

Options for Combining Pervaporation Membrane Systems with Fermentors for Efficient Production of Alcohols from Biomass

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Prepared for Presentation at 2004 AIChE Annual Meeting, November 2004, Topical Conference T4

Abstract Although several separation technologies are technically capable of removing volatile products from fermentation broths, distillation remains the dominant technology. In this presentation, the status of an emerging membrane-based technology called pervaporation for the recovery of biofuels such as ethanol is reviewed and options for integrating pervaporation units with fermentors will be discussed. Pervaporation is an attractive technology because of the potential to selectively separate alcohols and water. Several issues and research priorities which will impact the ability of pervaporation to be competitive for biofuel recovery from fermentation systems will be identified.

Introduction The production of renewable biofuels has been receiving increased attention due to the phase out of methyl t-butyl ether (MTBE) as a fuel oxygenate, the reliance on sometimes problematic sources of fossil fuels, and the effect of non-renewable fossil fuel combustion on the earth's climate. Currently, the conversion of corn to ethanol accounts for the vast majority of liquid biofuels produced in the United States. Only a few decades ago, the ethanol produced from corn contained less energy value than the energy required to produce that ethanol [1]. Over time, efficiency gains in the corn-to-ethanol conversion process have reversed this situation [1]. Unfortunately, some of these efficiencies are only possible at the large scale, thereby fueling the drive to large corn-to-ethanol plants. For example, the median capacity of corn-to-ethanol plants under construction in the year 2004 was 40 million gallons per year (MGY) (150 million liters per year) [Source: BBI International].

While corn will remain a sizeable fraction of the starting material for liquid biofuels for the foreseeable future, other carbon sources will be required if renewable biofuels are to make more significant inroads into the world's energy portfolio. A variety of biomass materials are available for production of liquid biofuels, both intentionally grown for this purpose and that which is a side product or waste material from another process. Some of these waste materials, such as corn stover, are co-located with current large-scale ethanol production facilities. Many more sources of lignocellulosic material will be distributed in nature. The amount of this distributed biomass waste is significant, although often overlooked.

In order to utilize this distributed biomass, a process train which can convert lignocellulosic materials to biofuels such as ethanol or butanol in an efficient, cost-effective manner at a small scale is needed. The stages of this process train must be reassessed individually and collectively in order to arrive at the most efficient small scale system. For example, recovery of ethanol from the fermentation broth has long been ceded to distillation for corn-to-ethanol operations. The economies of scale and the degree of heat integration which are achieved at the large scale make distillation economically and energetically efficient. However, the advantages of distillation over competing separations technologies for biofuel recovery fade as

the scale of the operation is reduced, thereby opening the door for other technologies such as gas stripping, liquid-liquid extraction (perstraction), vacuum stripping, membrane distillation, vacuum membrane distillation (VMD), sorption, and pervaporation.

Fundamentals of pervaporation Pervaporation is a process in which a liquid stream containing two or more miscible components is placed in contact with one side of a non-porous polymeric membrane or molecularly porous inorganic membrane (such as a zeolite membrane) while a vacuum or gas purge is applied to the other side. The components in the liquid stream sorb into/onto the membrane, permeate through the membrane, and evaporate into the vapor phase (hence the word “pervaporate”). The resulting vapor, referred to as “the permeate”, is then condensed. Due to different species in the feed mixture having different affinities for the membrane and different diffusion rates through the membrane, a component at low concentration in the feed can be highly enriched in the permeate. Thus, the permeate composition may widely differ from that of the vapor evolved after a free vapor-liquid equilibrium process. A schematic diagram of the pervaporation process is shown in Figure 1. The main process units of a pervaporation process: feed source, feed pump, heater, membrane module, condenser, and vacuum pump, are shown in Figure 2.

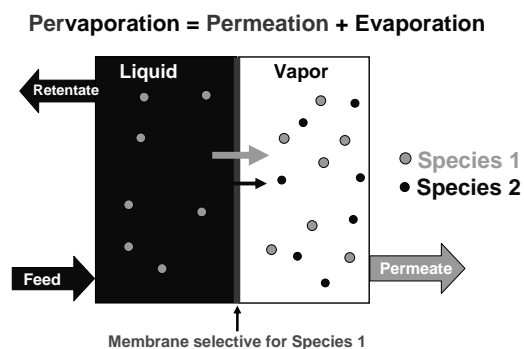


Figure 1. Schematic diagram of pervaporation process.

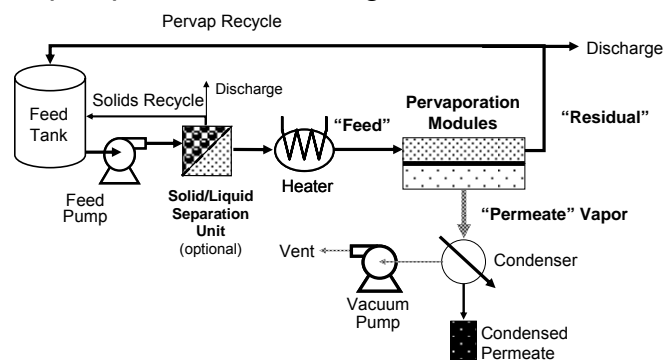


Figure 2. Flow diagram for generic pervaporation system.

The properties of the membrane material dictate the separation achieved in the process. If the membrane is hydrophobic, then organic compounds will preferentially permeate relative to water and the permeate will be enriched in the organic compounds. Alternatively, if the membrane is hydrophilic, then water will be enriched in the permeate and the organic compound in the feed liquid will be dehydrated. For the production of biofuels, pervaporation can be applied to both the recovery of alcohols from water and for the dehydration of the alcohols to meet fuel dryness specifications.

The maximum pervaporation transport driving force (and therefore maximum flux through the membrane) is achieved at the maximum feed concentration, the minimum permeate partial pressure of the target species, and the maximum feed liquid temperature. Obviously, there are limits to each of these. For example, feed temperature is limited first by the boiling point of the feed mixture and secondarily by the temperature sensitivity of components of the feed. The tradeoffs associated with a maximal operating temperature are highlighted in Table 1. Unless limited by the presence of temperature sensitive feed liquid components, the advantages of operating at a high temperature typically outweigh the disadvantages. For example, the membrane area required to remove a given amount of ethanol from water is on the order of ten times higher at 30 °C than at 80 °C. Potential temperature sensitive components can be either biotic in nature, such as enzymes or living microorganisms, or abiotic, such as certain

aroma/flavor compounds. Several flowsheet scenarios are available for processing such streams with pervaporation as has been well outlined by Groot *et al.* [2,3] and Mulder and Smolders [4].

Table 1. Advantages and disadvantages associated with operating a pervaporation system at the maximum possible temperature.

Advantages	Disadvantages
<ul style="list-style-type: none"> • Highest flux • Highest permeate pressure (reduced vacuum requirement) • Lowest permeate condensation costs (ability to operate at higher coolant temperatures) • Yields system with the lowest required membrane area 	<ul style="list-style-type: none"> • Harmful to temperature sensitive compounds and microorganisms • Higher likelihood of precipitate formation • Increased heater capital costs • Requires high temperature heat source • Requires heat exchanger to recover heat from residual stream • Increased material property requirements • Requires more insulation

Integration of Pervaporation with Fermentation Systems A comparison of different author's research on alcohol generating fermentations is difficult due to the number of variables which enter into the reported results such as: type, strain, growth phase and loading of microorganism; source, pretreatment, and concentrations of nutrients and substrate; temperature and temperature history; pH and pH history; oxygen concentration; fermentor design/mixing. Adding the variables associated with separation technologies to the fermentation variables yields an even more complex system from which few direct comparisons are possible. However, a number of general trends and observations can be made from this body of research:

- 1) Fermentor productivity will increase upon application of a solvent removal technology if the microorganisms exhibit inhibition by the solvent product at concentrations readily achieved in the fermentor.
- 2) Increasing the concentration of viable cells in the fermentor will increase the solvent productivity of the fermentor, all other variables being equal.
- 3) Integrating a solvent recovery unit with a fermentor enables the use of more concentrated substrate solutions which increases the productivity of the fermentor and reduces the amount of water processed in the system.
- 4) A variety of separation technologies, including pervaporation, are technically viable to recover biofuels from fermentation broths.

Solid-Liquid Separation As noted previously, the most cost-effective pervaporation system is most likely one which is operated at the maximum possible feed temperature. Therefore, if temperature sensitive materials are present, then the pervaporation system will either have to be operated at a temperature lower than the operational optimum, the sensitive materials will need to be removed prior to being exposed to harsh conditions, or a certain incapacitation of the sensitive materials will need to be accepted. In most biofuel fermentation scenarios, the most temperature sensitive materials are microorganisms. As a result, microfiltration (MF) and centrifugation are both viable separation options as the solids separation unit shown in Figure 2. As a barrier-based technology, membrane filtration has the advantage that it will, theoretically, remove all solids above the design range of the filter. MF is capable of removing most fermentative microorganisms. If proteins or enzymes must be retained as well, then

ultrafiltration (UF) or nanofiltration (NF) may be required. In centrifugation, no absolute or relative cutoff standard exists. In addition, centrifugation is only able to separate materials based on density differences. Thus, fermentor solids with a density similar to that of the broth will be difficult to remove by centrifugation. Several studies have noted the presence of solids in the clarified centrate stream from centrifuges whereas the high clarity of the permeate from membrane filters has been observed. The main vulnerability of membrane filtration is potential fouling of the membrane surface or of the internal pores. Membrane fouling has been addressed through module design (rotating disk filters, vibrating modules, tubular membranes, ceramic membranes, open flow channels, turbulence enhancing inserts) and operating procedures (high cross-flow feed liquid velocity, air sparging, backflushing, cleaning regimens). The solid-liquid separation device before the pervaporation system not only removes temperature sensitive broth components, thereby allowing pervaporation operation at elevated temperatures, it also protects the pervaporation modules from fouling by solids in the broth.

Based on the above discussion, a pre-pervaporation solid-liquid separation device, although not required, would reduce the fouling potential of solids in the fermentor broth and enable the use of the full range of pervaporation module options. The recovered biosolids could also be returned to the fermentor to increase the productivity of the fermentor by increasing the concentration of viable cells in the reactor. The addition of any separation device to the system adds capital and operating costs. Thus, an economic tradeoff exists between the increased efficiency of pervaporation combined with the increased fermentor productivity vs. the increased complexity of adding a pre-pervaporation separation device.

Membrane Materials for Alcohol Recovery by Pervaporation Many membrane materials have been studied for the purpose of recovering organic compounds from water by pervaporation. The ability of a membrane to separate species 1 from species 2 is most often reported as the separation factor, α_{12} , as defined by:

$$\alpha_{12} = \frac{\left(\frac{C_1^v}{C_2^v} \right)}{\left(\frac{C_1^L}{C_2^L} \right)} \quad \text{where } C_i^L \text{ and } C_i^V \text{ are the bulk liquid and vapor concentrations (mol/m}^3\text{) of species } i$$

The current benchmark hydrophobic pervaporation membrane material is poly(dimethyl siloxane) [PDMS], often referred to as “silicone rubber”. Reported ethanol-water separation factors for “pure” PDMS membranes range from 4.4 to 10.8. The broad range in ethanol-water separation factors for PDMS membranes is typical of performance parameters reported in the literature for a given polymer and separation situation. The breadth in values arises from a variety of factors, including the source of the polymer starting materials, method of casting the film, crosslink density, thickness of the selective layer, microporous support material (if any), and test conditions. Reported butanol-water separation factors for PDMS also cover a fairly broad range – 40 to 60 – which is 6 to 10 times that of ethanol-water.

Much effort has been expended searching for polymeric materials with better ethanol-water separation performance than PDMS. Unfortunately, seldom have materials been reported to improve upon PDMS. One material which has received significant attention is poly[1-(trimethylsilyl)-1-propyne] or “PTMSP” – a high free volume polymer displaying a permeability higher than that of PDMS. The ethanol-water separation factor for PTMSP has also been reported to be higher than that of PDMS, ranging from 9 to 26. Unfortunately, PTMSP

membranes have, so far, proven to deliver unstable performance, with flux and selectivity declining with time, although efforts continue to improve the stability of PTMSP.

While no organic membrane has yet to challenge PDMS as the benchmark hydrophobic pervaporation membrane material, inorganic membranes based on hydrophobic zeolites, such as silicalite-1, have shown both higher ethanol-water separation factors and ethanol fluxes than PDMS membranes. Silicalite has been reported to deliver ethanol-water separation factors ranging from 12 to 72 with a typical value around 40 – four to five times that of PDMS. As with inorganic membranes in other areas, silicalite-1 membranes are expected to be more expensive than polymer membranes on a unit area basis. However, they may be cost effective on a per unit ethanol basis owing to the higher separation factor and flux afforded by the silicalite-1. Efforts to produce silicalite-based modules on a larger scale are ongoing including development of tubular silicalite membranes at Bio-Nanotec Research Institute, Inc. (BNRI, part of Mitsui & Co, Ltd., Tokyo, Japan) and of multi-channel monolithic membranes at CeraMem Corporation (Waltham, Massachusetts USA).

Due to the difficulty and cost of manufacturing defect free commercial-scale silicalite membranes, several groups have investigated the potential of mixed matrix membranes consisting of silicalite particles dispersed in PDMS. In fact, a membrane of this type was, until recently, available from Sulzer Chemtech. The range of ethanol-water separation factors for silicalite-PDMS mixed matrix membranes is from 7 to 59, overlapping the ranges reported for both PDMS and silicalite alone.

Future Trends in Pervaporation Membranes The preceding discussion provides a glimpse of the most attractive materials for the recovery of ethanol from water which are either currently available or under development. It appears that PDMS will, at least for the near term, continue to be the dominant organic membrane material for the recovery of alcohols from water. Development of silicalite-based membranes, both pure and in mixed matrix form, will continue, likely culminating in commercial membranes of this type available within 2-5 years.

Effect of fermentation broth components on pervaporation membranes and modules

The literature contains several anecdotal observations regarding the impact, both positive and negative, of fermentation broth components on the performance of a variety of pervaporation membranes and modules. However, only a few of these attempted a systematic study to unravel the often overlapping effects of broth components on pervaporation membranes. To complicate matters, several studies have indicated no significant effect of fermentation broth on pervaporation performance of various membrane materials. Broth components which have been mentioned as impacting pervaporation performance include: viable and dead whole cells and cell debris, suspended solids, sugars (glucose, xylose), organic acids (acetic, L-malic, succinic, butyric), dissolved solids (NaCl), glycerol, alcohols, pH, and fatty acids. Given the uncertainty, additional experimental observations are needed to understand the impact of broth components on pervaporation performance.

Energy Considerations Molecules which end up in the permeate experience a phase change from liquid to vapor which requires energy to fuel the evaporation. Since the membrane is never infinitely selective, heat must be applied to evaporate not only the desired permeate species, but the undesired permeating species. When pervaporation is operated at an elevated feed temperature (and therefore elevated permeate temperature), the heat released during

condensation can be removed with a simple forced air heat exchanger. Under these circumstances, the heat of evaporation is the dominant energy sink in the pervaporation process. Thus, the energy cost of delivering a unit of ethanol as condensed permeate is roughly the sum of the energy required to evaporate both the desired ethanol and the undesired water in the permeate. The heat of evaporation on a mass basis is significantly higher for water than for ethanol (2260 vs. 838 kJ/kg). For example, if the permeate contains 50 wt% ethanol, 1 kg of water is evaporated per 1 kg of ethanol with 73% of the energy involved required for the water component. Therefore, in order to achieve highly energy efficient recovery of alcohols from water, high alcohol-water separation factors are desired.

Several conclusions can be made from an analysis of evaporation energies and strategies to reduce energy usage, including recovering the heat of condensation using heat pumps. First, using heat-integrated distillation systems as a benchmark and requiring a residual ethanol concentration of 0.02 wt%, pervaporation systems with ethanol-water separation factors greater than 15 are required to improve upon the benchmark if condensation heat recovery is employed while separation factors greater than 40 are required if condensation heat recovery is not employed. If the residual ethanol requirement is relaxed (or if the ethanol recovery requirement is reduced), then even pervaporation systems with separation factors of 8 or 10 are sufficiently energy efficient while still maintaining ethanol recoveries in excess of 90%.

Conclusions Pervaporation is an emerging technology with significant potential to efficiently recover alcohols and other biofuels from fermentation broths. Based on the information in this presentation, a number of issues must be addressed for pervaporation to be economically viable, energetically attractive, and enlisted for biofuel recovery:

- 1) Increased energy efficiency - improved ethanol-water separation factor and heat integration
- 2) Reduction of capital cost for pervaporation systems - reduction in the membrane/module cost per unit area and increase in membrane flux to reduce required area
- 3) Longer term trials with actual fermentation broths to assess membrane and module stability and fouling behavior
- 4) Optimized integration of pervaporation with fermentor - filtration to increase cell density in fermentor and allow higher pervaporation temperatures, removal/avoidance of inhibitors
- 5) Synergy of performing both alcohol recovery and dehydration by pervaporation with dephlegmation fractional condensation technology
- 6) Updated economic analyses of pervaporation which provide comparisons to competing technologies on even bases at various biofuel production scales.

As part of our research and development activities into the sustainable production of biofuels, the USEPA's Pervaporation Team will be contributing to four industry-led, U.S. government-funded research projects which seek to address the issues outlined above.

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