

Membrane Pervaporation

An Experimental Experience in Novel Separations for Green Engineering

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Abstract

Pervaporation membrane processes represent a state-of-the-art separation for the specialty chemical, pharmaceutical and petrochemical industries. In its industrial application, pervaporation can be used for solvent purification, reuse and recovery – thus enabling green process design for the environment. At Rowan University we have successfully immersed student teams in learning the principles, design and applications of membrane pervaporation through a project-based experience in our engineering clinics. Through this experimental project, students have learned about the industrial uses of membrane technology. Students also learn about the various process aspects of pervaporation, from selecting the proper membrane for the desired separation to examining performance parameters, membrane transport, vacuum operation and cryogenic vapor trapping, not normally taught in chemical engineering curricula. Most importantly, students see how membrane processes can be used in “green process” operation and design.

Introduction

Membrane technology is being incorporated into many areas of chemical engineering for process and product concentration and purification. One of the leading-edge membrane technologies, pervaporation, has applications in the growing engineering areas of:

- pharmaceutical engineering/biotechnology
- hazardous waste management
- specialty chemical and biochemical production
- food and beverage processing
- reuse and recovery systems engineering

Its use in green engineering for sustainable process design will be the focus of the experimental development described in this paper. In particular, pervaporation has received much notice for its ability to partially or totally replace complex processes such as azeotropic or extractive distillation which use additional chemicals. Pervaporation can be used in an organic solvent recovery and purification mode in chemical, pharmaceutical and petrochemical processes, thus enhancing the sustainability of the overall manufacturing process.

Other membrane processes, e.g., reverse osmosis, ultrafiltration, microfiltration and gas permeation exist that can also be integrated into the curriculum and are described elsewhere [1, 2, 3, 4, 5, 6, 7, 8].

Background

Pervaporation selectively separates a liquid feed mixture, typically using a nonporous polymeric membrane. The generally accepted mechanism for pervaporative transport is solution-diffusion [9]. Transport in a pervaporation process is generally considered to follow three steps:

- 1) Sorption of the liquid mixture on the feed side of the membrane
- 2) Diffusion through the membrane
- 3) Desorption on the permeate side of the membrane to the vapor phase

Preferential solute permeability, which is based on solubility and diffusivity of the solute in the membrane, must exist for effective separation of the solute from a feed mixture. The chemical potential gradient across the membrane from the feed (liquid) side to the permeate (vapor) side is the driving force for separation.

In a simple pervaporation process, a liquid feed mixture flows past the membrane and a vacuum is maintained on the permeate side (Figure 1). The permeate produced is in the vapor phase and can be condensed as needed. The retentate remains a liquid. An effective separation is achieved since the permeate becomes "rich" in the component(s) that preferentially permeate the membrane while the retentate becomes "lean" in those component(s).

The effectiveness of pervaporation is measured by two parameters, flux and selectivity. Consider a binary mixture of components A and B. The flux is the rate of permeation per membrane area and can be expressed for the total permeate or for each specific component.

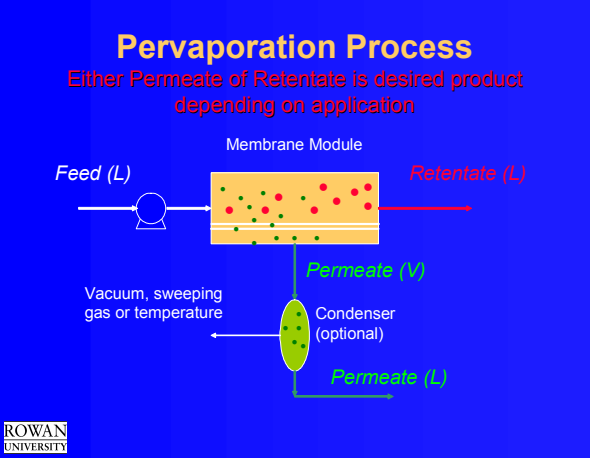
- J_T = total flux
- J_A = flux of component A
- J_B = flux of component B

The flux has dimensions of mass/(area•time), [M/L²•t]. Typical units would be kg/m²hr. The flux can be measured by knowing the mass of permeate collected, membrane area, and time of the experimental run. The flux can also be defined by the phenomenological expression:

$$J_i = -L_i(\Delta\mu_i/l) \tag{1}$$

where L_i = phenomenological transport coefficient

Figure 1. Pervaporation process



$\Delta\mu_i$ = chemical potential driving force across the membrane

l = membrane thickness

Selectivity is a measure of the membrane's separation efficiency. It is a ratio of the mass fractions of components A and B for the permeate and the feed.

$$\alpha = (y_A/y_B)/(x_A/x_B) \quad (2)$$

where y_A = mass fraction of A in the permeate

y_B = mass fraction of B in the permeate

x_A = mass fraction of A in feed

x_B = mass fraction of B in feed

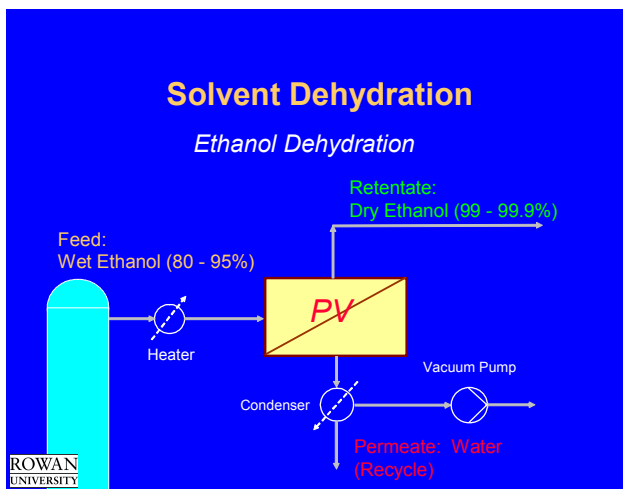
Equation 2 is for the selective permeation of component A. A value greater than unity indicates the preferential permeation of A over B, and a value less than unity indicates the selective permeation of B over A. The separation effectiveness is sometimes expressed as an enrichment factor, β . The enrichment factor is the ratio of a component's concentration in the permeate to its concentration in the feed.

$$\beta = y_A/x_A \quad (3)$$

Pervaporation has the capability of separating a wide range of organic chemicals from process effluent streams. Pervaporation can be used to dehydrate organic solvents that are "contaminated" with water in order that they be recovered and reused. Pervaporation can also be used to selectively remove trace amounts of organic contaminants from waste and byproduct streams. The result of this process is two-fold. First, if the organics are successfully removed from the aqueous mixture, the now purified water can be recycled, or discharged without environmental consequences. Secondly, the newly recovered solvent can be further purified by a dehydration process, and reused in the process stream if needed. Thus pervaporation can be looked upon as an environmentally and economically advantageous process [10].

The first successful commercialization of pervaporation technology was organic solvent dehydration. Commercial plants to dehydrate solvents such as isopropanol, acetone, ethanol, etc.

Figure 2. Solvent dehydration process schematic for EtOH-H₂O



are in world-wide operation (Figure 2) [9]. These systems use hydrophilic membranes to selectively permeate water and produce a "dry" organic retentate.

Commercial pervaporation systems for organic removal from aqueous mixtures have been successfully applied in environmental, biotechnology and food/beverage applications [9, 10]. By far the most promising and challenging area for growth is the application of pervaporation technology to organic-organic separations common to the petrochemical and specialty chemicals industry [9].

Previous research by the author has focused on organophilic pervaporation to separate a variety of organic-water mixtures [11, 12, 13, 14, 15, 16]. The objective of the

current work is to study in detail how various process parameters affect the separation of dilute amounts of ethyl acetate from aqueous solutions. This work then forms the basis for further modeling and design as applied to the actual plant effluent streams.

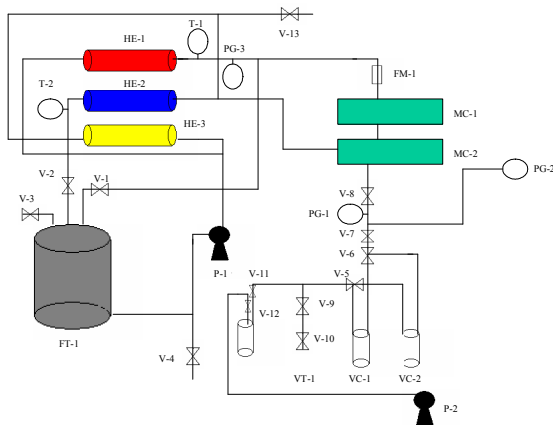
Laboratory Development

The Zenon PV-LAB unit (Zenon Environmental, Inc., Burlington, Ontario, Canada) that was used in this project is a bench-scale system designed to provide pervaporation testing for dehydration of solvents and selective removal of organic solvents from liquid streams. The pervaporation test cell accommodates membrane sheets and provides a cross flow with sufficient turbulence for the separation of process fluids without adverse mass transfer effects. The maximum feed tank capacity of the system is 10 liters. The maximum feed flow rate is 12 liters/min. The major components of the Zenon

system are a seal-less feed pump, pervaporation test cell, feed tank, feed heater, two cold water heat exchangers, three permeate impingers/condensers, and vacuum, pressure, and temperature gauges. All components are interconnected with necessary piping, valving, wiring, and controls, on a self-contained rugged steel frame (Figure 3).

The unit is quite versatile in its control of process parameters. Feed temperatures can be

Figure 3b. Pervaporation system schematic



The unit is designed to achieve high vacuums (~1 torr or less). Permeate-side pressure is controlled using a valve downstream of the membrane cell, but upstream of the condensers. The pressure is regulated by closing the valve it to increase the permeate-side pressure, fully open is the lowest pressure. Instead of using this feature, a vacuum break (air bleeding technique) with a fine regulating valve downstream of the condensers can be employed. The unit has three brass

Figure 3a. Pervaporation system in operation



regulated with a feed heater that can produce a maximum feed around 90°C. A cold water heat exchanger is placed in the retentate line and can be used to further regulate temperature or connected to a brine source for reduced temperature studies. Feed flow rate can be controlled up to 12 liters/min with a valve in the feed loop bypass line. Permeate-side pressure can be controlled and is measured with a 0 - 40 torr (mmHg) vacuum gauge. Downstream or permeate-side pressure is maintained with a vacuum source. A laboratory vacuum pump (~0.1 torr capability) is connected to the Zenon system through heavy-walled flexible tubing.

impingers with glass collection bottles, each which serve as condensers and can collect approximately 15 ml of permeate (although other size bottles can be attached). Dewars with the appropriate condensing fluid, e.g., liquid nitrogen, are placed under the glass condenser bottles and raised and lowered by a simple lab jack during the run. Thus, students learn about cryogenic trapping of organic and water vapor mixtures.

One of the important features of the system is the membrane test cell. The cell accepts standard flat sheet membranes, therefore permitting evaluation of either commercially available sheets or those made in one's own laboratory. The membrane area available for permeation is 79.1 cm² (the membrane permeation area is rectangular with rounded corners with nominal dimensions of 5.65 x 14 cm). The test cell has a rectangular design with appropriate headspace that permits true cross-flow to occur. The design of the cell and capacity of the feed pump improve cell turbulence to produce Reynolds numbers in excess of 10,000. Reynolds numbers of this magnitude are necessary to minimize mass transfer boundary layer effects in performing studies on the removal of trace volatile organics from water and in maximizing the separation of partially miscible systems. A complete discussion of pervaporation system experimental design has been described elsewhere by Slater and Lipski [17]

Laboratory Project

The project activity described below takes place in the Junior and Senior engineering clinics where multidisciplinary teams (~3 students/team) work on open-ended projects in various areas, many linked to industry or a faculty grant from a state or federal agency [18, 19]. These projects emanate from a particular discipline, are lead by that department's faculty, and typically involve an industrial mentor. These student teams are matched by the faculty Project Manager (PM) to best achieve the best results in the individual projects. Teams may combine various fields of expertise within a classic discipline (environmental, water resources and structural) in CEE, (biochemical and polymer) in ChE or science with engineering (Chem and ChE). Students are required to produce a written report or paper/ journal publication and present an oral report at the end of the semester.

The goal of the project is to evaluate the use of pervaporation technology in a green engineering role for sustainable process design. To meet this objective, student teams need to investigate the use of organic solvents (which will be eventually recovered and purified by pervaporation) in the chemical process industry. This could come from examining the production of a pharmaceutical, specialty or commodity chemical, or petrochemical product. Students are asked to get basic process design information, such as they would find in the Kirk-Othmer Encyclopedia of Chemical Technology [20] and do life cycle assessment on the product produced [21]. This will show the flows of energy and materials from "cradle to grave" and the impacts on the environment. Through this analysis, the student team can see the challenges and needs for separation processes.

Once the student team identifies an area to use pervaporation, then they can propose and conduct bench-scale experiments to get preliminary data to do scale-up and design calculations. For the case mentioned in this paper, the students have chosen to investigate a pharmaceutical production where organic solvents such as acetone, ethanol, ethyl acetate, methyl ethyl ketone, isopropanol, toluene are commonly used.

The challenge in a process upgrade for sustainable design is two-fold. There are dilute solvents streams that can be concentrated and further reused in the process. Here, students will

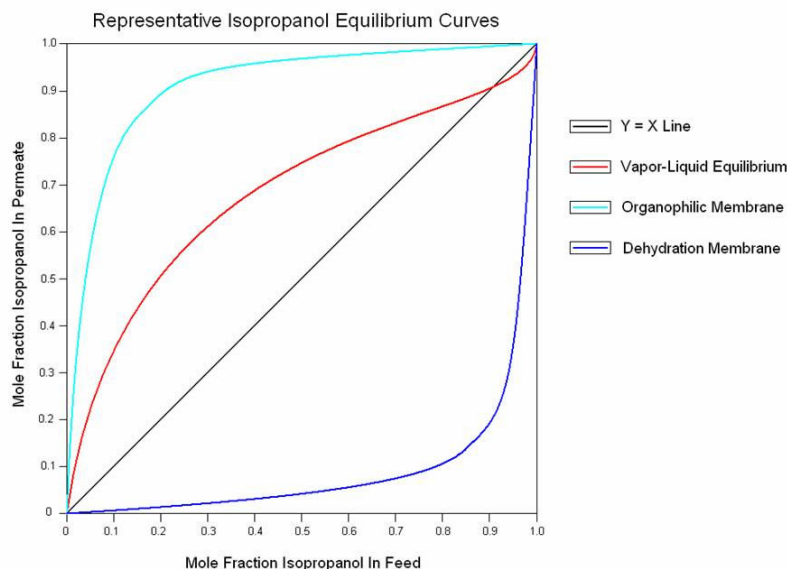
need to investigate the use of organophilic membranes to selectively permeate and concentrate the organic from water mixtures. In this application the membrane pervaporation system may compete with more conventional chemical process technology such as liquid-liquid extraction. The other “end” of the operation is where the solvent “rich” streams have varying concentrations of water from 20 to a few percent. In this application of pervaporation, a hydrophilic membrane is used to selectively permeate water from the feed stream, producing a retentate that is essentially pure organic solvent. Therefore, any solvent streams that would have been treated as waste and either discharged or disposed of can now be reused, therefore minimizing the need to manufacture them which results in lower energy and raw materials usage.

Experimental Studies

The following section describes the basic experiments that a student group can perform to examine membrane performance. These experiments are used to examine both basic feasibility of using a particular membrane for a given separation and to understand the effect of the process parameters (feed concentration, temperature and permeate-side pressure) on membrane performance.

A membrane feasibility experiment can be used to determine selectivity and flux in the separation of a particular chemical mixture. A good choice for an initial experiment is the

Figure 4. Pervaporation “operating” curve vs. VLE in isopropanol-water separation



(~10% w/w water) (Figure 4). A feed temperature in the range of 50 - 90°C can be used with a permeate-side pressure ~10 torr (mmHg) absolute. A high feed flow rate, ~10 liter/min, should be used. These experimental conditions should be held constant during the run. The experiment will produce a permeate that is mostly water. Flux and selectivity calculations are performed. An initial experiment like this is an important study, especially if the student hasn't performed any other type of membrane separation experiments. This test will also give the student confidence in operating the system and collecting data.

dehydration of an organic solvent. Some of the common organic streams that are dehydrated in industry are ethanol, isopropanol, acetone, and tetrahydrofuran. Isopropanol is a good candidate since sufficient literature data exists to compare results. This run should use a hydrophilic membrane that is commercially available, such as the Sulzer dehydration membranes. A typical polymer used as a dehydration membrane is poly(vinyl alcohol), PVA. The run can be performed with a water concentration close to the azeotropic composition of an isopropanol-water mixture

A variation on the basic introductory experiment is to use an organophilic membrane, e.g., a silicone-based polymer, to selectively remove an organic from a dilute aqueous mixture. This could simulate the removal or recovery of products from fermentation operations such as ethanol, butanol, acetone, etc. The study could also simulate removing an organic from a contaminated industrial waste stream or in recovering a solvent and concentrating it for reuse. A dilute organic concentration, in the range of ~5% w/w is used and the process temperature and permeate side pressure are again held constant. During this experiment the permeate is enriched in organic. Similar flux and selectivity calculations are performed.

An experiment like the one described above is good if laboratory time is limited, although it produces minimal data. The study allows the student to understand the basics of pervaporation, and the unique features of this membrane operation such as vacuum operation, cryogenic trapping, and properly handling membranes. These experiments take a longer time to complete than typical reverse osmosis or gas permeation experiments because of the process complexities and the time needed for a new membrane to reach steady state. A complete examination of the process engineering aspects of pervaporation is only possible after examining the effect of process parameters on pervaporative performance. Studies can be aimed at investigating the effect of feed solute concentration, feed temperature, permeate-side pressure, and feed flow rate on flux and permeate concentration. These experiments usually take an entire semester to generate enough data for correlations.

The next logical experiment involves determining the effect of feed solute concentration on pervaporation performance (Figure 4). This experiment is also useful in generating an "operating curve" of the pervaporation process and comparing that to a standard vapor-liquid equilibrium (VLE) curve for the same binary mixture (as done in distillation). Either the selective water permeation or the selective organic permeation example could be used. This experiment would simply vary the feed concentration from 0 to 100% (in appropriate intervals) and measure the permeate concentration and flux that are produced. The permeate concentration can be measured with a gas chromatograph (GC). This experiment is not too practical for time purposes since the system must come to steady state for each run, and it would take separate laboratory periods for each run. A shorter variation of this experiment generates data in the range of interest (usually 0 - 20% of the feed concentration of the preferentially permeating species). This experiment shows that as the concentration of the preferentially permeating component in the feed is increased, so is the transport of that component through the membrane. This increases the total flux and permeate composition.

Information on scale-up and system design can be generated by examining the effect of other process parameters on pervaporative performance. Temperature is a good candidate for study. Regardless of the separation being performed, as temperature increases so does the flux. This occurs in an Arrhenius-type manner. Figure 5 shows an example of typical student data for

Figure 5. Effect of temperature on pervaporative flux for diacetone alcohol-water dehydration

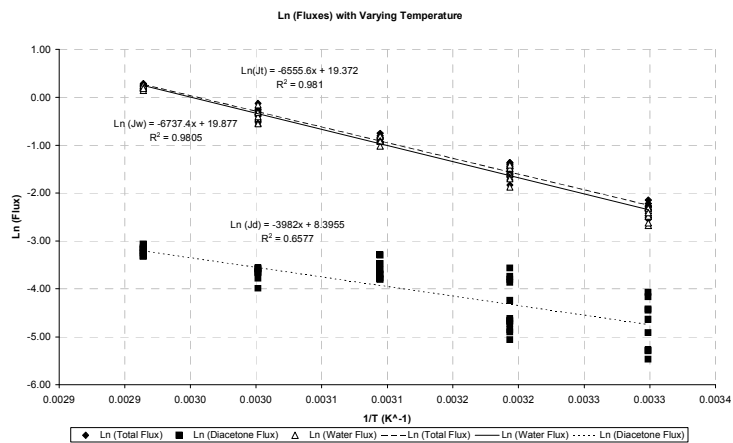
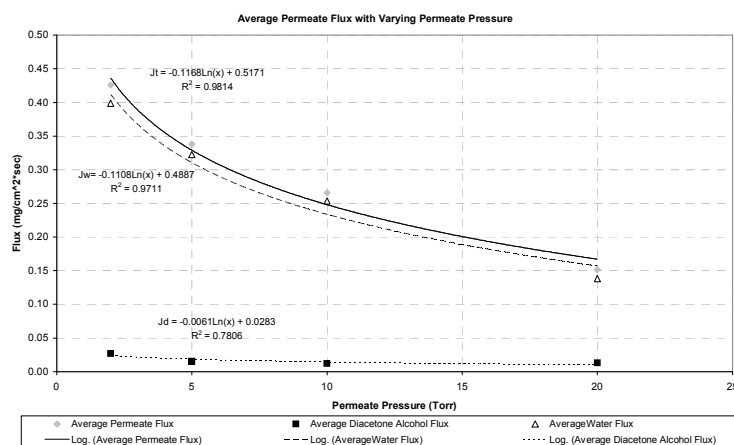


Figure 6. Effect of Permeate-side pressure on pervaporative flux for diacetone alcohol-water dehydration



effect of Reynolds number on the mass transfer coefficient. The students can also take the data collected from the basic permeability experiment and estimate the various stream concentrations using a simple material balance.

Conclusions

An experimental project in membrane pervaporation for organic solvent separation provides a valuable experience for chemical engineering students. Through an experimental project students are exposed to many aspects of the theory, design and application of membrane pervaporation. Students examine the effect of process parameters, feed concentration, feed temperature and permeate pressure on pervaporative performance. They can develop empirical correlations that can be later used in process design. Students can investigate the use of pervaporation technology in solvent recovery and reuse in a chemical manufacturing operation. This part of the project enables the understanding of green engineering design for sustainable manufacturing.

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a temperature study. The activation energy of separation can be calculated from this relationship. The permeate-side pressure can also be varied (Figure 6). As absolute permeate pressure is increased, permeate flux decreases. The student can calculate the limiting pressure to have a chemical potential difference across the membrane. The student can also note that feed pressure does not influence pervaporative performance. The effect of cross flow velocity past the membrane surface can be varied by controlling the feed flow rate. The student can then investigate the

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Biographic Sketches

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