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Separation of diluted butanol–water solutions via vapor phase by organophilic membranes based on high permeable polyacetylenes

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ABSTRACT

The diluted organic-water solutions are convenient products of biomass treatment to biofuels (e.g., ABE fermentation). A continuous membrane-assisted method by example of butanol recovery from fermentation media is considered in present work. The method is based on combination of the gas stripping (convenient process) with membrane vapor separation (with preferable butanol vapor permeability). In comparison with known membrane pervaporation method the suggested one possesses such advantageousness as an expanded membrane module area and resistance to fouling. Main attention is put on fundamental aspects of separation: (1) the contribution of liquid/vapor phase transition and (2) vapor selective properties of organophilic membranes. Two polymers: poly-1-trimethylsilyl-1-propyne (PTMSP) and poly-4-methyl-2-pentyne (PMP), and two their block copolymers (with PTMSP–PMP ratio 60:40 and 25:75) are suggested as membrane materials for this purpose. Vapor permeability of water, butanol and butanol–water solutions are determined for selected polymers and block copolymers at different temperatures and butanol–water solution concentrations. Apparent activation energy and temperature parameter of permeability of water and butanol vapors in PTMSP and PMP membranes are obtained. The methodology of study can be used for the systematic research of the vapor permeability membrane properties influence on separation of liquid multi-component mixtures with taking into account of liquid/vapor equilibrium.

1. Introduction

The development of energy production from renewable sources would provide saving of natural resources and improving of environment [1]. Last years the interest to different kinds of biofuels (such as biomethane, biohydrogen, biodiesel, bioalcohols) grows up permanently. Biobutanol is considered as one of the most perspective biofuel due to its great physical–chemical properties: high energy content, high octane number, low volatility and others [2–4]. Butanol is also used for production of plasticizers and solvents in chemical industry; it is a good extracting agent and solvent for pharmaceutical and perfumer industry. Nowadays the major part of butanol is produced by propylene oxo-synthesis, i.e., from petroleum. Alternative technology of butanol production that was widely used at the beginning of 20th century is fermentative treatment of biomass. This process is well known and ecologically clean but it has essential drawback, that is, low final content of butanol (which is inhibitor of bioprocess) in fermentation broth (about 1 wt%) [5]. Therefore such technology demands application of lower energy consuming separation system for recovery and concentrating of butanol [6–9].

Traditional methods of liquid mixtures separation are distillation, extraction and adsorption [10,11]. Membrane methods of liquid mixtures separation were developed relatively recently but they are already considered as reagent- or adsorbents-free technologies possessing higher energy efficiency in comparison with distillation [12]. Pervaporation is one of the most appropriate membrane methods for butanol recovery and concentration from fermentation broth. Nevertheless it has such significant disadvantage as direct contact of membrane with bio-medium that leads to membrane fouling by microorganisms and non-volatile organic substances [12]. Additionally, it has restrictions for membrane area contacted with bio-medium inside of bioreactor to provide efficient removing of butanol as inhibitor.

Alternative membrane-assisted method of butanol recovery from fermentation broth is considered in this paper. The method is based on combination of gas stripping and membrane vapor separation (Fig. 1). The gas stripping is used for the transfer of butanol from liquid fermentation solution into vapor phase in accordance with the positive deviation of vapor–liquid equilibrium from Raoult law for butanol–water solutions at lower alcohol concentrations. Actually, the vapor phase membrane method is used for butanol recovery from fermentation broth

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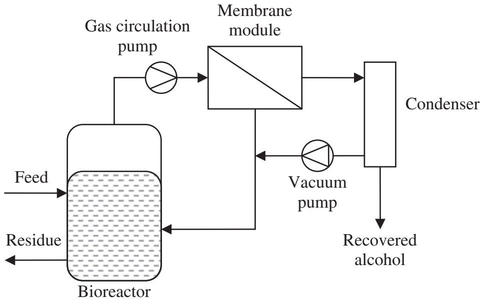

Fig. 1. The principle of bioalcohol recovery by combination of gas stripping with vapor phase membrane separation method.

just after gas stripping [11,13]. Such approach allows carrying out the continuous recovery of butanol from bioreactor as pervaporation does and to avoid drawbacks of pervaporation. Also, this method can be applied for recovery of ethanol or any other volatile products if appropriate membrane is selected.

The recovery of butanol which is minor impurity in water requires the application of organophillic membranes which are more permeable toward organic molecules (e.g., butanol) than toward water that is typical for rubbery membrane materials, for example, for polydimethylsiloxane (PDMS). PDMS-based membranes are the widest studied membranes in the area of bioalcohols recovery from fermentation media by pervaporation technique. However, the permeance of PDMS membranes and resistance to biomedia attack are not sufficient for its industrial application [12,14]. Nowadays glassy organophilic polyacetylenes are considered as promising materials for membrane separation of organic/water solutions because they could provide production of high permeable membranes. For example, a well known poly-1-trimethylsilyl-1-propyne (PTMSP) is the most permeable polymer up to this day [15,16]. PTMSP has been widely investigated in a large number of studies as pervaporation membrane material for alcohol–water mixtures separation [16]. Poly-4-methyl-2-pentyne (PMP) is a “carbon” analogue of PTMSP and rather new membrane material. PMP shows high mass transfer coefficients for gases and vapors and demonstrate higher stability towards different organic solvents compared to PTMSP [17]. Main attention is put on fundamental aspects of separation: (1) the contribution of liquid/vapor phase transition and (2) vapor selective properties of organophilic membranes. Actually, these two stages are realized in pervaporation at once. Two polymers: poly-1-trimethylsilyl-1-propene (PTMSP) and poly-4-methyl-2-pentene (PMP), and two their block copolymers (with PTMSP–PMP ratio 60:40 and 25:75) are suggested as membrane materials for this purpose. Vapor permeability of water, butanol and butanol–water model diluted solutions is determined for selected polymers and block copolymers at different temperatures and butanol–water solution concentrations. Apparent activation energy and temperature parameter of permeability of water and butanol vapors in PTMSP and PMP membranes are obtained. In whole, the methodology of study considered can be used for the general study of the vapor permeability membrane properties influence on separation of liquid multi-component mixtures with taking into account of liquid/vapor equilibrium.

2. Experimental

2.1. Materials

Synthesis of PTMSP, PMP (chemical structures are shown in Fig. 2) and their block copolymers was carried out according to the procedures described earlier in [17–19]. PTMSP–PMP ratio in two block copolymers was 60:40 and 25:75. The composition of block copolymers was determined by an elemental analysis performed by the pyrolysis chromatography using a Carlo Erba instrument (Italy). The intrinsic viscosities of polymer solutions in CCl_4 were measured at 25 °C with the aid of an Ubbelohde type viscometer. The molecular masses of polymer samples were determined by gel permeation chromatography (GPC) of polymer solutions on a Waters 600 Powerline system equipped with a differential refractometer Waters R401 as detector and two columns: 2 × PLgel 5 μ MiniMIX-C. Synthesized polymers were characterized by differential scanning calorimetry (DSC) performed in the 20–350 °C range (Mettler Toledo DSC-823e instrument), ^{13}C NMR (spectra registered by a Bruker instrument MSh-300 operated at 75.47 MHz) and IR-spectrometry (spectra recorded by a IFS-Bruker-113-V instrument in the 4000–200 cm^{-1} range). The obtained data is presented in Table 1.

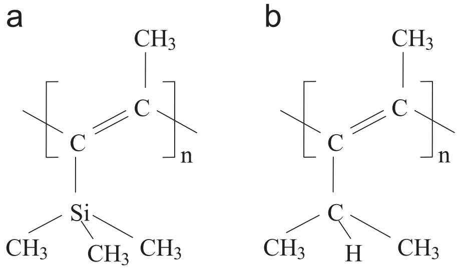

Fig. 2. Chemical structure of PTMSP (a) and PMP (b).

Table 1
Characteristic of studied polymers.

Polymer	T_g (°C)	[η] (dL/g)	M_w (g/mol)	M_w/M_n	*cis-/trans*-ratio
PTMSP	> 280	0.6 (toluene)	250,000	1.6	65/35
PMP	260	3.4 (CCl_4)	1000,000	2.5	35/65
PTMSP–PMP (60:40)	–	–	350,000	2.2	–
PTMSP–PMP (25:75)	–	–	630,000	2.7	–

Dense PTMSP films were cast from dilute toluene solution (3 wt%), PMP and co-polymers films were cast from cyclohexane solutions (2 wt%). Obtained films were dried in vacuum at ambient temperature till the constant weight. The thickness of polymeric films was 30 μm for PTMSP and PMP films, 28 μm for PTMSP–PMP (60:40) copolymer film and 25 μm for PTMSP–PMP (25:75) copolymer film. For vapor permeability measurements distilled water and butanol (≥ 99.7%) from Fluka were used as received.

2.2. Experimental setup

Transfer of water, alcohols and mixed vapors was studied using lab-scale setup shown in Fig. 3. Membrane cell and vessel with liquid (water, alcohol or mixture) were together placed in a gas thermostatic oven. Gas-carrier (nitrogen) was supplied through vapor saturator with liquid phase studied in order to obtain saturated vapor. Flow rate of gas-carrier was varied in the range of 5–8 cm^3/s. Total pressure (vapors and gas-carrier) in the upstream part of membrane cell was equal to 1 bar, downstream part of membrane cell was evacuated by membrane vacuum pump. Pressure in downstream part was measured by digital vacuum manometer Edwards High Vac (M). Operating area of