

RESEARCH ARTICLE



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Comparison of Energy Consumption in Pervaporation with Molecular Sieve Processes for Ethanol Water Azeotrope Separation

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Abstract

Objective: To compare energy consumption in pervaporation with conventional molecular sieve adsorption process for production of unhydrous ethanol using commercial pervaporation membrane P64 PEPSI C4064.1C. Method/Analysis: Experimental pervaporation system setup with commercial pervaporation membrane P64 PEPSI C4064.1C is used for separation of ethanol water mixture (95% (v/v) ethanol) at vacuum 10-15 torr. For analysis Karl Fischer titration method is used. Based on experimental results electrical as well as thermal energy consumption for 100 KLPD capacity pilot plant is calculated and compared with conventional molecular sieve adsorption process. Findings: Comparison for commercial membrane P64 PEPSI C4064.1C with reported data shows that separation factor as well as total flux related to separation factor is consistent with other hydrophilic membranes. The energy consumption for pervaporation process includes the external heating and cooling required for the feed and permeate streams, as well as the electrical power associated with pumps for re-circulating feed and maintaining vacuum. To separate 100 KLPD ethanol mixture with 95 vol % ethanol by pervaporation process, 10500 kg steam is required whereas 50500 kg steam is required for separation by adsorption process. Total electrical energy for pervaporation process is 76 Kw as compared to 270 kw required for adsorption process. Novelty: This study demonstrated that Electrical energy required for pervaporation process is almost 72 % less than molecular sieve adsorption process. There is no extra energy requirement for External additive addition and separation/sieve regeneration. Based on these results a pervaporation based separation process plant with low energy consumption can be designed for separation of ethanol water mixture.

Keywords: Pervaporation; Energy; Membrane; Molecular sieve; Azeotrope

1 Introduction

Ethanol-Water mixture containing 95% ethanol by volume forms minimum boiling azeotrope. However, azeotropic mixture separation is difficult by widely used conventional distillation. Almost 40 % part of the energy used in a chemical plant is based on distillation and other related methods.

In India Grain, molasses and sugar industry are the major sources for production of fuel grade ethanol.

Three processes mentioned below are used for production of fuel grade ethanol:

- 1. Molecular sieve adsorption (PSA) technology.
- 2. Use of benzene and other organic solvents for moisture removal from ethanol.
- 3. Use of solvents like ethylene glycol to remove moisture from the rectified spirit (azeotropic mixture).

In industrial practice for separation of azeotropic mixture, a third component, entrainer used acts as breaker for azeotrope. High Capital and high energy cost are the major disadvantages of azeotropic distillation process ^(1,2). Another conventional separation process Molecular sieve adsorption (PSA) technology requires more energy and high pressure steam ⁽³⁾. On account of energy prices and efficiency there is need for development of alternative separation processes which are less energy consuming and more efficient to conventional separation processes is essential.

Pervaporation is a separation process based on evaporation of one of the components of the liquid mixture and could be a promising alternative. Vapor Pressure Difference, Membrane Selectivity, Mass Transfer and Driving Force are the main characteristics of pervaporation. Pervaporation relies on the vapor pressure difference between the liquid mixture on one side of the membrane and the vapor phase on the other side. Components with higher vapor pressures have a higher tendency to permeate through the membrane. In pervaporation process membrane is used as a separation medium. Pervaporation involves mass transfer of the vaporized components through the membrane. The rate of mass transfer is influenced by the membrane's permeability, thickness, and surface area. Membrane selectivity is crucial in determining which components preferentially permeate the membrane. The ideal pervaporation membrane should be selectively permeable to the target components while rejecting others. Membrane materials and their interactions with specific components, separation is possible. The main advantage of pervaporation is the low energy consumption compared with traditional processes such as distillation. Additionally, it could be more economical, safe, and ecofriendly^(4,5).

Research on Membrane distillation is going on in the laboratory, bench scale and even in pilot scale. As per suggestions by Muhammad and Rosentrater Membrane distillation may not be a viable option for a commercial scale up and membrane based separation, especially pervaporation is a better option over other methods, especially Membrane distillation⁽⁶⁾.

For Extraction process organic solvents are being replaced by inorganic salts and ionic liquids but commercial scale demonstrations are not reported in literature. Another attractive option is adsorption, but it is more costly and needs to be made much more cost effective⁽⁶⁾.

According to the research carried out for the energy consumption in a hybrid PV process for the separation of toluene and octane, 56% less energy is required for separation compared conventional extractive distillation process⁽⁷⁾.

In pervaporation, separation is based on the solution-diffusion interaction between the dense permselective layer of the membrane and the solvent/water mixture⁽⁷⁾. The membrane processes pervaporation (PV) is less energy demanding and more effective than conventional processes.

However, there are limitations with pervaporation which includes Membrane Stability, Selectivity Challenges, Temperature Sensitivity, Non-Ideal Mixtures, Economic Viability and Scaling Up. Pervaporation membranes may face stability challenges, such as degradation or fouling over time. Harsh operating conditions, chemical interactions with the feed, and impurities in the mixture can impact membrane stability. Achieving high selectivity for specific components can be challenging. Membrane materials may exhibit selectivity towards one component over another, but achieving absolute selectivity can be difficult, especially for mixtures with similar properties. While temperature can enhance separation efficiency, high temperatures may lead to increased energy consumption and potential degradation of the membrane. Finding an optimal temperature range is crucial. Pervaporation may face limitations with non-ideal mixtures, such as azeotropic systems or mixtures with closely related boiling points. The separation efficiency in such cases may be lower. The cost of membrane materials, fabrication, and maintenance can impact the economic viability of pervaporation. Research is ongoing to develop cost-effective membranes and improve overall process economics. Scaling up pervaporation processes from laboratory-scale to industrial-scale operations can pose engineering challenges. Achieving consistent performance and addressing issues related to large-scale module design and operation are important considerations.

Understanding these theoretical principles and limitations is essential for researchers and engineers to design and optimize pervaporation processes for specific applications. Ongoing research focuses on energy consumption of pervaporation and conventional molecular sieve adsorption for separation of ethanol water and expanding the practicality of pervaporation in various industries.

Energy consumption of pervaporation and conventional molecular sieve adsorption for separation of ethanol water have been analyzed using commercial pervaporation membrane. Shivohm membrane system, Maharashtra, India is the manufacturer of membrane. It is explained that how pervaporation could be a promising alternative to conventional molecular sieve adsorption processes. Detail item wise energy comparison is carried out which is missing in previous reported literature.

Overview of the factors affecting the design of PV processes utilizing these membranes to remove water from common organic solvents is reported in literature. Process variables included: solvent type, water permeance, water/solvent selectivity, initial and final water concentrations, operating temperature (PV), temperature drop due to evaporation (PV) and permeate pressure⁽⁸⁾. Experiments in present study are based on variation in process variables included Operating temperature, Permeate pressure.

Results conclude that a process plant based on pervaporation process with low energy consumption compared to conventional adsorption process can be designed for separation of ethanol water mixture.

2 Methodology

Review of membranes and their properties is reported in literature⁽⁹⁻¹²⁾. Flat sheet membrane module with commercial membrane P64 PEPSI C4064.1C based on PVA-PAN composite, supplied by Shivohm Membrane systems, Kabnur, Mahrashtra, India was used for experimental trials. Membrane area 0.8 m^2 was used for lab scale trials. The final vacuum applied for trials was 10 Torr. 10 L Feed containing Ethanol water mixture with 95 % (v/v) ethanol was maintained at 60 °C. Experimental run was carried out for 10 hrs. Pump of capacity 0.5 Hp fitted with VHP is used for circulation of feed.

Figure 1 shows a schematic diagram for pervaporation process in recirculation and single pass modes. Feed pump is necessary for circulation of feed to the membrane unit. Permeate stream from membrane unit travels to chiller/condenser where water vapors are condensed and retentate is recycled to feed tank. A heater, membrane modules, a cooler/condenser and a vacuum pump assembly completes the set up. In recirculation mode, the reject stream from the membrane modules is recirculated back to the feed tank, while in single pass mode the reject stream from the membrane modules is discharged and not recycled back to the process.

As shown in Figure 1, the energy-consuming elements are heating of the feed stream, cooling/condensing of the permeate stream, the feed pump and vacuum pump. Thermal energy elements are feed heating energy (Qh) and permeate cooling energy (Qc) whereas the electrical energy elements are electrical power associated with feed pump (Ef) and vacuum pump (Ev). The latent heat of condensation of the water vapor form permeate stream could be recovered and used for heating the feed.



Fig 1. Experimental setup

2.1 Molecular sieve process

A molecular sieve plant for ethanol water separation generally uses two or more vessels packed molecular sieves. Two vessels are used for dehydration of ethanol. One vessel will be in regeneration from while other will be used for dehydration. Super-heated ethanol water vapors are fed to the vessel which adsorbs the water. In the other vessel the water is removed from the molecular sieves by desorption. In many cases this is done by a combination of employing a moderate vacuum and feeding a small amount of dry ethanol product to the vessel. The vapor from the vessel in the regeneration mode is fed to the recycle tower which also serves to evaporate the wet ethanol feed to the super-heater. Feed in the first vessel is at 2.72 atm while output stream from second vessel is at 0.13 atm. Superheater duty for first vessel is 133.93 kW While condenser duty after second vessel is -136.00 kW. In the first vessel 99 mol % water is removed and stream with 99 mol % water is sent to second vessel where small amount of dry ethanol is also mixed. Water get desorbed and condensed upto 45.9 mol % ethanol and 54.1 mol% ethanol mixture. In Table 1 a comparison is made between a molecular sieve drying unit and a pervaporation unit for a typical Ethanol dehydration unit with 100 KLPD capacity. The comparison includes the thermal and electrical energy consumption.

Table 1. Energy consumption comparison for pervaporation and molecular sieve process for ethanol water mixture separation.	(100
KLPD pilot plant)	

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Item	Pervaporation	Molecular Sieve					
Steam (kg/24 Hr)	10500 kg	50500 kg					
Pumps power	21 kw	55 kw					
cooling tower	0	400 m3/hr, 80 kw, 50 kw pump, 30 kw fan					
Air compressor	0	18 kw					
Chiller	30 TR, 45 KW	0					
Vaccum pump	10 kw	eductor, 45 m3/hr, 37 kW, 0.1 bar abs					
Total electricity	85 Kw	270 Kw					

The mathematical equations used for thermal and electrical energy calculation are as follows:⁽¹¹⁾

Heating (Qinit) required to increase the temperature of the feed reservoir (TRes) to the required temperature is calculated using equation:

$$Q_{initial} = m_i c_{pf} \left(T_{fi} - T_{res} \right) \tag{1}$$

Heating energy (Qh) required to maintain the feed as well as recirculating stream to the desired feed temperature is calculated using equation:

$$Q_h = m_{c_{pf}} \left(T_{fi} - T_{fo} \right) \tag{2}$$

The thermal energy (Qc) required to condensate the water vapour and subcooling from condensation temperature to Tpo is calculated as:

$$Q_c = m_p \lambda + m_p \int_{tpi}^{T_{pc}} c_{p,g} dT + m_p \int_{T_{pc}}^{T_{po}} c_{p,d} T$$
(3)

The electrical power consumption required for circulating the feed stream through the PV system is given by equation:

$$E_f = \frac{\Delta p_N v_f}{T p^1} \tag{4}$$

The electrical power consumption of a vacuum pump in the PV unit can be estimated using equation:

$$E_V = -m_r \int_{T_{in}}^{T_{int}} c_p dT \tag{5}$$

where

$$T_{out} = T_{in} \left[1 + \frac{1}{\eta p} \left(\left(\frac{P_{out}}{p_{in}} \right)^{\frac{\gamma - 1}{\gamma} - 1} \right) \right]$$
(6)

3 Results and Discussion

Commercial hydrophilic membrane P64 PEPSI C4064.1C performance was compared with the hydrophilic membranes reported in literature⁽¹³⁾. Comparison in Table 2 shows that separation factor as well as total flux related to separation factor is consistent and concludes that membrane area required for separation is less as compared to membranes reported in literature.

Membrane material/Support	Feed concentration (wt%)	Feed Temperature (°C)	Separation factor	Flux (g.m ⁻² .h ⁻¹)				
PAC-polyvinylpyrrolidone	96	20	3.2	2200				
Poly(vinyl chloride)	96	40	63	3				
Cellulose acetate	96	60	5.9	200				
Chitosan	96	40	2208	4				
P64 PEPSI C4064.1C	93.75	60	92.76	180				

Table 2. Commercial h	vdrophilic mer	nbrane P64 PEPSI	C4064.1C com	parison with re	ported data
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Experimental results based on P64 PEPSI C4064.1C are discussed below.

Figure 2 shows the effect of feed temperature on permeate flux obtained at 10 torr vacuums. As the feed temperature increased, the water vapor pressure on the feed side increased exponentially. The vapor pressure on the permeate side was held constant. The increasing vapor pressure in feed due to temperature rise causes increase in the driving force and the water flux. An increase in temperature also increases the diffusion coefficient for transport through the membrane. It is observed that flux obtained increases from 0.05 kg/m^2 .hr to 0.18 kg/m^2 .hr by increasing the feed temperature from 35° C to 60° C. After 60° C increase in temperature causing no significant increase in water flux after 60° C. Although feed temperature in the reported data varies from 20 °C to 60° C, here 60° C is finalized for experiment as flux at this temperature is higher as compared to other temperatures. As compared to the literature data flux is improved compared to chotisan and PVC membrane material support⁽¹³⁾.



Fig 2. Effect of feed temperature on permeate flux (10 Torr vacuum)

Figure 3 shows the water % (w/w) remaining in the retentate part (ethanol rich phase) with the time. Initial water in the retentate was 6.2 %. After 10 hrs of experimental run water % observed was 0.14 % (w/w).

Figure 4 shows effect of vacuum on the first hour permeate flux through membrane. The water flux increased from 0.05 to 0.18 kg/m^2 .hr as the permeate pressure is decreased from 30 torr to 10 torr. With decreasing permeate pressure (i.e., increasing vacuum), as the feed side vapor pressure remains unchanged, the transmembrane vapor pressure difference is increased. This leads to an increased driving force and consequently an increased water flux.

Figure 5 shows the graph for total flux through membrane with time at the feed temperature 60 °C and pressure 10 torr. Initial total flux was 0.18 kg/m².hr using membrane area 0.8 m². As the time increases permeate quantity through membrane decreases. During the 10 th hr flux obtained was 0.01 kg/sq. meter.hr. The driving force for the pervaporation process is the partial vapor pressure difference of permeant between the feed and permeate conditions. One of the reasons for decreasing flux is increase in ethanol concentration at the interface of membrane causing less water to permeate through membrane. As time



Fig 3. The water % (w/w) remaining in the retentate part (ethanol-rich phase) with the time



Fig 4. The effect of vacuum on the first hour of permeate flux

increases, decreased driving force causes water to permeate less. The difference between vapor pressure at the feed/membrane interface on the feed side and at membrane interface on the permeate side decreases with the time at constant vacuum. For the experimental run at 10 torr and 60 $^{\circ}$ C separation factor achieved is 92.76, which is higher than reported literature data⁽¹⁴⁾.



Fig 5. The total flux with time at the feed temperature 60 $^\circ C$ and pressure 10 torr

The pervaporation module results obtained using P64 PEPSI C4064.1C membrane in this study have been used as the basis to estimate the energy consumption required for Pilot plant with capacity 100 KLPD ethanol water feed (ethanol 95 % v/v). Table 2 shows comparison results. Total electrical energy required for Pilot plant is 76 kW while 10500 kg low pressure steam is required to increase and maintain feed temperature to 60 °C. 30 kW energy is required for 20 Tr capacity chiller to condense and cool permeate.

The high pressure steam required for molecular sieve process is significant. 50500 kg high pressure steam is required for ethanol water separation by molecular sieve in comparison to 10500 kg low pressure steam for pervaporation. It is noteworthy that these values are indicative only and highly variable depending on the flux obtained experimentally. The heat of condensation removed in the condenser is almost equal to the intermediate heat required for permeate evaporation. Cooling tower and air compressor in molecular sieve process consumes additional 178 kW heat in comparison to pervaporation.

4 Conclusion

Total electrical energy for pervaporation process is 76 kW as compared to 270 kW required for adsorption process. Electrical energy required for pervaporation process is almost 72% less than molecular sieve adsorption process. For pervaporation process low pressure steam is useful which is not beneficial in molecular sieve process with high pressure steam. Decreasing permeate pressure cause the transmembrane vapor pressure difference to increase upto 10 torr pressure which is finalized figure for operation which leads to an increased driving force and consequently an increased water flux. Experimental run carried out concludes operation time of 10 hrs is required for production of concentrated/unhydrous ethanol with membrane area and pressure specified. Based on these results a process plant based on pervaporation process with low energy consumption can be designed for separation of ethanol water mixture using P64 PEPSI C4064.1C membrane.

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