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## REVIEW ARTICLE

### SEPARATION OF ETHANOL WATER BY HYBRID DISTILLATION PERVAPORATION SYSTEM

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#### ABSTRACT

As separation techniques, pervaporation occupies a special place in the chemical industry. It is the only membrane process primarily used to purify the chemicals. Pervaporation, in its simplest form, is an energy efficient combination of membrane permeation and evaporation. Separation of the alcohol-water mixture by hybrid distillation pervaporation has received increasing attention in industry. Normally Conventionally azeotropic distillation is used to remove the water from an azeotropic ethanol/water mixture. The aim of this paper is to show the comparative study of pervaporation over a conventional azeotropic distillation for the separation of ethanol water mixture. It shows how pervaporation is better option over a conventional method due to its various factors like lower operating costs resulted from lower energy consumption, reduced waste water treatment and the absence of a chemical entrainer, reduction in capital cost and operating cost. All these aspects are pushing the development and adoption of new better technology over a conventional one. Despite the fact for the adoption of new technology like pervaporation, chemical engineers will need all of their skills to select the very best application and maximize the benefits to their plant.

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## INTRODUCTION

Pervaporation, in its simplest form, is an energy efficient combination of membrane permeation and evaporation. It's considered an attractive alternative to other separation methods for a variety of processes. For example, with the low temperatures and pressures involved in pervaporation, it often has cost and performance advantages for the separation of constant-boiling azeotropes. Additionally, pervaporation has emerged as a good choice for separation heat sensitive products. Pervaporation can be used for breaking azeotropes, dehydration of solvents and other volatile organics, organic/organic separations such as ethanol or methanol removal, and wastewater purification.

### Pervaporation

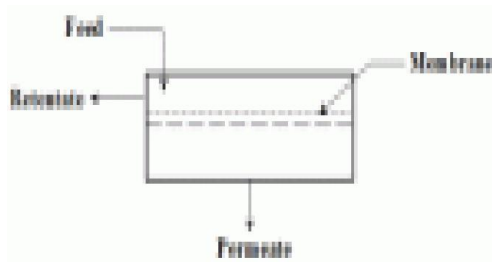
Pervaporation involves the separation of two or more components across a membrane by differing rates of diffusion through a thin polymer and an evaporative phase change comparable to a simple flash step. (<http://www.cheresources.com/content/articles/separation-technology/pervaporation-an-overview/> referred on 15/10/2015)

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A concentrate and vapor pressure gradient is used to allow one component to preferentially permeate across the membrane. A vacuum applied to the permeate side is coupled with the immediate condensation of the permeated vapors. Pervaporation is typically suited to separating a minor component of a liquid mixture, thus high selectivity through the membrane is essential. Liquid transport in pervaporation is described by various solution-diffusion models. The steps included are the sorption of the permeate at the interface of the solution feed and the membrane, diffusion across the membrane due to concentration gradients (rate determining steps), and finally desorption into a vapor phase at the permeate side of the membrane.

The first two steps are primarily responsible for the perm selectivity. As material passes through the membrane a "swelling" effect makes the membrane more permeable, but less selective, until a point of unacceptable selectivity is reached and the membrane must be regenerated. The other driving force for separation is the difference in partial pressures across the membrane. By reducing the pressure on the permeate side of the membrane, a driving force is created. Another method of inducing a partial pressure gradient is to sweep an inert gas over the permeate side of the membrane. These methods are described as vacuum and sweep gas pervaporation respectively.

(<http://www.cheresources.com/content/articles/separation-technology/pervaporation-an-overview/> referred on 15/10/2015)



(Courtesy by www.cheresources.com)

Fig. 1. Overview of pervaporation process

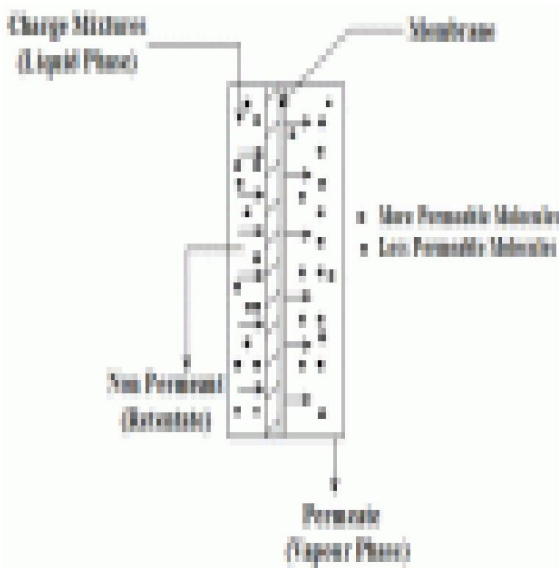


Fig. 2. Schematic of Liquid Permeation

Characteristics of the pervaporation process include: (<http://www.cheresources.com/content/articles/separation-technology/pervaporation-an-overview/> referred on 15/10/2015)

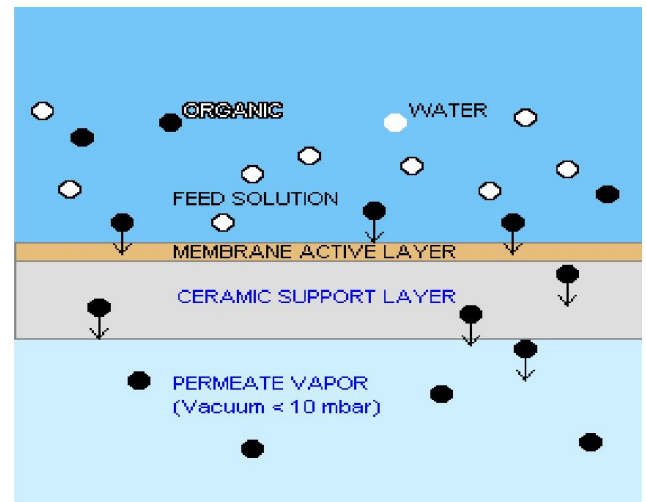
- Low energy consumption
- No entrainer required, no contamination
- Permeate must be volatile at operating conditions
- Functions independent of vapor/liquid equilibrium

**Application of Pervaporation**

- Dehydration of organic solvents (e.g., alcohols, ethers, esters, acids)
- Removal of dilute organic compounds from aqueous streams (e.g., removal of volatile organic compounds, recovery of aroma, and biofuels from fermentation broth)
- Organic-organic mixtures separation (e.g., methyl tert-butyl ether (MTBE) /methanol, dimethyl carbonate (DMC)/methanol). (Shao *et al.*, 2006)

**Mass Transfer Process along Membrane in Pervaporation**

The pervaporation of dilute organic-water mixtures has been relatively well described by a resistance-in-series model. The mass transfer process of a single component across the membrane occurs in 4 consecutive steps:



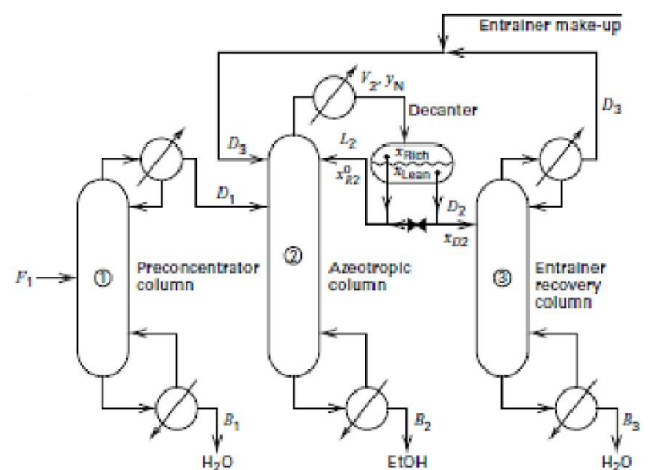
(Courtesy by www.cheresources.com)

Fig. 3. Mass Transfer Process Along Membrane in Pervaporation

- 1- Mass transfer from the bulk of feed to the membrane interface.
- 2- Selective absorption into the membrane at the feed side.
- 3- Selective diffusion through the membrane.
- 4- Desorption into the vapor phase at the permeate side. (Sridhar and Ramakrishna, 2003)

**Dehydration of Ethanol by Conventional Methods**

For the ethanol to be usable as a fuel, the majority of the water must be removed. Most of the water is removed by distillation, but the purity is limited to 95–96% due to the formation of a low-boiling water-ethanol azeotrope with maximum (95.6% m/m (96.5% v/v) ethanol and 4.4% m/m (3.5% v/v) water). This mixture is called hydrous ethanol and can be used as a fuel alone, but unlike anhydrous ethanol, hydrous ethanol is not miscible in all ratios with gasoline, so the water fraction is typically removed in further treatment to burn in combination with gasoline in gasoline engines.



Courtesy by: www.chemeng.ntua.gr

Fig. 4. Dehydration of Ethanol by Azeotropic Distillation

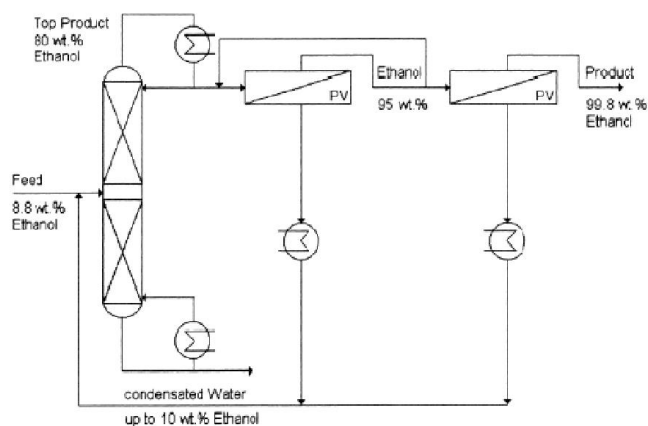
Conventionally azeotropic distillation is used to remove the water from an azeotropic ethanol/water mixture. The first process, used in many early fuel ethanol plants, is

called azeotropic distillation and consists of adding benzene or cyclohexane to the mixture. When these components are added to the mixture, it forms a heterogeneous azeotropic mixture in vapor–liquid–liquid equilibrium, which when distilled produces anhydrous ethanol in the column bottom, and a vapor mixture of water, ethanol, and cyclohexane/benzene.

When condensed, this becomes a two-phase liquid mixture. The heavier phase, poor in the entrainer (benzene or cyclohexane), is stripped of the entrainer and recycled to the feed—while the lighter phase, with condensate from the stripping, is recycled to the second column. Another early method, called extractive distillation, consists of adding a ternary component that increases ethanol's relative volatility. When the ternary mixture is distilled, it produces anhydrous ethanol on the top stream of the column. ([https://en.wikipedia.org/wiki/Ethanol\\_fuel/referred](https://en.wikipedia.org/wiki/Ethanol_fuel/referred) on 16/10/2015)

### Dehydration of Ethanol by Hybrid Distillation Pervaporation Process

The pervaporation distillation hybrid process is employed to separate ethanol–water mixtures by plitting azeotrope and finally to dehydrate the ethanol. A new system is developed combining a distillation column followed by two PV units with different types of hydrophilic membrane. First a high flux–low selectivity membrane to split the azeotrope and second a low flux–high selectivity membrane as a polishing step.



**Fig. 5. Separation of Ethanol from water by Hybrid Distillation Pervaporation**

A simplified process layout is shown in Fig. 4. The top product of the distillation column, 80 wt% ethanol, was concentrated to 99.8 wt% ethanol using the PV units. The permeate from the PV units was recycled to the distillation column. The hybrid process can thus replace the four distillation columns commonly required in the conventional azeotropic distillation process. This method to be considerably cheaper compared to the conventional process, mentioning in particular the reduced energy requirement and the avoidance of entrainers for distillation.

Alternative process layouts with only one PV unit as final step in the ethanol dehydration process were proposed by Tusel and Bru Eschke and Fleming. Depending on the layout of the PV unit, the ethanol concentration of the product was between 99.5 and 99.95 wt%. It could be shown that these processes were an effective solution for saving investment costs as well as operating costs compared to conventional distillation. The lower operating costs resulted from lower energy consumption, reduced waste water treatment and the absence of a chemical entrainer. Pervaporation also overcame distillation problems related to impurities in the ethanol such as aldehydes and methanol. (Pervaporation-based hybrid, 1998)

### Conclusion

Comparative study of dehydration of ethanol for different shows that hybrid distillation of pervaporation method is better because of certain advantages. In hybrid distillation pervaporation system very low energy required compared to conventional system. Use of carcinogenic chemical like benzene as entrainer can be eliminated. Many economical study shows that capital cost and operating cost can be reduced compared to conventional methods.

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