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# Performance evaluation of silica membrane for water–n-butanol binary mixture

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ABSTRACT

The pervaporation performance of a commercial silica membrane (Pervatech BV) was evaluated for dehydration of aqueous n-butanol solutions. The influence of the operation parameters, such as feed composition, temperature and permeate pressure was experimentally investigated in terms of permeation flux, separation factor, permeance and membrane selectivity. The membrane exhibited high flux, 3.53 kg/m$^2$ h, combined with a separation factor equal to 150, at 70 °C and for 10 wt.% water in feed. The mole fraction of water in the permeate ranged from 98.7% to 99.2% at 70 °C. The information collected is of most importance to design and optimize a pervaporation process for the dehydration of n-butanol, which can be integrated with an intensified technology, the simulated moving bed reactor, used in the synthesis of the green fuel, 1,1-dibutoxyethane.



## 1. Introduction

During the last two decades, there has been a continuous improvement in the production methods due to the increasing competitiveness in the market. Those factors have led industry to search and invest into new technology in order to improve its production performance at low costs [1]. Membrane – based technology is currently regarded as a new frontier of chemical engineering and has been widely used in various applications in medicine, food and petrochemical industry, energy and environmental fields [2,3]. Membrane separation processes have many advantages over the existing separation processes such as high selectivity, low energy consumption, moderate cost to performance ratio, compact and modular design [4]. A promising membrane based technique is Pervaporation (PV).

PV is used to separate a liquid mixture by partly vaporizing it through a permselective membrane (Fig. 1). The feed liquid mixture flows along one side of the membrane, and a fraction of it (permeate) is recovered in the vapor state on the other side of the membrane, by means of vacuum or sweep gas. The mass transport through the membrane is induced by maintaining a low vapor pressure on the permeate side, eliminating thereby the effect of osmotic pressure [5].

PV is as an attractive alternative to the traditional separation techniques; to date different PV applications have been investigated as [1,6,7]: (i) dehydration of organic solvents (e.g. alcohols, ethers, esters, and acids), (ii) removal of dilute organic compounds from aqueous streams (e.g. removal of VOCs, recovery of aroma and biofuels from fermentation broth), and (iii) organic–organic mixtures separation (Methyl tert-butyl ether (MTBE)/Methanol (MeOH), Dimethyl carbonate (DMC)/MeOH).

Membranes are the key for the separation efficiency of any membrane process. Therefore, an extensive research has been done in order to find an optimized membrane material, having selective interaction with the desired component of the liquid feed solution in order to obtain high values of permeation flux and separation factor [8]. The performance of a membrane material depends on its structure (geometry, porosity, pore size, thickness and nature of the top layer), but also on its properties (synthesis composition, temperature, hydrophobicity or hydrophilicity) [9].

For PV and especially for dehydration of solvent mixtures, numerous membranes have been reported [4,9–28]. Both organic and inorganic membrane materials have been tested. Until now, mostly polymeric membranes have been used at industrial scale [4].

Cross-linked poly(vinyl alcohol) (PVA) polymer based membranes show high water permselectivity, but with relatively low permeation flux [10]. Polymer membranes are cheaper than ceramic inorganic membranes, but they exhibit limited thermal,

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**Nomenclature**

| | |
|---|---|
| $A$ | membrane area ($m^2$) |
| $D$ | diffusion coefficient ($m^2/s$) |
| $D_0$ | pre-exponential factor of Eq. (10) ($m^2/s$) |
| $E_D$ | activation energy of diffusion (J/mol) |
| $E_p$ | activation energy of permeation (J/mol) |
| $E_J$ | apparent activation energy (J/mol) |
| $\Delta H$ | enthalpy of adsorption (J/mol) |
| $J_i$ | permeate flux of component $i$ (mol/($m^2$ s)) |
| $J_0$ | pre-exponential factor of Eq. (8) (mol/($m^2$ s)) |
| $J_{tot}$ | total permeate flux (mol/($m^2$ s)) |
| $l$ | thickness of the selective layer of the membrane (m) |
| MRD | mean relative deviation |
| $n_{exp}$ | number of experiments |
| $P$ | permeability coefficient (mol/(m s Pa)) |
| $P_0$ | pre-exponential factor of Eq. (12) (mol/(m s Pa)) |
| $P^0$ | saturation pressure (Pa) |
| $P_{perm}$ | total pressure on the permeate side (Pa) |
| $Q$ | permeance (mol/($m^2$ s Pa)) |
| $R$ | ideal gas constant (J/(mol K)) |
| $S$ | solution coefficient (mol/($m^3$ Pa)) |
| $S_0$ | pre-exponential factor of Eq. (11) (mol/($m^3$ Pa)) |
| $t$ | time variable (s) |
| $T$ | temperature (K) |
| $w$ | mass fraction |
| $x_i$ | liquid mole fraction of component $i$ in the feed side |
| $y_i$ | mole fraction in the vapor phase of component $i$ |

*Greek letters*

| | |
|---|---|
| $\gamma_i$ | activity coefficient of component $i$ |
| $\alpha$ | process separation factor |

*Subscripts*

| | |
|---|---|
| $i$ | component $i$ ($i$ = water, n-butanol) |
| *calc* | calculated |
| *exp* | experimental |

mechanical and chemical stability, giving place to the interest on development of more stable multipurpose membranes.

In the last ten years many attractive, high-flux inorganic membranes with good thermal and chemical stability have been developed for the separation of molecular mixtures [11]. They exhibit better structural ability than organic membranes without the problems of swelling or compaction, withstanding harsh chemical environments and high temperatures [12]. Two types of inorganic membrane materials are being used in the dehydration of organic solvents: hydrothermally synthesized zeolite membranes and sol–gel derived silica membranes.

Zeolites have emerged as quite noble and attractive membrane materials, which have been tested in laboratory and pilot scale production [13,14]. They have very narrow pore size distribution and therefore they show high molecular sieving ability. High quality NaA zeolite membranes, with both high selectivity and permeability, have been synthesized, for the dehydration of solvents, by different research groups [15–19]. Nevertheless, the cost of zeolite membranes (linked to their present development) is still significantly high to make their use economically viable [29].

Silica or silica – based membranes are a promising inorganic material highly selective with high flux rates during pervaporation. They have, in general, wide pore size distribution, consisting of micropores formed as silica network pores, medium sized pores formed as either inter-particle pores and/or grain boundaries, and large pores as pinholes [20]. Prepared by the sol–gel method, they comprise an extremely thin active top layer on coarse layers or porous supports [21–24].

Recently, hydrophilic zeolites and silica membranes, stable at elevated temperatures and pressures, have become commercially available (Mitsui Engineering & Shipbuilding Ltd.; Netherlands Energy Research Foundation ECN; Pervatech PV; Sulzer Chemtech).

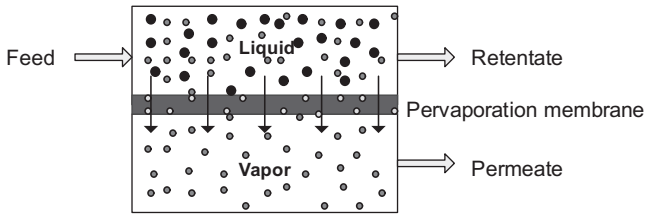


**Fig. 1.** Schematic representation of the pervaporation process.

In Table 1 is listed the performance of commercial organic and inorganic membranes for the dehydration of various organic solvents [27,30–38]. It can be concluded that commercial inorganic membranes (silica and zeolites) offer a great application potential in the dehydration of organic solvents. Silica membranes (from ECN and Pervatech) exhibit high permeation flux rates (1.0–5.2 kg/$m^2$ h) with good separation factors (10–4100) in the temperature range of 60–80 °C. Zeolite membranes present the highest water selectivities, up to 16,000, but with lower fluxes than silica membranes. This can be clearly seen in Fig. 2.

According to the literature data presented in Table 1 and Fig. 2, it can be concluded that the commercial microporous silica membrane from Pervatech BV reveals a good compromise between water permeation flux and selectivity in the dehydration of alcohols. Therefore, the pervaporation performance of the silica Pervatech membrane will be assessed, in this work, for n-butanol dehydration. An extensive study of the effect of the operating conditions (permeate pressure, feed concentration and temperature) will be presented and discussed in terms of the pervaporation parameters (permeation flux, separation factor, permeance and selectivity).

These will be useful data to design and optimize a complete production plant for the synthesis of the green fuel, 1,1-dibutoxyethane (DBE), using simulated moving bed reactor (SMBR) technology. In the DBE synthesis by SMBR, two outlet streams are obtained: (i) the extract stream comprising water/n-butanol and (ii) the raffinate stream comprising DBE and n-butanol [39]. The efficient recover of n-butanol from both streams is of the most importance for the viability of the DBE production process.

## 2. Theory – analysis of pervaporation membrane performance parameters

The selective ability of a pervaporation membrane, as in a gas separation membrane, can be estimated by performance parameters like the total permeation flux through the membrane and the separation factor of the desired component.

The total permeation flux, $J_{tot}$ (kg/$m^2$ h), can be determined experimentally by using the following equation:

$$J_{tot} = \frac{m}{A * t} \quad (1)$$