highest butanol flux equal to 43.1 g $m^{-2}h^{-1}$ was recorded at the feed pressure of 0.055 MPa. However, at higher feed pressures, the butanol flux decreased in opposite to the growing permeate fluxes – the feed started getting through the membrane while the extraction process still went on. At the feed pressure of 0.065 MPa, the feed flow across the membrane began to dominate over the extraction mechanism.

6. Conclusions

The experimental results confirm that the membrane extraction of butanol from aqueous solutions can be successfully performed with the help of [HMIM][TCB] IL. The feed pressure is the most important factor in the system determining the final concentration of butanol in the permeate. At lower pressures, the mass is transferred between the water-butanol vapor and the IL, and this process is not highly efficient (the butanol flux of up to 3 g $m^{-2}h^{-1}$ and its concentration in the permeate of up to 8 wt% were achieved). The increase of the feed pressure causes the aqueous butanol solution to fill the membrane pores, thus enabling the liquid–liquid extraction process. Under these conditions, the best results were achieved – the butanol flux and its concentration reached 43.1 g $m^{-2}h^{-1}$ and 14.8 wt%, respectively. The application of the hydrophobic and selective IL makes the separation process even more productive. However, further the pressure increase led to the process breakdown – the feed passed *t* membrane pores and the resulting concentration of butanol in the permeate dropped.

Symbols:

J^i — Flux of component *i*, g $m^{-2}h^{-1}$
m^i — Mass of component *i*, g $m^{-2}h^{-1}$
A — Surface area of the membrane, m^2
t — Time, h

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