Highly Efficient Membrane-based Techniques in Separation of Harsh Mixtures

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Abstract. Membrane-based techniques are always praised as energy-saving and efficient methods to retrofit some conventional technological processes that are usually high energy-consumption, especially distillaiton in separation of azeotrope. This work reviews the recent progresses of separation processes by membrane-based techniques for liquid mixtures which are difficult to be separated by normal distillation. Membrane-based techniques such as membrane distillation, pervaporation, and membrane structured packing are concretely described. In addition, a membrane hybrid process is presented. Compared with conventional separation, membrane-based techniques and membrane hybrid processes will play important role in the separation of liquid mixture due to the investment, operating cost, safety and separation efficiency.

1. Introduction

For years, distillation has continued to be one of the most vital processing steps in the separation of petroleum hydrocarbons and related compounds. Many mixtures of organic liquids with water in certain composition have azeotropic points, at which the liquid has the same composition as the vapor in equilibrium. Such mixtures can not be separated by normal distillation except complicated distillation processes such as azeotropic distillation and extractive distillation. Although separation columns have been workhorses of the chemical industry for decades, the direct contact of two fluids sometimes leads to difficulties such as flooding, unloading, foaming and emulsion, and how to produce suitable interface to maximize mass transfer rate still remains a challenge [1].

Separation of azeotropic, closely boiling, isomeric or heat-sensitive liquid mixtures by membrane-based techniques have been studied extensively due to their potential industrial utility. Being economical, safe and eco-friendly, these membrane-based techniques are considered to be a promising alternative to conventional energy intensive technologies like azeotropic or extractive distillation in liquid mixtures separation [2]. On the other hand, the membrane hybrid process of distillation and pervaporation has been emerged recently. The key advantages of such hybrid process are the ability to split azeotropes and the reduction in operating cost.

2. Membrane separation process

Membrane separation technology is an innovative technology and has been employed in many fields like energy, electronics, chemical engineering, environmental protection and other industry. Membrane-based techniques such as membrane distillation, pervaporation and novel membrane contactor, offer great advantages over existing mass transfer process such as low energy consumption, moderate cost to performance ratio, compact and modular design.

2.1. Membrane distillation

As shown in Figure 1, membrane distillation (MD) is a typical process driven by temperature difference and affinity difference. In MD process, a heated aqueous feed solution is brought into contact with a hydrophobic microporous membrane. Then volatile component evaporates at the feed side, crosses membrane in vapor phase and condenses in the cold liquid/vapor interface inside membrane module. The membrane forms a separation between the warm, vaporizing retentate stream and the condensed product. An et al examined superhydrophobic membrane distillation for dyeing wastewater using PDMS/PVDF hybrid electrospun membrane [3]. Shon imbedded carbon nanotube to PVDF-co-hexafluoropropylene to improve mechanical and hydrophobic properties [4]. Yet there are so many research aiming to elevate hydrophobic properties of membrane [5], their real effect to wetting resistance may not be absolute, especially for low surface tension liquids [6].

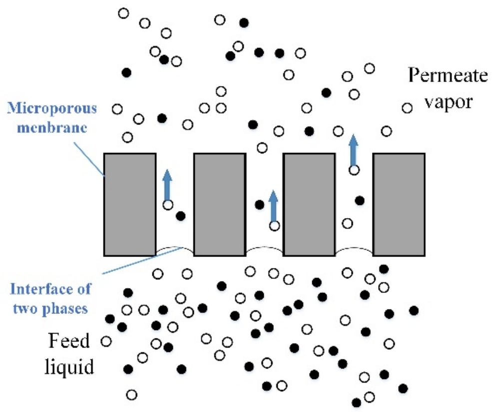

Figure 1. Schematic diagram of membrane distillation

2.2. Pervaporation

Pervaporation (PV) is a improved membrane process for liquid separation and the membrane usually serves as a separating barrier. PV separation is based on the relative solubility and diffusivity of each component in membrane material. Pervaporation membranes fall into homogeneous membrane [7] and composite membrane [8]. In PV process, an aqueous feed solution is brought into contact with a dense membrane. One of the components can preferentially be solved and diffuse in membrane due to its higher affinity with the membrane, and release into vapor phase at the downstream side of membrane, as shown in Figure 2. The separation of compounds employing PV method can be classified into three major fields, including dehydration of aqueous-organic mixtures [9], removal of trace volatile organic compounds from aqueous solutions and separation of organic-organic solvent mixtures [2]. Especially, pervaporation demonstrates incomparable advantages in separating heat-sensitive, close-boiling, and azeotropic mixtures due to its mild operating conditions, no emission to the environment and no involvement of additional species into feed stream.

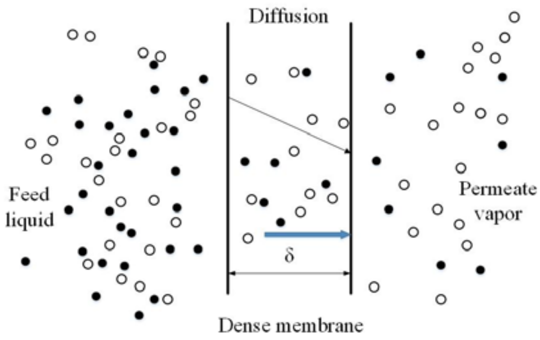

Figure 2. Schematic diagram of pervaporation

2.3. *Novel membrane contactor*

Membrane contactor is a novel process in which fluids contacted flow are on opposite sides of a suitable membrane and fluid/fluid interface forms at the mouth of each membrane pore. Mass transfer occurs by diffusion across the interface. Because the fluids have their own channels, the operational problems such as flooding, loading, foaming and emulsions easily occurring in conventional contact are totally absent. Besides, large surface area per unit volume is successfully achieved.

Since Zhang and Cussler proposed firstly the concept that hollow fibers were used as a new type of distillation packing to separate IPA from water, as shown in Figure 3 [10, 11], many researches have been put into effect. Zhang et al. continually investigated the behaviors in separation of different alcohols-water solutions [12, 13, 14]. Yang et al. made use of microporous hollow fiber structures packing to separation propylene/propane and iso-/n-butane [15, 16]. Li et al. employed ceramic hollow fiber contactor to distillation of benzene and toluene [17]. In order to improve separation efficiency of distillation column with hollow fibers, membrane module design [18] and surface-coated modification of membrane [10, 20, 21] have been paid more attention.

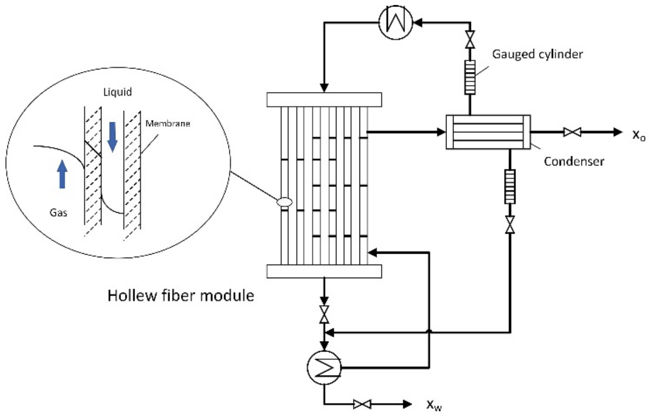

Figure 3. Schematic process for hollow fiber structured packing distillation

3. Hybrid process

A hybrid process is a process package consisting of different unit operations, which are interlinked and optimized to achieve a predefined task [22]. To our best knowledge, distillation process is most commonly applied in industry. Either a pressure-swing distillation is used with the consequences of extra cost, or azeotropic/extractive distillation is applied through a third component as entrainer with unfavorable side effects. In many cases, PV alone may not supply product suitable for further processing or waste disposal in accordance with environmental standards. To overcome the restrictions, the promising technology is the hybrid process of the combination of distillation and pervaporation system that can be applied for the separation of low volatile and azeotropic mixtures. Of course, the number of distillation column and PV unit can be increased as required.

Lee et al. [23] employed pervaporation to reactive distillation system to eliminate required column for the separation of a methanol and methyl acetate azeotrope, enhancing the efficiency of the transesterification reaction and the energy savings(up to 71%), as shown in Figure 4 (a). Tremblay et al. [24] proposed a new hybrid pervaporation-distillation process for ethanol recovery, as shown in Figure 4 (b). The vapor stream entered the bottom of a membrane unit and flowed upwards through the module countercurrently contacted with the liquid that the condensed vapor refluxed to the top of membrane unit and flowed down the surface of membrane through action of gravity. Thus, enrichment of volatile components in vapor phase and selective pervaporation of water run in parallel.

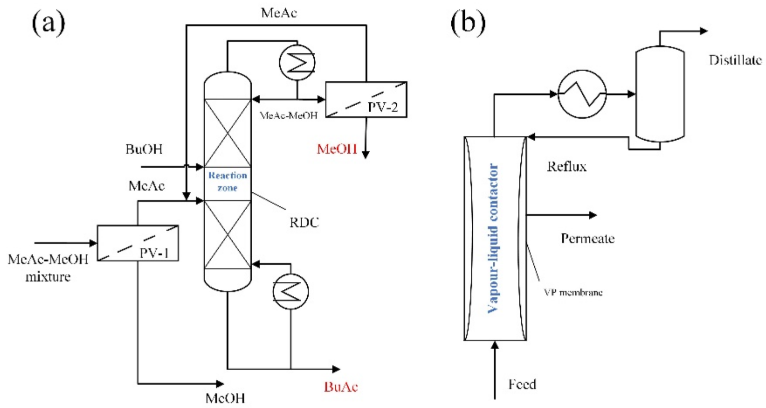

Figure 4. Schematic hybrid process of a reactive distillation-pervaporation (a) and new distillation-pervaporation (b)

4. Current & Future developments

A detail comparison among conventional separation technique, membrane process and membrane hybrid process can be found in Table 1.

Table 1. Comparison of different technologies for liquid mixtures separation

Technology	Investmet	Advantages and disadvantages
Azeotropic distillation	High	High energy consumption,toxic entrainer, impurity of product, industrialization
Extractive distillation	High	High energy consumption, extractive agent residue in product, industrialization
Membrane distillation	Low	Low energy consumption, excellent separating effect, in the process of industrialization
Pervaporation	Low	Low energy consumption, prematuration of membrane manufacture, industrialization
Membrane contactor	Low	Low energy consumption, simple equipment, wide operational flexibility, high separation efficiency, in the process of industrialization
Hybrid process	High	Low energy consumption, low operating cost, complex process, high separation efficiency, in the process of industrialization

In addition, there is too much potentiality and space for membrane-based technology to deal with waste water as a clean and pre-environment method. It is believed that high energy consumption, complex and high investment conventional separation process will be gradually constituted by novel membrane separation technology in the near future. Recent research developments in these fields are also showing a very broad perspective for these new separation processes to take up real challenges in the chemical or petrochemical industry.

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