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A REVIEW PAPER ON PERVAPORATION

Engineering

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ABSTRACT

In membrane separation process, pervaporation is promising technology nowadays because of its applied to wide variety of the material from organic material to water purification. Review of the pervaporation shows that it can be applied to material where conventional process is not performing well or energy intensive or use of any other material. Over review show that pervaporation will be used for more and more system.

KEYWORDS

Pervaporation, Membrane Separation, Ethanol – Water, Butenol- Water

INTRODUCTION

Pervaporation is a membrane-based method employed to separate liquid mixtures by allowing selective vaporization through a specialized membrane. Pervaporation processes have been utilized in commercial applications for many years, specifically for dehydrating alcoholic solutions, extracting organics from aqueous solutions, for separating organic mixtures and many other applications in chemical industry. Pervaporation, as opposed to distillation, is often a more energy-efficient method for separating mixtures containing water, mainly due to the enhanced selectivity resulting from the membrane's permselectivity. The membrane's performance is a crucial factor in determining the process's viability. In this paper the basics and application of the pervaporation system for separation is reviewed.

PERVAPORATION:

Pervaporation is the combination permeation & evaporation through non porous membrane. The feed is directed along one side of the membrane, and a portion of the feed, known as the "permeate," migrates through the membrane to exit in vapor form on the opposite side. The vapor side of the membrane is either maintained under a vacuum or flushed with an inert carrier gas stream. The permeate is eventually collected in a liquid state through condensation. The liquid product contains a higher concentration of the component from the feed mixture that permeates the membrane more quickly. The remaining feed materials that cannot pass through the membrane constitute the "retentate."(1)

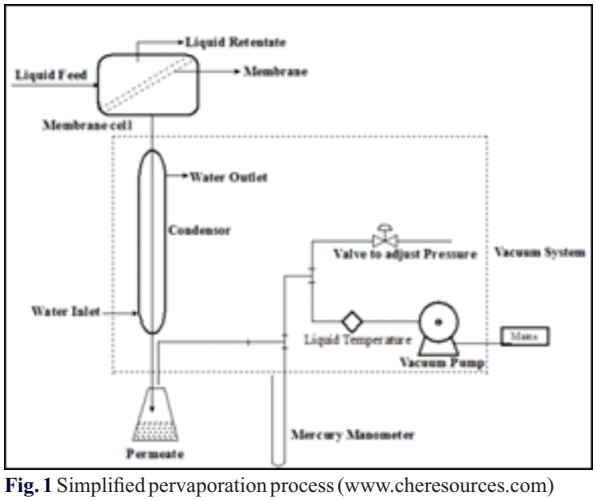

Fig. 1 Simplified pervaporation process (www.cheresources.com)

Regarding membrane types, we can categorize them into two distinct classes based on the component that is selectively permeated.

Hydrophilic membranes: These membranes are designed to separate the target compound, which is typically water, from an aqueous-organic feed mixture by allowing it to preferentially permeate through the membrane. Examples of membrane materials in this category include Polyvinylalcohol(PVA), Polyvinylalcohol/ Polyacrylonitrile (PVA/PAN), Polyetherimide (PEI), and 4,4'-oxydiphenylene pyromellitimide (POPMI).

Organophilic Membranes:

In contrast, organophilic membranes are tailored to separate organic target compounds from an organic-organic feed mixture by favoring their permeation through the membrane. Common membrane materials in this class typically include PDMS and PVA/PAN.

Characteristics of the pervaporation process include:
1. Low energy consumption
2. No entrainer required, no contamination
3. Permeate must be volatile at operating conditions
4. Functions independent of vapor/liquid equilibrium

Low energy consumption and independence of vapor/liquid equilibrium makes pervaporation an attractive process for separation of azeotropes and mixtures with low relative volatility. (1)

PERVAPORATION CHARACTERISTICS:

Molecular flux Molecular flux is the amount of a component permeated per unit area per unit time:

$$J_i = \frac{Q_i}{A\,t}$$

Where,
J_i = Flux of component
Q_i = Moles of component "i" permeated in time "t"
A = Effective membrane surface area (cm^2).

Permselectivity Performance of a given membrane is expressed in terms of permselectivity as:

$$\alpha = \frac{X_i^p / X_j^p}{X_i^f / X_j^f} = \frac{V_i^p \rho_i^p / V_j^p \rho_j^p}{V_i^f \rho_i^f / V_j^f \rho_j^f}$$

Assuming the density of the components in the feed is the same, then:

$$\alpha = \frac{V_i^p / V_j^p}{V_i^f / V_j^f}$$

Where,
ρ = Density
X = Weight fraction
V = Volume fraction Superscripts "p" and "f" denote "permeate" and "feed" respectively while "i" and "j" represent individual components.

Permeability Coefficient The molecular flux for pervaporation can be related to the permeability coefficient by:

$$J_i = -P_i \left[\frac{P_i^o X_{r,i} - P Y_{p,i}}{L} \right]$$

Where,

Pi = Permeability coefficient of component "i". 0 Pi = Saturation pressure of pure component "i" in the mixture.
P = Total pressure.
Xr i, = Mole fraction of component "i" in liquid feed.
Yp i, = Mole fraction of component "i" in permeate
L = Membrane thickness

APPLICATION OF PERVAPORATION FOR SEPARATION

As Conventional Separation process are not capable to separate ethanol water in fermentation process use of membrane separation process increasing rapidly. Separating ethanol from water mixtures is a critical aspect of ethanol production from biomass. Continuous fermentation and separation processes can be effectively managed using both ultrafiltration and pervaporation methods. Pervaporation is particularly useful for extracting ethanol from the permeate generated by ultrafiltration. The research and exploration of the pervaporation technique for ethanol-water mixture separation have yielded noteworthy findings. These findings include results for membranes that exhibit a preference for permeating ethanol, as well as membranes that favour the permeation of water. The combination of pervaporation and ultrafiltration offers the opportunity for the continuous and selective removal of ethanol from a fermentation reactor. Following ultrafiltration, the resulting ethanol-water mixture can undergo purification through a two-stage pervaporation process, employing homogeneous, composite, or asymmetric membranes. (2)

A novel organic-inorganic hybrid membrane has been developed, demonstrating remarkable performance in dewatering applications. The exclusive precursor employed in the sol-gel synthesis of the selective layer is 1,2-bis(triethoxysilyl)ethane (BTESE), which is organically linked. The microporous structure of this layer enables the selective sieving of smaller molecules from larger ones.

In the dehydration of n-butanol with 5% water content, the membrane exhibits an impressive separation factor exceeding 4000, along with rapid water transport exceeding 20 kg/m² per hour at 150°C. These characteristics are attributed to the material's high adsorption capacity and the sub-micron thickness of the selective layer. Importantly, the selectivity remains consistent for nearly one and a half years under continuous process testing conditions. Additionally, the membrane demonstrates exceptional hydrothermal stability and a high resistance to acid contamination. A gradual decrease in performance, with reduced flux and separation factor, is only observed at a pH level lower than 2. These features highlight the broad potential for industrial applications of this hybrid membrane material due to its stability and effective separation capabilities. (3)

Thin microporous silica membranes were fabricated on the external surface of hollow fiber ceramic substrates. This approach offers the advantage of relatively fast and cost-effective production of membranes with a large surface area. It also results in low support resistance and a high membrane surface area-to-module volume ratio, exceeding 1000 m^2/m^3, which outperforms traditional tubular membranes. The characterization of these membranes involved techniques such as scanning electron microscopy (SEM), secondary neutral mass spectrometry (SNMS), single gas permeance measurements, and pervaporation. The results showed that the membranes exhibit high helium permeance (ranging from 1.1 to 2.9 × 10^{-6} mol m^{-2} s^{-1} Pa^{-1}), excellent helium/nitrogen permselectivity (approximately 100 to 1000), and gas permeance with Arrhenius-type temperature dependence. These characteristics suggest that the membranes are microporous and have a low number of defects. Furthermore, it was determined that the contribution of the hollow fiber substrate to the overall mass transport resistance is minimal, even for rapidly permeating gases like helium. This means that the small dimensions of the substrate allow for further enhancement of the silica layer without significantly increasing the support resistance. In the context of applications, when dehydrating n-butanol (at 80°C with 5% water content), the membranes initially exhibited high flux and selectivity (2.9 kg/m² h and 1200, respectively). Similar results were observed for the dehydration of dimethylformamide (DMF). Over time, the water permeance of most membranes stabilized at around 1 kg/m^2 h bar^{-1}, with selectivities ranging from 5 to 25. The excellent performance of these hollow fiber membranes, coupled with their advantages over other support geometries, positions them as promising candidates for various applications. (4)

Membranes with a preference for allowing water to pass through while impeding other substances can enhance the efficiency of ethanol dehydration processes. Silica membranes are known for their gas separation capabilities, but their effectiveness in dehydrating ethanol/water mixtures has been explored in this study. The study investigates the performance of carbonized template molecular sieve (CTM SS) membranes in dehydrating ethanol/water mixtures. The top layer of the membrane, derived from silica, was found to have a thickness of approximately 20nm using the XPS sputtering technique. However, the silica tends to penetrate the porous structure of the γ-alumina layer to a depth exceeding 90nm. Over the course of 200 minutes of operation, the selectivity of water to ethanol (H2O/EtOH) increased from approximately 1 to 5.6. This increase was attributed to a gradual pore filling by adsorbed water and ethanol, which hindered the transport of ethanol. Consequently, smaller water molecules were favored in moving to the permeate side of the membrane. The total mass flux remained relatively constant at around 1.5 kg/m²/hr when using a 10% ethanol feed. Notably, a selectivity of up to 9.5 was achieved when using azeotropic feed solutions with 95% ethanol, demonstrating the potential of this technology for a wide range of ethanol dehydration applications. When the feed was pressurized up to 400 kPa, the permeate flux doubled, but this also enhanced the transport of ethanol over water. (5)

Pure silicalite membranes were created on porous supports made of sintered stainless steel or alumina discs. The silicalite layer was thoroughly characterized using X-ray diffraction, scanning electron microscopy (SEM), and mercury porosimetry. The examination revealed that individual crystals within the membrane were intricately intergrown in three dimensions, forming a polycrystalline phase. The membranes displayed remarkable thermomechanical stability as they remained intact even after thermal treatment in a vacuum or calcination to remove the organic amine trapped in the channels of the silicalite. This indicates the high resilience of the membrane. To assess its liquid separation potential, the membrane was subjected to pervaporation using an aqueous ethanol solution. The results demonstrated a high ethanol permselectivity, with a separation factor (EtOH/H2O)) exceeding 60 for a 5% aqueous ethanol solution at 30°C. This high permselectivity suggests the absence of cracks and pores between the silicalite grains within the membrane. Further investigations, including adsorption experiments with ethanol and water on silicalite, revealed that the exceptional permselectivity can be attributed to the membrane's ability to selectively adsorb ethanol, making it an effective tool for separating ethanol from water in liquid mixtures. (6)

Pervaporation experiments were conducted using a commercial hydrophilic ceramic membrane supplied by PERVATECH. The study used the dehydration of an ethanol/water system as a model for pervaporation investigations. The experiments encompassed a temperature range of 303-343K, ethanol concentrations in the feed ranging from 10% to 90% by volume, and feed flow rates spanning from 0.5 to 10 L/min. The study focused on analyzing the impact of operational parameters on permeate fluxes and separation factors. It was observed that water flux was significantly influenced by temperature, with an increase in temperature leading to an increase in water flux. However, this rise in temperature decreased the membrane's selectivity for water molecules. Furthermore, water flux decreased as the ethanol concentration in the feed increased but increased with higher feed flow rates. The optimal operational conditions for the pervaporation process were determined as follows: a temperature of 333 K, a feed flow rate of 6 L/min, and a feed with 90% ethanol concentration. These conditions yielded high values of water flux and separation factor. The findings from this study align well with similar research reported in the literature. (7)

Blend membranes were created using a combination of a natural polymer, chitosan, and a synthetic polymer, poly(vinyl alcohol) (PVA). The preparation involved a solution casting process and crosslinking using a urea formaldehyde/sulfuric acid (UFS) mixture. Chitosan served as the foundational component in the blend system, while the concentration of PVA was adjusted within the range of 20 to 60 wt%. The compatibility of the blend was investigated through differential scanning calorimetry, and Fourier transform infrared spectroscopy was employed to analyze the crosslinking of the membranes. These membranes were then put to the test in pervaporation for the dehydration of isopropanol and tetrahydrofuran (THF) near their azeotropic compositions at a temperature of 308°C. The performance of the membranes was evaluated by calculating their

flux and selectivity. Swelling experiments were conducted in water and organic mixtures at 308°C to provide insights into the results obtained from the pervaporation tests. Notably, the blend membrane containing 20 wt% PVA, when tested with THF and isopropanol feeds containing 5 and 10 wt% water, exhibited remarkable selectivity values of 4,203 and 17,991, respectively. Flux increased with higher concentrations of water in the feed, and the highest selectivity was achieved with the blend membrane containing 20 wt% PVA. This study is unique due to the novel use of the UFS mixture as the crosslinking agent, which contributed to the exceptional performance of the blend membranes in the pervaporation process. (8)

A chitosan membrane with an 84% degree of deacetylation underwent crosslinking using toluene-2,4-diisocyanate and was tested for its effectiveness in dehydrating isopropanol through the pervaporation method. Both pure and crosslinked membranes were subjected to characterization using Fourier transform infrared spectroscopy and wide-angle X-ray diffraction to explore intermolecular interactions and crystallinity, respectively. Additionally, dynamic mechanical thermal analyses were conducted to assess the thermal and mechanical stability of the membranes. Sorption studies were carried out using water, isopropanol, and various feed mixtures to gain insights into polymer-liquid interactions and the mechanisms involved in pervaporation separation. The membrane exhibited significant potential for breaking the aqueous azeotrope of 87.5 wt% isopropanol, boasting a high selectivity of 472 and substantial water flux of 0.39 $kg/m^2 h^{-1}$. The study delved into the influence of operating parameters, such as feed composition, membrane thickness, and permeate pressure, on membrane performance metrics like flux and selectivity. (9)

The study delved into the pervaporation behavior of mixtures comprising toluene and various alcohols, namely methanol, ethanol, and propanol, using a linear low-density polyethylene membrane. The investigation spanned different feed compositions and relied on parameters like the swelling ratio, permeation rate, and selectivity to determine the characteristics of the process. In all cases, it was observed that toluene exhibited a preference for permeating through the membrane, resulting in separation factors as high as 66, with fluxes ranging from 0.1 to 1.4 $kg/m^2 \cdot h$. Predictions based on the Flory-Huggins theory indicated that the membrane selectively absorbs toluene. The experimental findings revealed that as the toluene content in the feed increased, the pervaporation flux also increased, but the selectivity decreased. Furthermore, it was observed that the pure-alcohol fluxes decreased with increasing molecular size. (10)

CONCLUSION:

Recently the use of pervaporation for separation of alcohol water mixture is increased. The separation of difficult mixture like close boiling, azrotrope, etc can be done by the pervaporation. Both kind of membrane can be used for the pervaporation. Initially polymeric membrane were used for the separation, but currently use of composite membrane are in demand. Given that pervaporation is a membrane-based process, it offers the possibility of integrating separation steps with the reaction itself, leading to significant enhancements in reaction efficiency, yields, and overall process economics. This opens up promising opportunities for separating esterification products or byproducts. Ongoing research aims to create advanced membranes with increased fluxes, enhanced selectivity, and greater chemical resistance, thereby expanding the potential applications of pervaporation-esterification hybrids.

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