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High performance dual-layer hollow fiber fabricated via novel immiscibility induced phase separation (I^2PS) process for dehydration of ethanol

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ABSTRACT

This pioneer study discloses a novel immiscibility induced phase separation (I^2PS) process to fabricate high performance dual-layer hollow fiber for dehydration of ethanol via pervaporation. The I^2PS process takes the advantages of phase separation phenomena occurring in immiscible blend dopes made of incompatible polymers. The immiscible blend dopes were simultaneously extruded through a triple orifice spinneret and fabricated into dual-layer hollow fibers consisting of an outer protective layer and an inner selective layer. A dense selective layer is formed at the outer-surface of the inner-layer due to the incompatibility between the polymer solutions of both inner and outer-layers as well as the shielding effect of the outer protective layer that provides a sufficient time for the formation of an almost defect-free selective layer during the phase inversion process. It is found that the phase inversion kinetics of the outer-layer dope solutions as well as the nature of outer-layer materials play great roles in determining the morphology of the outer protective layers and subsequently affects the permeance of the resultant hollow fibers. On the other hand, the selectivity of the as-spun fibers was found to be controlled by the outer surface of the inner-layer. The novel dual-layer hollow fiber spun from the combination of cellulose triacetate (CTA) and Ultem® possesses a high water permeance (29.33 mol/m^2 h kPa) or water flux (1.77 kg/m^2h at 50° C) coupled with reasonable water/ethanol selectivity (824 mol/mol) as compared to the pervaporation membranes available in the literatures. Heat treatment may enhance the selectivity of the aforementioned hollow fibers with some sacrifices of permeance. The present study may illuminate an innovative approach for hollow fiber fabrication in the future.

1. Introduction

The awareness of global warming and energy crisis has been increased due to the excessive extraction and lavish consumption of fossil energy. These phenomena prompted the exploration of alternative energies that offer the harmonious integration between renewability, sustainability as well as environmental conservation. Biological based energy such as bioethanol has been widely used to substitute fossil fuel in transportation and agricultural sectors. The total ethanol production in the United States for 2010 reached 49 billion liters as compared to 41 billion liters in 2009 indicating the increasing demand of ethanol in the market [1]. It is worth noting that almost 90% of gasoline in the United States is blended with ethanol. However, the separation and purification of fuel grade ethanol (anhydrous ethanol) by traditional distillation process was reported as an energy intensive process [2,3]. Therefore, significant efforts have been made to optimize the current separation process as well as to explore the alternative separation techniques which aim to further reduce the production cost of fuel grade ethanol [3–5].

Previous studies have suggested the potencies of pervaporation process to outperform conventional distillation and adsorption process in dehydration of alcohols [6,7]. The advantages of pervaporation process can be listed as energy efficient, small footprint coupled with flexibility and simplicity in the process control and module fabrication [7]. Most importantly, pervaporation process is not limited by the azeotropic restriction which makes it a rate-controlled process rather than a thermodynamic equilibrium process [8].

Membrane materials and morphological design are the key features in the aforementioned technology. Early development of pervaporation membranes has been focused on the flat sheet membranes made from hydrophilic materials such as poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), chitosan and alginate [9–11]. However, these materials are often prone to severe swelling phenomenon and crosslinking is needed to stabilize the structure and enhance the membrane selectivity [12]. Thus, pervaporation membranes with a balance of hydrophilic and hydrophobic characters are strongly preferred. The first commercial pervaporation membrane was developed by Gesellschaft für

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Trenntechnik (GFT) which utilized a composite membrane configuration whereby a thin layer of crosslinked PVA was coated on a porous poly(acrylonitrile) (PAN) support cast on a non-woven fabric [13]. This membrane configuration allows the effective separation to occur at the thin selective layer. As a result, the permeation flux can be greatly enhanced with a satisfactory selectivity.

From an application point of view, membranes fabricated in a hollow fiber configuration possess several advantages over the flat membranes such as: higher packing density, self-supporting structure and self-containing vacuum channel if the shell fed mode is applied [12,14,15]. Recently, dual-layer hollow fibers have gained popularities among membrane scientists in various fields of separations [16–25]. Depending on the application, this sophisticated hollow fiber spinning technology requires a strict selection of polymer materials for both inner-layer and outer-layer as well as the appropriate control of spinning parameters in order to harvest the synergistic advantages of both inner-layer and outer-layer materials. Particularly in the field of pervaporation, the application of dual-layer spinning technology was reported to significantly reduce the materials cost as the high performance yet expensive material can be used as the outer selective layer while the inner supporting layer can be fabricated from a cheaper material [26]. In addition, the dual-layer hollow fiber can be tailor-made to have a greater swelling resistance through proper selection and combination of materials for both outer and inner-layers [25,27]. Jiang et al. [28] reported that the usage of polymer materials that were miscible for both inner and outer-layer (such as polysulfone and matrimid®) can induces the formation of interpenetration network at the interface between inner-layer and outer-layer. The as-spun fibers were found to possess superior performance approaching ceramic membrane in the dehydration of *t*-butanol via pervaporation process.

On the other hand, the hollow fibers employed in pervaporation and gas separation are required to possess a defect-free dense selective layer to achieve high separation efficiency. However, the fiber with a defective selective layer is usually obtained through the non-solvent induced phase separation (NIPS) process. In this process, a strong non-solvent such as water is commonly used as the external coagulant to induce the formation of dense selective layer by a rapid phase inversion process. Silicon rubber coating and heat treatment were frequently used to seal the defective fibers [29–31]. Besides, a defect-free hollow fiber can be attained by formulating the dope solution containing volatile, non-volatile solvent and non-solvent [21,32]. However, a significant decline of the membrane permeance is commonly observed mainly due to the excessive densification of the selective layer.

Therefore, this study attempts to propose an alternative hollow fiber spinning method to fabricate high performance dual-layer hollow fibers by means of the immiscibility induced phase separation (I^2PS) process. In this proposed mechanism, the selective layer is formed at the outer surface of the inner-layer and it is triggered by the immiscibility of inner-layer and outer-layer polymers. The schematic of the proposed concept is illustrated in Fig. 1. This preliminary concept is demonstrated by fabricating dual-layer hollow fibers for dehydration of ethanol via pervaporation process. A total of three types of outer-layer materials were selected from a range of hydrophobic, hydrophilic, rubbery and glassy materials in order to elucidate and investigate the robustness of the proposed method. All of the as-spun dual-layer hollow fibers possess an outer-layer that functions as the shielding layer to protect the ultra-thin selective layer beneath from direct contact with the feed mixtures and to minimize the swelling effects. Through this method, highly permeable hollow fibers with a reasonable selectivity for ethanol dehydration have been fabricated. To the best of authors' knowledge, no study has been reported on the fabrication of novel pervaporation hollow fibers based on the proposed method.

2. Experimental

2.1. Materials

The outer-layer polymer materials, 6FDA-HAB-BisAHPF co-polyimide (PI), was synthesized via chemical imidization route

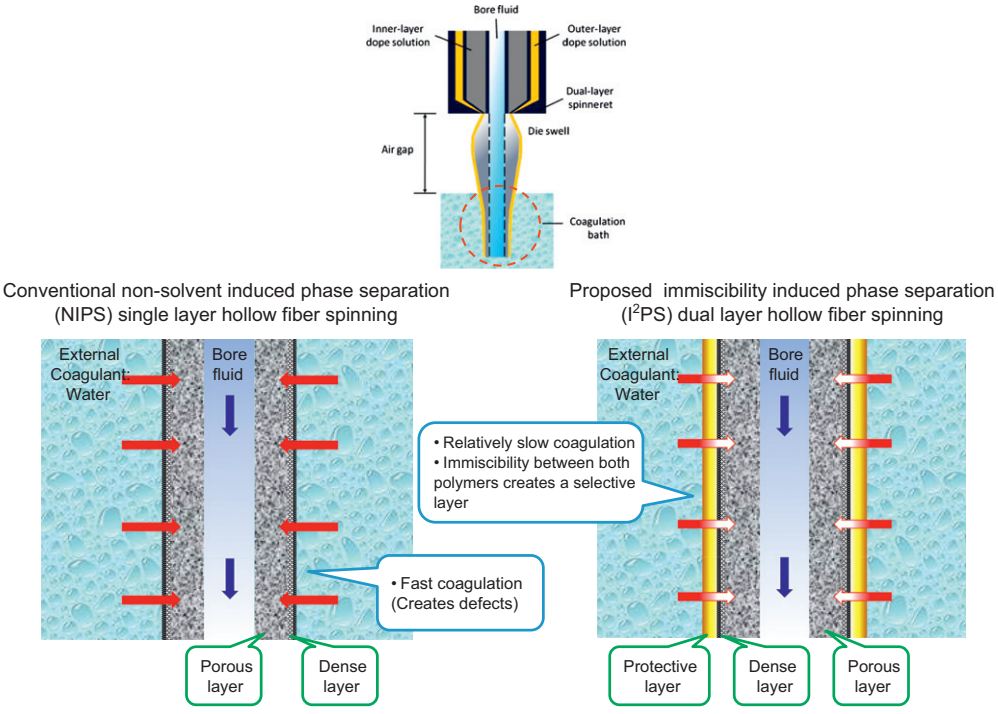

Fig. 1. Schematic of the proposed spinning method as compared to NIPS.