A cascaded pervaporation process for dehydration of acetic acid

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HIGHLIGHTS

- Cascaded PV has been utilized for the separation of acetic acid–water.
- The CAPE-OPEN to CAPE-OPEN (COCO) simulator was employed to assist the study.
- Comparison between three different PV configurations has been performed.
- Dehydration of acetic acid was achieved, obtaining 99.7 wt% acetic acid.

ARTICLE INFO

ABSTRACT

Pervaporation is advantageous in separating close-boiling point mixtures, azeotropes, thermally sensitive compounds and purification of chemicals. However, one pervaporation unit may not be economically feasible to simultaneously provide a high purity of compounds in both the retentate and the permeate streams. In this study, a cascaded pervaporation method is developed aiming to dehydrate 85 wt% acetic acid solution from a basis feed of 100 kg/h. First, pervaporation experiments were performed using lab-made PPSU membranes. In pervaporation, the separation factor depends on the intrinsic properties of the membrane and on the operating conditions. These aspects cause a variation of the separation factor in pervaporation from 2 to 24. The process with one pervaporation unit, a cascaded PV system, and a cascaded PV with recycle stream is evaluated. This study demonstrates an efficient dewatering of acetic acid from an initial feed of 85 wt% acetic acid, obtaining 99.7 wt% acetic acid at rate of 72.8 kg/h using a cascaded PV with recycle stream. The large membrane area requirement in PV due to the low flux may be the main limitation for PV. Therefore, the development of new membranes exhibiting a high flux and a high selectivity are vital to decrease the membrane area, which may improve the potential for realizing these processes on a commercial scale.

1. Introduction

Pervaporation (PV) is well-known separation processes for liquid/liquid separations. It is commonly applied for the separation of organic aqueous solutions such as water/alcohol (Chiang and Hu, 1991; Hirotsu et al., 1988; Liu et al., 2005) and organic acid/aqueous solutions (Alghezawi et al., 2005; Asman and Sanli, 2003; Chen et al., 2011; Deng et al., 1994; Jullok et al., 2011), and more recently, for organic–organic separations (Luis et al., 2012; Parvez et al., 2012). PV is a non-pressure driven process that requires a vacuum at the downstream of the membrane to allow separation by partial vaporization through a dense and selective membrane. This process offers the most economical option for feeds with low water content (Chemtech, 2004).

Separation of acetic acid from water using distillation is difficult and energy-intensive due to the close boiling points of water and acetic acid, leading to large number of trays in the distillation column to perform the separation, which increases the associated costs (Chien et al., 2004). Stand-alone PV processes and cascade not making use of distillation (e.g., cascaded–PV) can improve the overall efficiency of the separation while reducing the energy consumption. In this work, the separation of acetic acid and water was studied experimentally for PV and the possibility of combining series of PV was studied. The simulation part was modeled using the CAPE-OPEN to CAPE-OPEN (COCO) simulator with inclusion of custom models using Matlab.

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2. Materials and methods

2.1. Experimental

2.1.1. Materials

Polyphenylsulfone (PPSU, Radel® R-5000) with an average molecular weight of 50,000 g mol^{-1} was obtained from Solvay Advanced Polymer Belgium and dissolved in N-methyl-2-pyrrolidinone (NMP), purchased from Sigma Aldrich, Belgium. Acetic acid (HAc) was supplied by Chem Lab Belgium. Demineralised water with a conductivity of 5.6 μS/cm is produced using a reverse osmosis system. The laboratory scale PV membranes were synthesized using phase inversion, immersion-precipitation. Three different PPSU concentrations were used, denoted as 25-PPSU, 27.5-PPSU and 30-PPSU. Details of the membrane synthesis have been described elsewhere (Jullok et al., 2011, 2012).

2.1.2. Pervaporation experiments

A pervaporation study using the synthesized membranes was conducted using a Lab Test Cell Unit (Sulzer Chemtech) as shown in Fig. 1. Several concentrations of acetic acid and aqueous mixtures (i.e., 3–45 wt% water) at 50 °C were studied. The feed solution containing a mixture of acetic acid and water was filled in a 3 L stainless steel tank. The self-made flat sheet membrane was then dimensioned for a 1.963×10^{-3} m^2 effective membrane surface area (diameter=5 cm) before being mounted onto the membrane cell unit. The feed solution was circulated over the membrane using a centrifugal pump and left overnight to allow the membrane-feed mixture equilibrium. Due to the dense structure of the membrane top layer, the sorption of liquid into the dense layer to reach equilibrium between membrane and feed mixture normally takes a long time at ambient conditions. Thus, overnight immersion will ensure that both the membrane and the feed solution are in equilibrium prior to PV experiments. Vacuum was not employed on the permeate side during this period to avoid any possibility of components to escape from the system. From a previous study (Jullok et al., 2011), the membranes were found to be stable throughout different immersion conditions; different feed concentrations and temperatures after 24 h. An increase of about 20% of the degree of swelling (DS) on the PPSU membrane from pure water to pure acetic acid immersion was observed, but those experiments were performed using an immersion technique, this is contacting both the porous sub-layer and the dense top layer with the solution. The DS was shown to be caused mainly by the sorption of liquid into the porous sublayer. In this work, since only the dense top layer of the PPSU membrane is exposed to the feed liquid in the PV unit and more diluted solutions in acetic acid are used, significantly lower swelling is expected. Afterwards, vacuum was used achieving pressures below
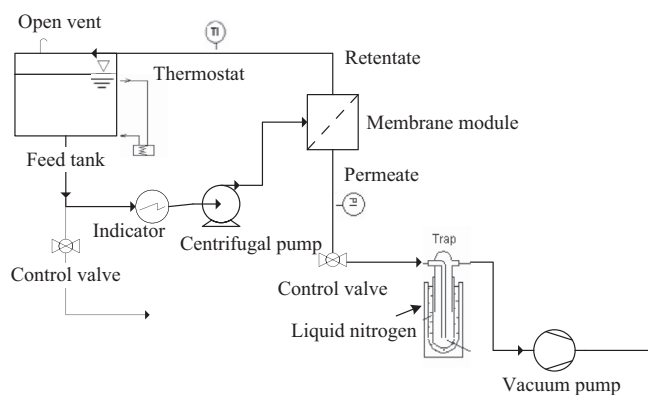
3 mbar and the experimental membrane flux was calculated as follows:

$$j = \frac{M_0 - M_f}{A.t} \tag{1}$$

where M is the initial and final weight collected (kg), t is the duration of the experiment (h) and A is the effective membrane area (m^2). In determining the partial flux of component i, J_i, the total permeate flux J is multiplied by the mass fraction of component i in the permeate. However, in gas separation, molar flux (j_i) is normally reported with unit cm^3(STP)/cm^{2}s since it allows direct comparison of PV data with the large body of gas permeation data (Baker et al., 2010)

$$j_i = J_i \frac{v_i^G}{m_i} \tag{2}$$

where v_i^G is the molar volume of gas i (22.4 l(STP)/mol) and m_i is the molecular weight of component i then, j_i is used to estimate the water or acetic acid permeability by applying Eq. (3).

$$\left(\frac{P}{l}\right)_i = \frac{j_i}{(\gamma x_i P^{sat} - y_i P_p)} \tag{3}$$

where P/l is the membrane permeability (P) to membrane thickness (l) ratio, i.e., the pressure-normalized flux or permeance in gas permeation units (GPU). The activity coefficient, γ, has been calculated using the Van Laar equation, and P^{sat} is the saturated vapour pressure calculated using the Antoine's equation. The mole fraction in the feed solution is defined as x, y is the mole fraction in the permeate and P_p is the permeate pressure obtained for the component during the PV. The permeate compositions were analyzed using a refractometer with an accuracy of ± 0.0005. The separation factor, β, and selectivity, α, were calculated using Eqs. (4) and (5) respectively:

$$\beta_{water} = \frac{y_{water}/yHAc}{x_{water}/xHAc} \tag{4}$$

$$\alpha_{water} = \frac{(P/l)_{water}}{(P/l)HAc} \tag{5}$$

2.2. Modelling of PV

The cascaded–PV system was modelled using the CAPE-OPEN to CAPE-OPEN (COCO) simulator with inclusion of custom models using Matlab. The interaction between all the simulation software components is based on the CAPE-OPEN specification standards. To build a simple membrane model using Matlab scripting language, Matlab Unit Operation was inserted. The ports are defined as feed, permeate and retentate. In order to solve the stream compositions, the permeate composition, X_p has to be calculated and must satisfy the target value of the separation factor, β, calculated experimentally using Eq. (4).

3. Results and discussion

3.1. Experimental performance

3.1.1. Pervaporation

In Fig. 2, it shows that all three PPSU membranes follow a similar trend: the separation factors at higher concentration of water (between 15–45 wt% water) were approximately constant and increase sharply as the concentration increases to higher than 85 wt% HAc in the feed solutions. This trend is consistent throughout the experiments, in which the separation factor ranged from 2 to 24. Transport of water across the membrane matrix is influenced by its solubility and diffusivity. Water molecules

Fig. 1. Schematic diagram of the experimental setup for PV.