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Membrane-Based Hybrid Processes: A Review

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Abstract: It has been widely recognized that membrane separation processes can offer many advantages over conventional mass transfer processes. A large number of membrane separation processes are currently being practiced in various sectors of industries. Despite the advantages, membrane processes often suffer from shortcomings when used individually. To overcome such limitations, membrane-based hybrid processes have been developed to maximize the productivity of the target separation processes. In this review, the membrane hybrid processes reported in the literature are classified into several categories and chosen examples of the processes are presented to show the general trends in the development of membrane-based hybrid processes.

Keywords: Membrane separation processes, mass transfer processes, membrane-based hybrid processes, target separation processes

INTRODUCTION

The increased world-wide competitiveness in production has forced industry to improve current process designs and also the increased importance of natural environment has compelled industry to develop new process designs. Consequently, the reorganization of present process designs (with the possible integration of new technologies into them), and the development of new process designs using alternative technologies is of growing importance to the industry.

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Membrane technologies have recently emerged as an additional category of separation processes to the well-established mass transport processes. Membrane separation technologies offer advantages over existing mass transfer processes. Such advantages can consist of (1);

- high selectivity,
- low energy consumption,
- moderate cost to performance ratio, and
- compact and modular design.

However, membrane processes have several inherent limitations. For example, a membrane system designed to treat waste water may be limited by the water's osmotic pressure, viscosity, temperature, and high concentration of suspended solids (2).

Therefore, the optimal separation process in many cases may be a 'Membrane-based hybrid process' that combines either a membrane process with a conventional process or a membrane process with the other membrane process. A hybrid process is appropriate when it offers significant advantage (such as lower capital and production costs or reduced energy requirements) over the exclusive use of conventional processes. Moreover, membrane hybrid processes may achieve separations that are otherwise impractical or altogether impossible to achieve with either conventional process.

In this paper, the studies reported in the literature on various membrane hybrid processes and their applications, process designs, etc. were reviewed to show the general trends in the development of membrane hybrid processes.

CLASSIFICATION OF MEMBRANE HYBRID PROCESSES

All membrane hybrid processes fall into the following two categories

1. processes that combine a membrane process with a conventional separation process (MCH) and
2. processes that combine a membrane process with another membrane process (MMH).

In the first category, to which most of the membrane hybrid processes belong, a conventional separation process is modified using a membrane process to achieve lower capital cost and/or while maintaining the cost, higher productivity and milder operational conditions, etc. In the second category, one or more membrane processes are integrated to a key membrane process to overcome the problems that arise when only a key membrane process is used.

The hybrid processes discussed in this paper are classified in Table 1.

Table 1. Classification of membrane hybrid processes

Hybrid process	Process 1	Process 2
MCH	Distillation	Pervaporation (PV)
	Esterification	Vapor-permeation (VP)
	Fermentation	Membrane gas separation (MGS)
	L-L phase separation	Microfiltration (MF)
	Biological oxidation	Ultrafiltration (UF)
	Air-stripping	Reverse osmosis (RO)
	Evaporation	Membrane distillation (MD)
	Pressure swing adsorption (PSA)	Membrane bioreactor (MBR)
	Flocculation	
	Powdered activated carbon (PAC)	
MMH	Membrane distillation (MD)	Microfiltration (MF)
	Electro dialysis (ED)	Ultrafiltration (UF)
	Nanofiltration (NF)	Nanofiltration (NF)
	Pervaporation (PV)	

MEMBRANE-CONVENTIONAL HYBRID (MCH) PROCESS

Many conventional separation processes have been practiced for a long time and become mature aided by extensive field experiences. Therefore, an enormous amount of information (e.g. process design, cost estimation, etc.) on those processes can be found in the literature. Based on such information, many studies on membrane hybrid processes (especially MCH process) have dealt with the following issues;

1. Membrane process tests,
2. Different hybrid configurations,
3. System optimization,
4. Economical consideration.

MCH Processes with Pervaporation (PV)

PV seems to have the widest application in chemical industry in conjunction with a conventional process such as distillation, esterification, liquid-liquid phase separation, biological oxidation, air-stripping, etc.

Pervaporation-Distillation Hybrid Process

Distillation seems to be the most studied field process when a hybrid process is formed with PV for the following two reasons (3).

- A large driving force in PV is realized when the liquid coming from the distillation column at a high temperature is fed to the upstream side of a PV membrane and permeates through the membrane to the downstream side where a reduced pressure is maintained.
- Selectivity is independent of vapor-liquid equilibria, which is of interest especially when liquid mixtures at their azeotropic points are separated and/or there is only a small difference in the boiling points of the components.

There are a number of studies on PV-distillation hybrid processes for the separation of azeotropic mixtures. It overcomes restrictions encountered when distillation alone is used, such as,

- addition of a solvent which should be removed in subsequent steps,
- pressure variations in the distillation columns, and
- a large number of trays required in the distillation columns.

Generally, PV-distillation hybrid processes not only offer a number of technical and ecological advantages but also economic advantages compared to azeotropic distillation.

Hömmerich and Rautenbach (4) studied a PV-distillation hybrid process for the production of MTBE (Methyl tert-butyl ether) in comparison with the conventional process made by HUELS, consisting of two high-pressure columns between 6 and 12 bar (Fig. 1-a).

One of the proposed hybrid systems is that the side stream of the distillation column is separated by PV (Fig. 1-(b)). The design and optimization studies were performed with the commercial program ASPEN PLUS®. The study revealed that a hybrid process combining a 6 bar distillation with a side stream separation by pervaporation could reduce the annual operating cost by 10 % (Fig. 1-(c)).

An economic analysis was performed by Hoof et al. (5), comparing different processes for the dehydration of isopropanol(IPA)/water mixtures. IPA of 99.5 wt% was aimed at as the final IPA purity. For simulation of the distillation process, ASPEN PLUS® was used. A subroutine for the design of PV systems, developed by the 'Institut für Verfahrenstechnik' RWTH Aachen, was used to simulate PV. Lab-scale pervaporation experiments were performed with both polymeric and ceramic membranes to provide experimental data required to run the subroutine.

There were four different cases to be tested:

1. Distillation-Pervaporation (D-P) hybrid with polymeric membrane,
2. D-P hybrid with ceramic membrane,
3. D-P-D hybrid with polymeric membrane,
4. D-P-D hybrid with ceramic membrane.

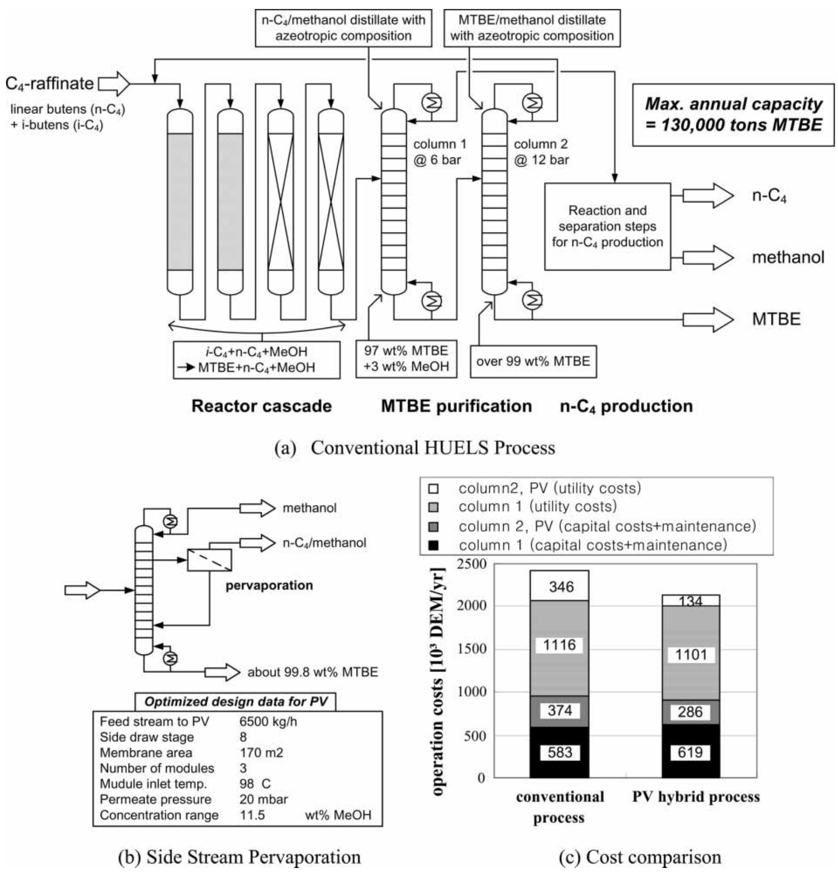

Figure 1. Flow schemes of (a) the conventional process and (b) hybrid process configuration and their cost comparison (4).

Among those, D-P hybrid with ceramic membrane was economically the most interesting process that led to a decrease in the total costs of approximately 49%. Figure 2 illustrates the overview of D-P hybrid with ceramic membrane that led to the best economic performance. Moreover, this process would save up to 48% of energy costs. As ceramic membranes can in general withstand higher temperatures, it might be possible to use even higher operating temperatures, leading to higher fluxes and, consequently a smaller membrane area.

Pervaporation-Esterification Hybrid Process

The conversion in esterification reactions is normally limited by chemical equilibrium. Thus, it can be enhanced by removal of water from the

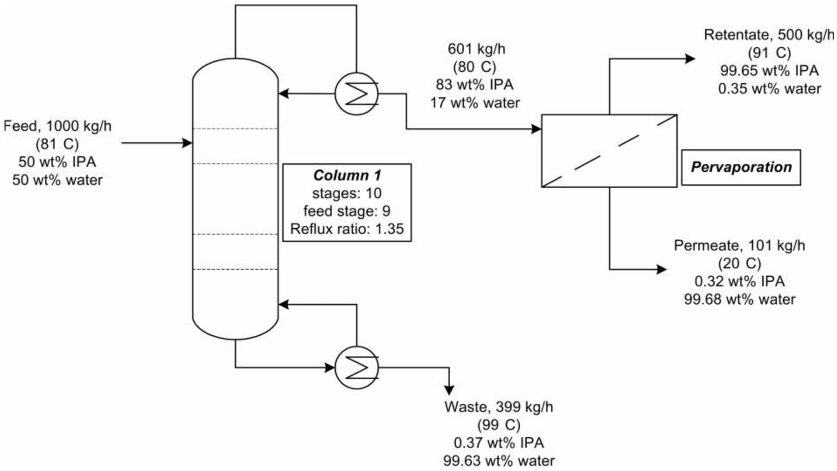

Figure 2. Hybrid system distillation-pervaporation with ceramic membranes (5).

reaction mixture to offer the opportunity to shift the chemical equilibrium. Thus, PV units are integrated into a recycle system to remove the product water continuously from the chemical reactor.

Bitterlich et al. (6) proposed an alternative hybrid process combining a reactor and a PV unit in esterification of butanol and acetic acid to produce butyl acetate. In the conventional process, an acid catalyst (sulphuric acid) used for esterification had to be removed from the reaction product by neutralization with sodium hydroxide. Water, the by-product of the reaction was removed by distillation. In an alternative process layout an immobilized acid in an ion exchange resin replaces the sulphuric acid. Hence, no neutralization was required. Furthermore, the distillation for the dehydration is replaced by a PV unit with hydrophilic membranes. The hybrid process therefore, overcomes the problems inherent in the use of sulphuric acid, i.e. waste treatment and acidic corrosion. The use of PV unit for dehydration can also achieve an increased flexibility due to the process design. The investigated alternative process for the synthesis of butyl acetate is displayed in Fig. 3.

Pervaporation-Liquid-Liquid Phase Separation Hybrid Process

Process water in the production of aniline is a sidestream of the process and contains aniline as a minor component. It is usually handled by biological treatment. However, biological treatment is not economical, particularly when the organic components are present in low concentration.

Meckl and Lichtenthaler (7) studied on a hybrid process where pervaporation was combined with liquid-liquid phase separation for the separation of aniline. Throughout this work, three membranes, poly(etherblockamide)

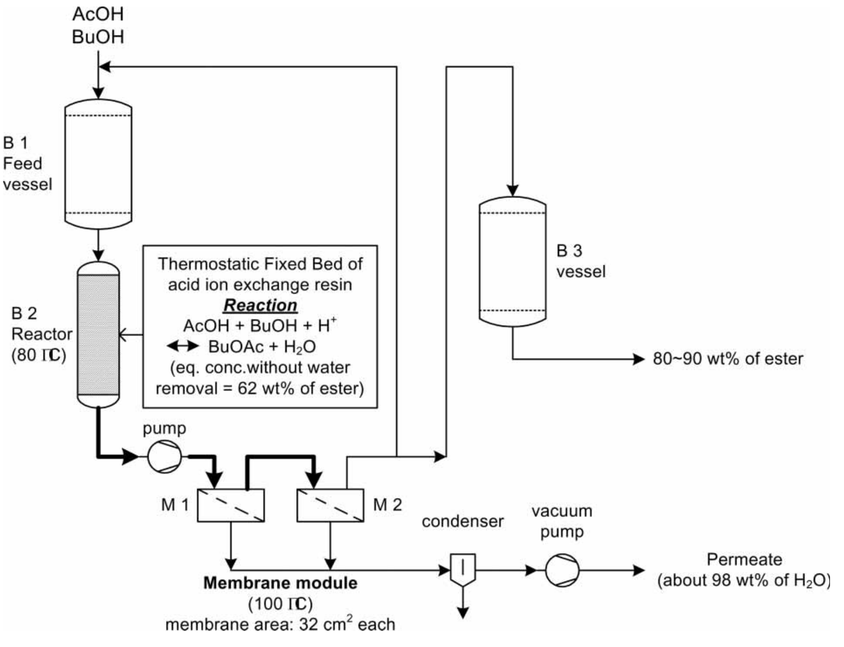

Figure 3. Layout of pervaporation-reactor hybrid process (6).

(PEBA)-membrane, polybutadiene (PB)-membrnae and poly(dimethylsiloxane) (PDMS)-composite-membrane were used for PV. It was concluded that the hybrid-process operating with the PEBA-membrane was the most economical. A typical hybrid process used in their research is shown in Fig. 4.

Pervaporation-Biological Oxidation Hybrid Process

Volatile organic compounds (VOCs) are present in effluents from industries such as petroleum refineries and chemical plants. The treatment of waste stream containing VOCs using pervaporation-biological oxidation hybrid process was studied by Oliveira et al. (8). As shown in Fig. 5, wastewater is recycled through the upstream chamber of a membrane module, while air flows through the downstream chamber of the module. VOCs permeate through the membrane preferentially and are carried away by the air stream into a bioreactor, where biodegradation of VOCs takes place. A model system with monochlorobenzene (MCB) as the VOC and Pseudomonas JS 150 as the degrading microorganism was used for the study. From the experimental results, it was shown that lower air flow rates, higher VOC concentrations, and higher bioreactor temperature significantly improved removal efficiencies. For example, when the MCB concentration in the membrane

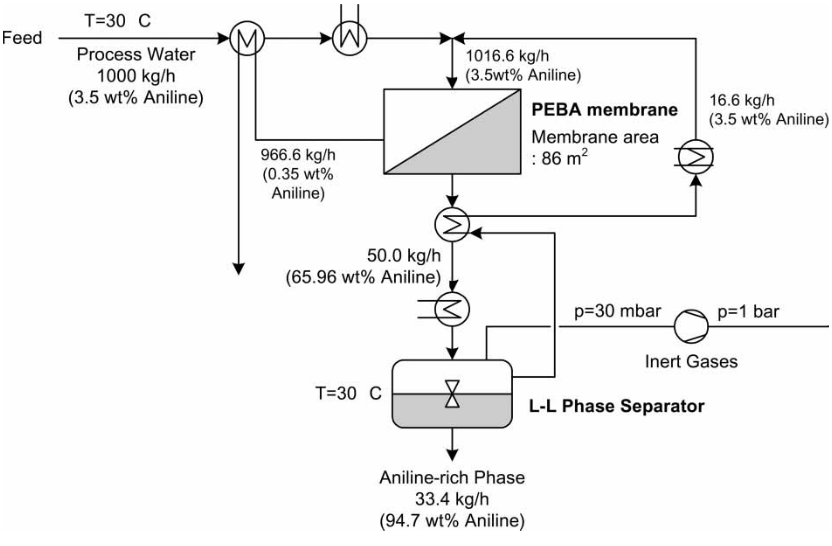

Figure 4. Layout of hybrid process for the removal of aniline from process water (7).

permeate was 17 gm^{-3} and the bioreactor was working at 15°C, removal efficiency was 95% (see Fig. 5).

Pervaporation-Air-Stripping Hybrid Process

Air-stripping-adsorption process is conventionally used for the removal of VOCs from wastewater or contaminated groundwater and pervaporation has a potential of providing a better alternative to the conventional process. Air stripping removes the more volatile components effectively while pervaporation can be designed such that it removes the less volatile components effectively. Thus, two processes are complementary. Shah et al. (9) proposed a pervaporation-air stripping hybrid process and studied numerically. As shown in Fig. 6, a part of wastewater is taken away from the middle of the air-stripping column and fed to the upstream side of a PV module. From the numerical analysis, it was concluded that the retentate should be returned to the same position at the air-stripping column from where the pervaporation feed was withdrawn (Fig. 6). It was concluded also, for this configuration, the optimum rate of withdrawal of the liquid from the column to the pervaporation module was equal to the liquid flow rate in the column.

Pervaporation-Evaporation Hybrid Process

Coolant liquids having ethylene glycol in the range of 20 ~ 30 wt% have been identified as hazardous organic waste. Waste coolant treatment by

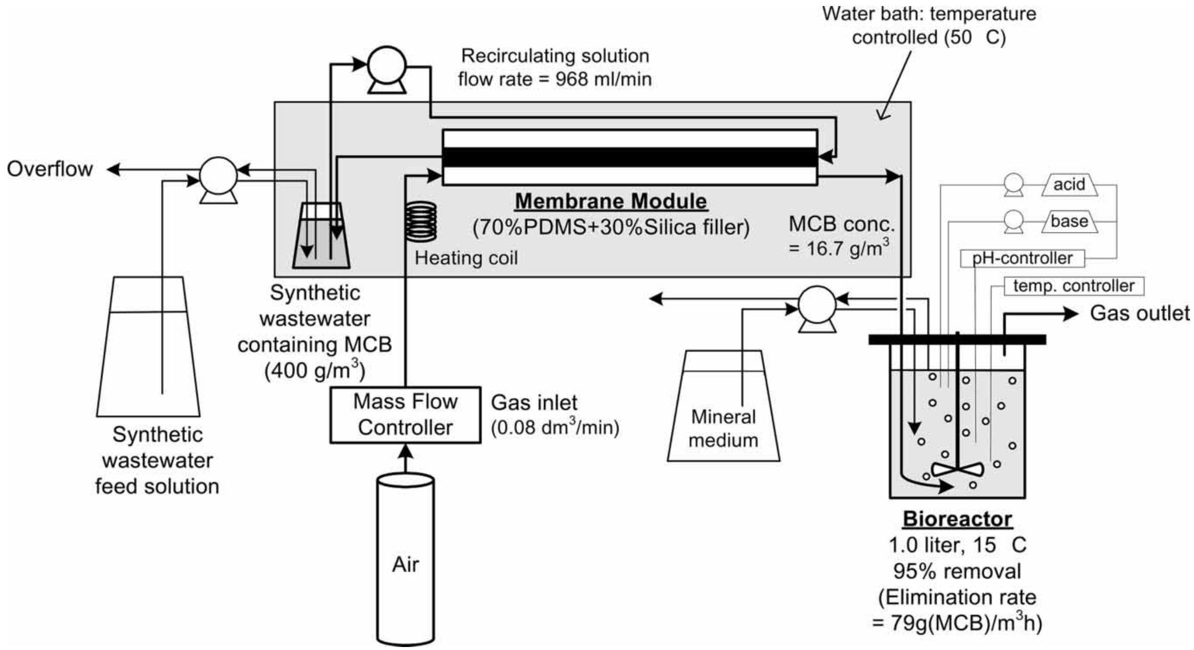

Figure 5. Experimental pervaporation-bioreactor hybrid process (8).

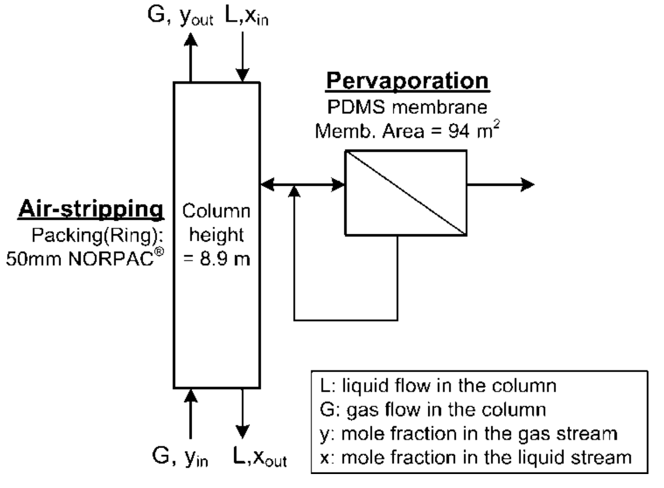

Figure 6. Optimum configuration of pervaporation-air stripping hybrid process (9).

incineration or disposal was proposed by the official legal regulations, if material recovery for reuse is not feasible. However, because of the high water concentration of the coolant liquid, incineration is not a suitable method. Therefore, glycol recovery is preferable, in particular if the process is less cost intensive compared to alternative methods. Another reason for recovery of the glycol is care for natural resources. For dewatering of the used coolant to a water content of less than 5%, a membrane hybrid process was developed by Jehle et al. (3). The process is outlined in Fig. 7. The hybrid process concept for glycol recovery was chosen as follows:

(a) MF or UF as a pretreatment to avoid clogging and minimizing scaling and fouling in the subsequent process stages.
(b) Evaporation (EV) for the concentration of the coolant liquid from 25% up to 70% glycol.
(c) PV to which the EV main product is transferred for further concentration (>95%).
(d) Final distillative purification process which separates the ethylene glycol with sufficient purity from the residues.
(e) RO for the final treatment of the water fraction from the EV and PV processes.

Based on the cost estimations, the membrane hybrid process gave better economic recovery of ethylene glycol from used coolant liquids compared to the present costs for incineration.

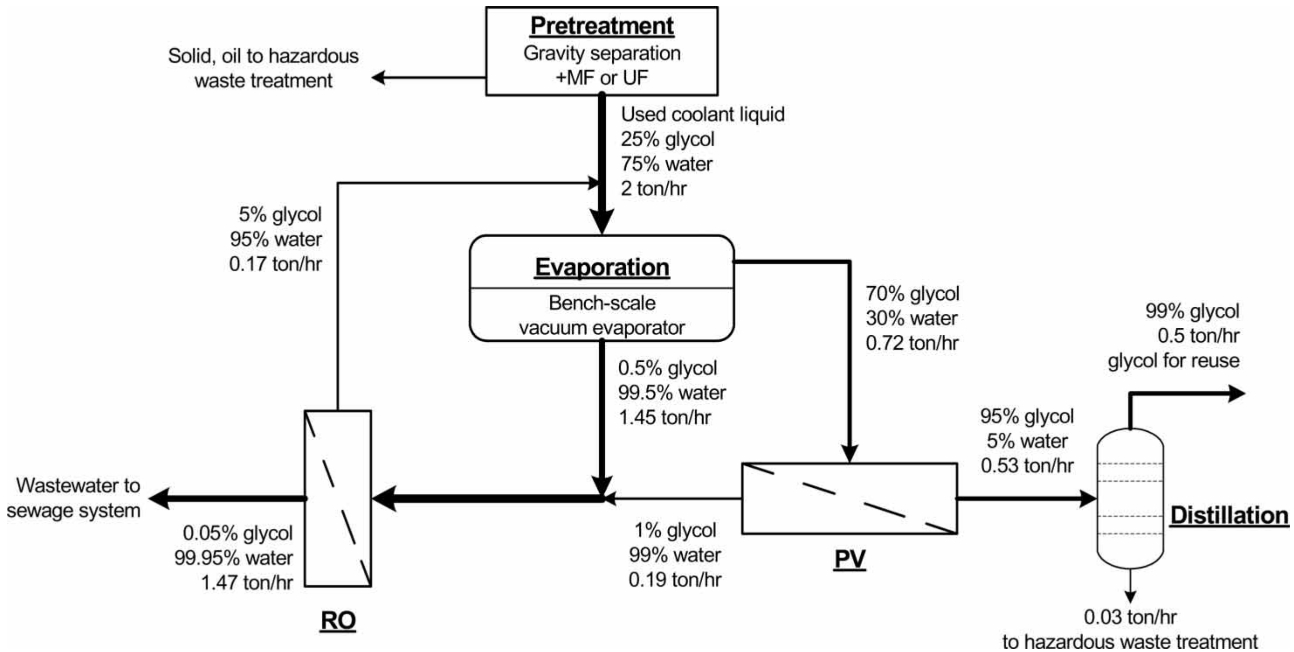

Figure 7. Mass flow diagram for glycol-water separation (3).

Vapor Permeation (VP) Included MCH Process

Vapor Permeation-Distillation Hybrid Process

Studies on VP hybrid processes in the literatures are all with distillation process. VP -distillation hybrid process is particularly interesting regarding membrane stability since the chemical and mechanical stress on the membrane can be significantly diminished in VP. Furthermore, no feed temperature drop occurs, thus keeping the driving force high and saving investment and energy costs due to missing reheater sections. The possible configurations of a PV-distillation hybrid process is shown in Fig. 8.

Moganti et al. (10) compared two different design methods for a given hybrid process (Fig. 8a) to find the optimal position and the optimal tray number, i.e. the Smoker's equation method and the minimum area method. Propane-propylene separation was chosen as a model system and the membrane properties were set by authors. The results obtained by both methods are very close and an analytical expression for the optimal placement of a membrane unit on a distillation column was derived.

Stephan et al. (11) did numerical calculations dealing with an olefin purification hybrid process using a distillation column and a facilitated transport vapor permeation membrane in different configurations (Fig. 8). By using a McCabe-Thiele based approach, the different configurations were analyzed to determine the optimal operating conditions for each configuration.

Pettersen and Lien (12) presented an explicit algebraic design model for vapor permeation which predicted membrane area within 20% and module cut rate within 2% accuracy. Based on this design model, some of the trade-offs in

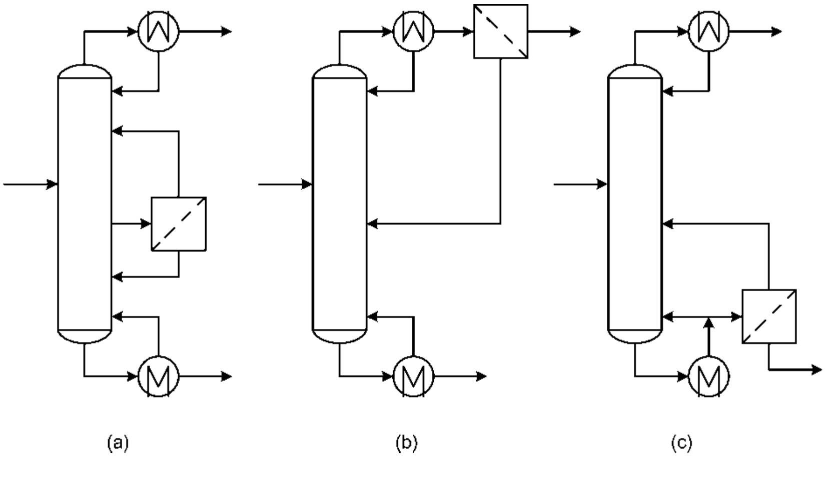

Figure 8. Various configurations for a PV-Distillation hybrid process (10–13).

a hybrid distillation and vapor permeation process (Figure 8b) are illustrated through parametric studies.

Pettersen et al. (13) compared the performance of three hybrid VP-distillation processes (Fig. 8) theoretically, using the separation of propylene and propane as a representative case. When the membrane is placed parallel to the column (Fig. 8a), the optimal position for the membrane feed stream was close to the column feed plate, which represents a potential pinch point in the column. The optimal membrane cut rate ($\theta =$ permeate flow rate/feed flow rate for membrane module) for this configuration was generally close to the mole fraction of propylene (x_M)in the membrane feed stream, that is, $\theta \approx x_M$. The comparison of the systems' performances indicated that placing the membrane in parallel (Fig. 8a) or on the bottom stream of the column (Fig. 8c) gave the best performance of the hybrid process.

Gas Separation (GS) Included MCH Process

Membrane gas separation (MGS) technologies are bulk processes. They are relatively light weight and maintenance-free. They also operate over a wide range of temperatures and pressures, and are portable. However, MGS system only can provide product gases of modest purities, and typically the permeate stream is at low pressure. Therefore, integration of MGS technology with other conventional processes has resulted in development of efficient gas separation processes that take advantage of the efficient bulk removal characteristics of membranes while overcoming possible limitations in purity. Most possible application fields are air separation and acid gas removal from natural gas.

MGS-Air Separation Technologies Hybrid Process

Beaver et al. (14) reviewed membrane hybrid systems with different air separation technologies such as pressure swing adsorption (PSA), cryogenics and catalytic removal.

The MGS-PSA hybrid processes could be used for the generation of high purity oxygen and nitrogen for lightweight systems on-board aircraft. In this application, nitrogen was needed for fuel tank blanketing and greater than 90% oxygen was needed for crew breathing. Figure 9 is an illustration of an integrated on-board gas generation system suitable for a large aircraft. The combination of membranes with adsorption was feasible due to the dramatic effect of increased oxygen concentration by the adsorption system.

One small-scale application involving MGS-cryogenics hybrid system was the CRYOGEN 10® of Carlisle Cryotronics. This unit is diagrammed in Fig. 10. The membrane separator was vertically configured in such a way

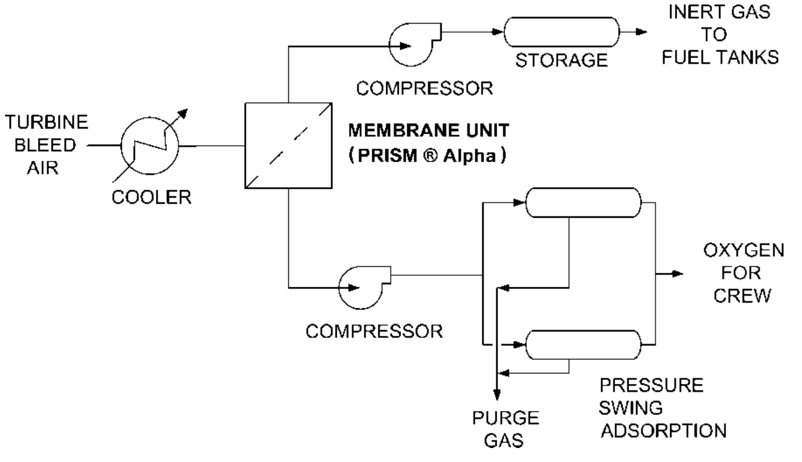

Figure 9. Integrated on-board gas flow diagram (14).

that the output from the filter was directed to the cold head which was situated within the liquid nitrogen Dewar flask. Input to this system was filtered compressed air and electrical power. The MGS-cryogenics hybrid system made this system a small, convenient, and relatively inexpensive method of making liquid nitrogen.

To overcome the limitation of MGS, the inability to produce very high purity, MGS-catalytic removal hybrid process was proposed. Figure 11 illustrates the process. Compressed air at 125 psig was cooled to 100° to 120°F and filtered to remove condensed or entrained liquids. The air was then fed into the gas membrane separators where the oxygen content was reduced to 0.5%. The purified nitrogen left the separators at approximately 110 psig. The oxygen enriched stream was discharged to the atmosphere at slightly above atmospheric pressure. The 99.5% oxygen-free nitrogen was further purified to 99.9995% oxygen-free nitrogen in the catalyst module. The nitrogen entered near the top of the catalyst tower where it was mixed with a small quantity of hydrogen gas. The gas mixture flowed downward through a palladium catalyst bed where the hydrogen reacted with the residual oxygen in the gas stream. The catalytic reaction reduced the residual oxygen content in the nitrogen gas stream down to 5 ppm.

Mercea and Hwang (15) developed PSA-continuous membrane column (CMC) process (Fig. 12). Oxygen was separated from the air, by a process in which the adsorption of N_2 on a zeolite was combined with a subsequent O_2 enrichment by permeation through polyimide hollow fiber membrane. It was found that a higher degree (38 l/h, 99.5%) of O_2 is obtained from air with the combined PSA-CMC process than by either one of the two processes.

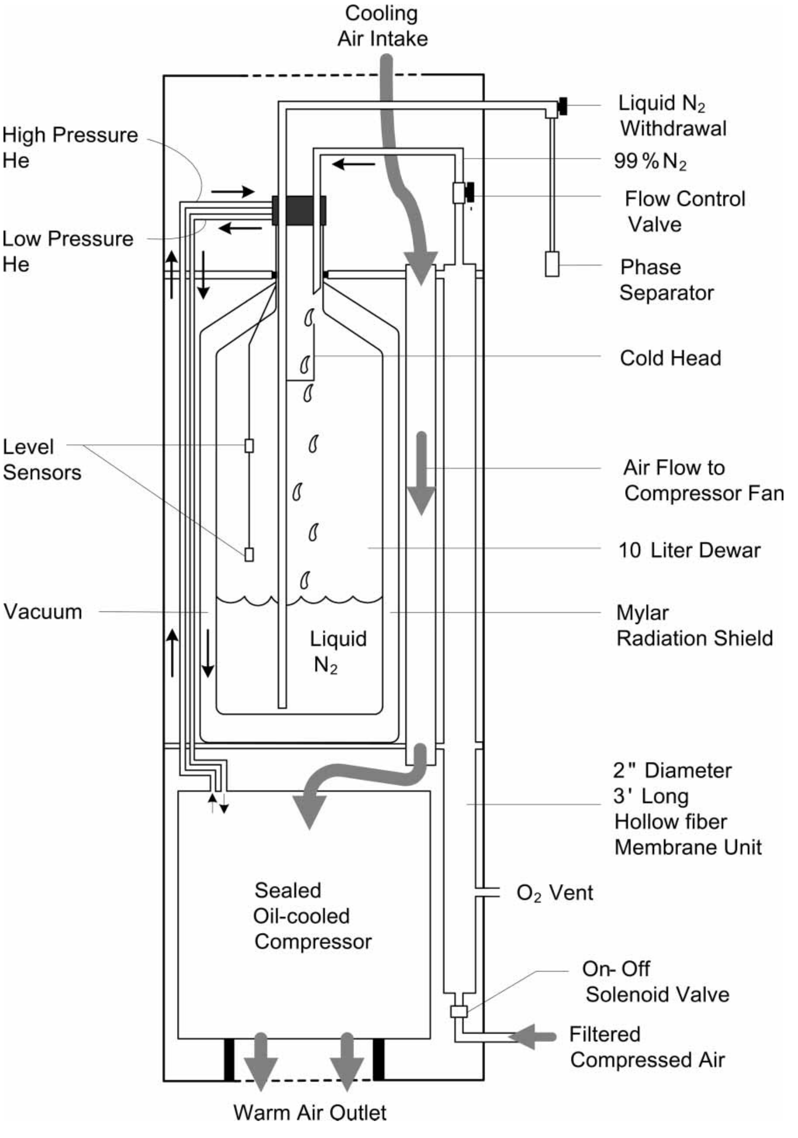

Figure 10. Diagram of small scale liquid nitrogen generator (Cryogen 10® Carlisle Cryotronics) (14).

MGS-Absorption Technologies Hybrid Process

Acid gases must be removed from natural gas in order to:

1. Increase the heating value of natural gas,
2. Decrease the volume of gas transported in pipe lines,

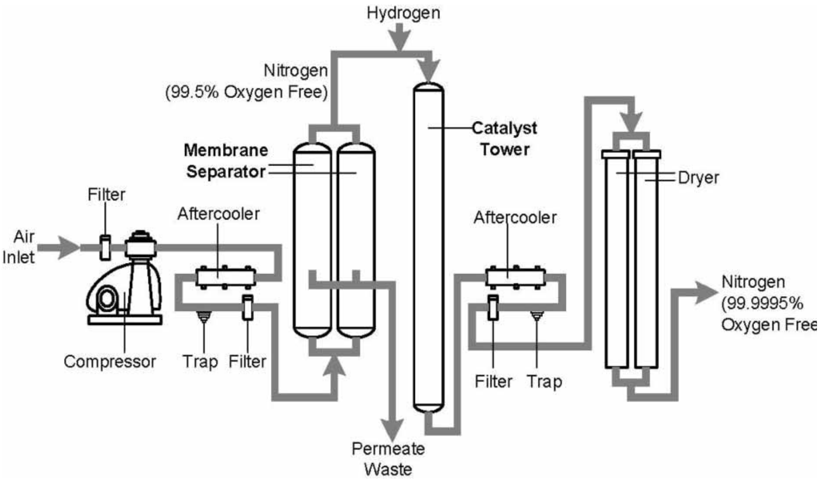

Figure 11. Membrane-catalytic oxygen removal hybrid process (14).

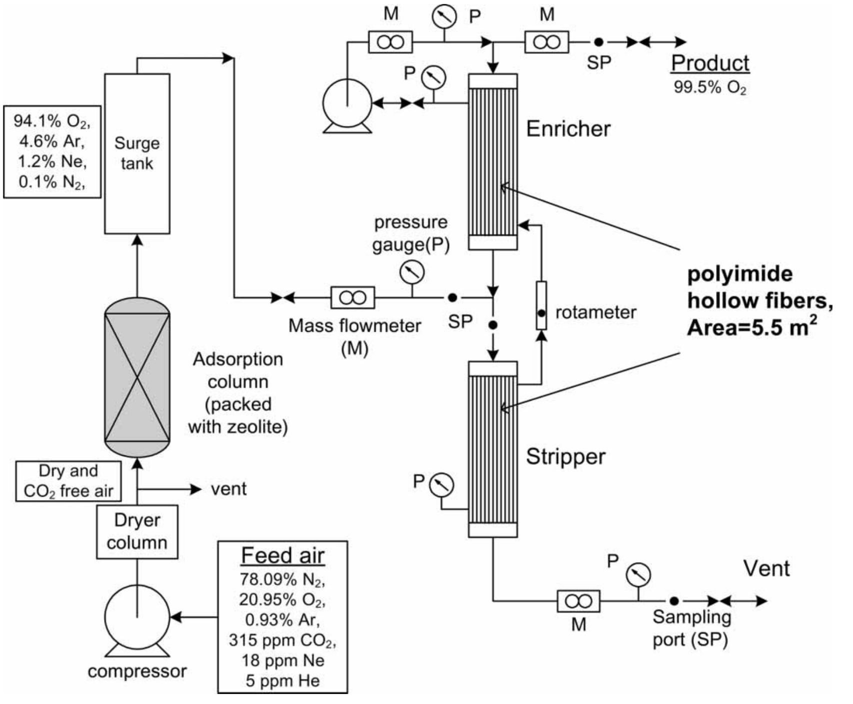

Figure 12. A schematic presentation of the PSA-CMC apparatus (15).

3. Reduce corrosion during the transport and distribution of natural gas and
4. Prevent atmospheric pollution by SO_2, which is generated during the combustion of natural gas containing H_2S.

The "sweetening" of crude natural gas, i.e., the removal of acid gases (CO_2 and H_2S), is conventionally achieved by absorption of these gases in various solvents. In spite of recent advances in the development of better solvents for acid gases, both in process design and energy integration, gas absorption processes are subject to the following limitations:

1. They are highly energy-intensive, especially when processing natural gas streams with high acid gas content,
2. They are capital-intensive at low flow rates of natural gas, and
3. They are not well-suited for offshore applications because of the size and weight of the required process equipment.

A process design study and an economical assessment were made of a hybrid process for the removal of up to 40 mole% CO_2 and up to 1mole% H_2S from crude natural gas by Bhide et al. (16). The process is shown in Fig. 13.

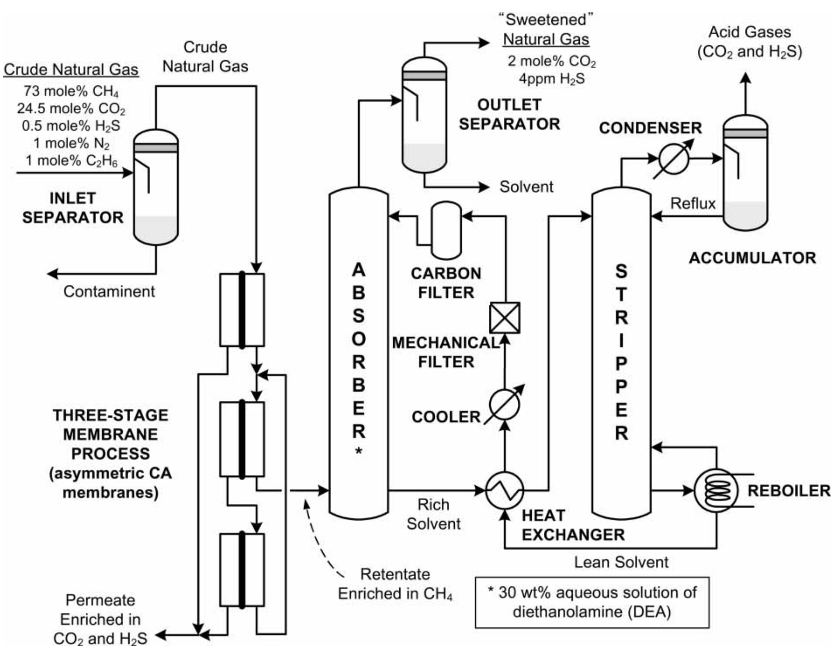

Figure 13. Flow diagram of a hybrid process for the removal of acid gases from crud natural gas (16).

Microfiltration (MF) Included MCH Process

Microfiltration-Adsorption-Flocculation Hybrid Process

Guo et al. (17) studied the effect of pretreatments namely floating medium flocculation (FMF) and powdered activated carbon (PAC) adsorption on organic and phosphorus removal. The schematic of MF-flocculation-adsorption hybrid process is shown in Fig. 14. The FMF was found to increase the phosphorus removal up to 97%. This preflocculation improved the dissolved organic removal only marginally (from 20% to 40%) whilst the pretreatment of adsorption increased the organic removal to more than 98%. The decline in filtration flux of MF was reduced by the incorporation of these pretreatment methods. The preflocculation combined with PAC adsorption also resulted in nine times higher critical flux. The experimental results showed that a pretreatment by flocculation and adsorption led to almost complete phosphorus and organic removal while reducing the membrane clogging.

Ultrafiltration (UF) Included MCH Process

Ultrafiltration-Fermentation Hybrid Process

UF membrane process combined with the conventional fermentation processes have been studied to make the whole process to have higher productivity, lower cost, more stable operation, etc.

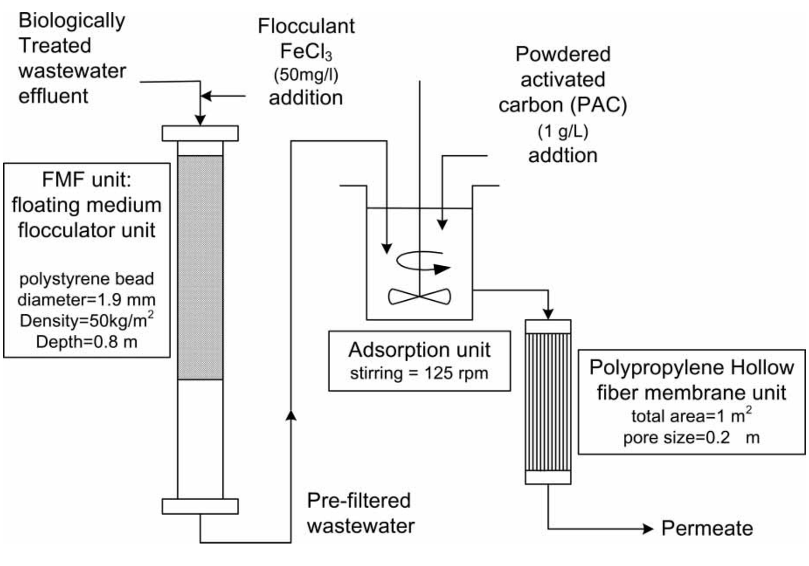

Figure 14. Schematic of MF-flocculation-adsorption hybrid process (17).

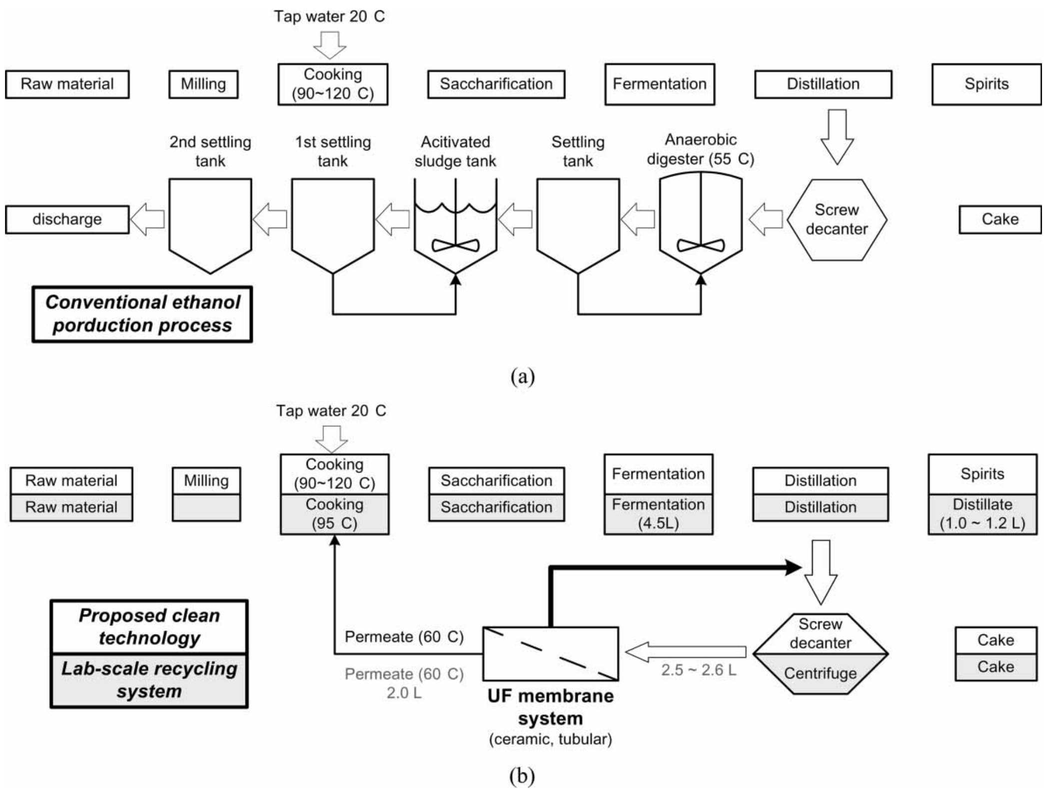

Figure 15. Flowsheet of (a) conventional ethanol production process and (b) proposed UF fermentation hybrid process for ethanol industry (18).

Kim et al. (18) developed a zero-discharge system for the alcohol fermentation industry using UF-Fermentation hybrid process by recycling distillery waste (stillage). Conventional alcohol fermentation process is shown in Figure 15a where the distillery waste is treated in anaerobic digester to decompose organic wastes before discharge. The major drawbacks of the conventional process were its high energy consumption and large variation of treatment efficiency with the change in raw materials used for the ethanol fermentation. The researchers proposed and evaluated a UF-fermentation hybrid process as shown in Fig. 15b. In this process, stillage was able to be recycled as cooking water for the next fermentation after treating it with UF. This new process was confirmed to have stable operation. This new clean technology for the ethanol production industry makes it possible to eliminate the stillage treatment steps by the conventional biological treatment processes such as anaerobic digestion and activated sludge steps, resulting in reduction of both land and energy cost.

Kirkman et al. (19) examined the impact and economic feasibility of retrofitting a UF system for lignin byproduct recovery and determined the potential benefit of reduced lignin throughput for those mills that are limited by the recovery furnace. Computer simulation with a computer simulation software, GEMS (Generalized Engineering Modeling and Simulation) was used to determine the material and energy balances for both conventional and hybrid processes. A simplified schematic of the mill, including the UF unit for processing 10% of the black liquor, is shown in Fig. 16. Simulation studies demonstrated that recovery of the high-molecular-weight kraft lignin by UF from a fraction of the black liquor flow is attractive from both an economic and an operational standpoint. The major impact on the kraft mill is the reduction in organic load to the recovery furnace which is positioned at the 'Recovery' box in the flowsheet. The benefits derived from such a reduction were:

1. Elimination of a production bottleneck at the recovery furnace. The resulting increase in production could return over 100% if lignin product is marketed.
2. Opportunity to run the furnace within thermal limits if it is currently overloaded.

Reverse Osmosis (RO) Included MCH Process

Reverse Osmosis-Evaporator Hybrid Process

Gienger and Ray (2) studied a RO-Evaporator hybrid process to minimize the energy needed to concentrate corn steep water. Steep water is the wastewater that results when corn is steeped to loosen the kernels for milling. This water contains approximately 6 wt% solids and the aiming concentration is 50 wt% using minimal energy. Figure 17 is a simplified schematic of the

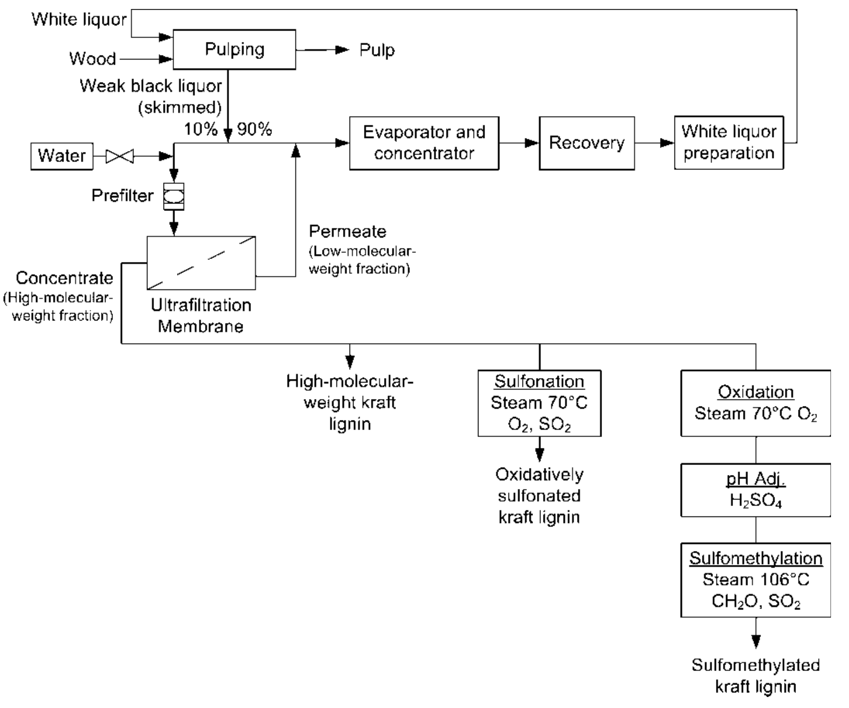

Figure 16. Flow sheet of a simplified mill including UF of kraft black liquor (19).

RO-Evaporator hybrid process investigated. The steep water (at 6 wt% solids) was pressurized and introduced into the membrane portion of the hybrid. The solution is dewatered via RO membranes, and the concentrated retentate (at max. 15 wt% solids) from the membrane is further concentrated (to 50 wt%

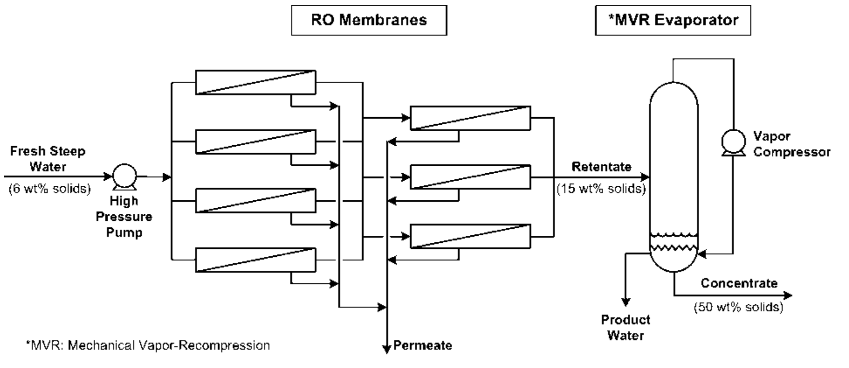

Figure 17. RO-Evaporator hybrid process to concentrate corn steep water for 6 wt% to 50 wt% solids (2).

solids) in the evaporator. From the economic consideration, an energy requirement of RO-evaporator hybrid process was about one third of the energy requirements of evaporator alone.

Membrane Distillation (MD) Included MCH Process

Membrane Distillation-Fermentation Hybrid Process

Gryta (20) investigated on ethanol production in bioreactor integrated with the membrane distillation (MD) system. The fermentation of sugar with Saccharomyces cerevisiae proceeds with the formation of by-products, which tends to inhibit the yeast productivity. The removal of by-products from the fermentation broth by MD process increased the efficiency and the rate of sugar conversion to ethanol. The separation of alcohol by MD enables achievement of a higher content of ethanol in the permeate than that in the broth. It was also observed that a beneficial effect of carbon dioxide on the ethanol transport through the membrane. The scheme of the experimental set-up of MD-fermentation hybrid process is shown in Fig. 18.

Membrane Bioreactor (MBR) Included MCH Process

Membrane Bioreactor-Fermentation Hybrid Process

The traditional, and still the most common, method of fermentation is the use of “free” cultures of microbial cells in a batch reactor. Batch fermentations have several problems, including

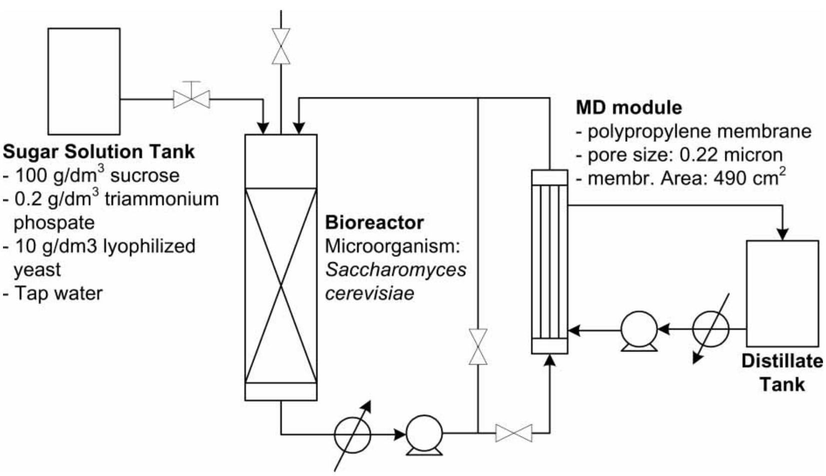

Figure 18. Scheme of the experimental set-up (20).

(a) their inherent inefficiency due to their start-up and shut-down nature,
(b) large capital costs for equipment, due to the low productivity,
(c) batch-to-batch variation in the product,
(d) the need to separate out the microbial cells at the end of the fermentation, and
(e) the long time needed for the fermentation, sometimes measured in days.

To overcome those limitations, Cheryan and Mehaia (21) studied a system in which a membrane bioreactor is coupled in a semi closed-loop configuration to a membrane module. The fermentation of cheese whey to ethanol was used as a model to show the membrane recycle concept. Cheese whey, which is a by-product of the cheese manufacturing industry, not only creates a potential pollution problem, but is also a waste of good quality protein and a renewable, easily fermentable carbohydrate source (lactose). The scheme in Fig. 19 shows a method for utilizing both major components of cheese whey. Cheese whey is first subjected to ultrafiltration to fractionate whey protein (in the retentate) and lactose (in the permeate). The permeate is then fed, together with nutrients, to a fermentation vessel where ethanol is produced from lactose by a bio-catalytic reaction. The fermentation broth is continuously withdrawn from the bottom of the fermentor and fed to the

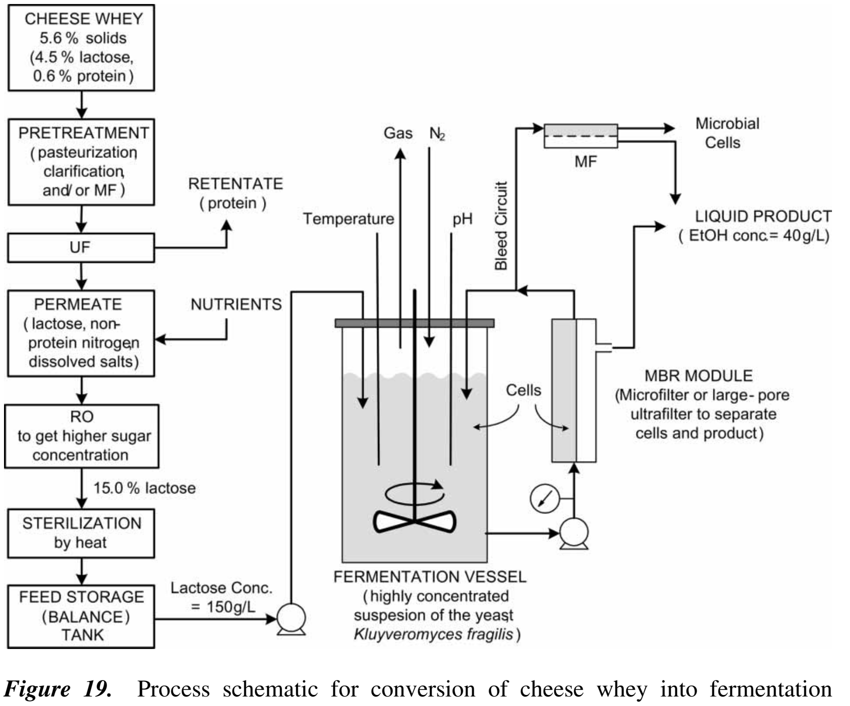

Figure 19. Process schematic for conversion of cheese whey into fermentation products with a membrane recycle fermentor (21).

upstream side of a membrane module (Membrane Recycle Fermentor: MRF), where the ethanol and substrate lactose are concentrated in the permeate. The cells remain in the retentate that is recycled to the fermentor. A part of the retentate from the MBR module is fed to a MF module where microbial cells are further concentrated. The permate from the MF module joins the permeate from the MBR module.

The membrane bioreactors provided an opportunity to vastly improve the performance and productivity of fermentations. Specific advantages of membrane recycle fermentors include:

- The inherently more efficient continuous process could be used.
- High dilution rates could be used, as a direct result of the high cell concentrations.
- Control of the environment was easy with the membrane recycle fermentors.
- The product stream from membrane bioreactor was free from microbial cells and other particulate material, which should reduce downstream processing costs.

MEMBRANE-MEMBRANE HYBRID (MMH) PROCESS

According to the available literature, some membrane-membrane hybrid (MMH) processes were proposed and researched. Some of MMH processes replaced conventional processes for higher efficiency, higher productivity, etc. and others found new target streams that needed to be treated for specific purposes. Compared to the studies on MCH processes, the amount of information in the literature on MMH processes is very limited, mainly because research on MMH processes started only recently. However, as the amount of research and industrial applications has increased, importance of MMH processes has also been more strongly recognized. In this section, MMH processes in which different membrane processes are combined for different purposes are described.

MF-RO Hybrid Process

Conventional wastewater treatment can not process municipal wastewater to the quality levels required for some receiving waters and most reuse applications, especially with respect to the reduction of the total dissolved solids content (TDS). On the other hand, RO can in principle produce water that will meet even the most stringent guidelines. Hence, replacement of conventional treatment systems by RO was considered. However, it has been clear since the early days of RO that extensive pretreatment is required for the feed to maximize the performance of RO membrane. Ghayeni et al. (22, 23) used hollow fiber MF as a pretreatment of RO feed for water reclamation from municipal wastewater (Fig. 20). The application of "critical flux" operation was introduced to optimize the flux through the MF membrane. Transmission of the polio virus through the 0.2 μm pore MF membrane was minimized by low pressure operation, with crossflow and in the presence of biomass. For feed containing significant levels of sewage bacteria, the passage of small bacteria was observed. Bacterial bioadhesion studies of various RO membranes showed significant differences between membranes, the least adsorptive being hydrophilic membranes. Figure 20 is pilot plant diagram with MF-RO hybrid process.

PV-RO Hybrid Process

Phenol is produced in the following processes;

1. phenolic-resin production;
2. the pulp and paper industry;
3. petrochemical refining and production;
4. coking.

Because phenol is so toxic and because even very small amounts when combined with free chlorine can impart a bad taste to drinking water, the US Energy Protection Agency (EPA) currently limits phenol concentrations in discharge waters to no more than 14 ppm.

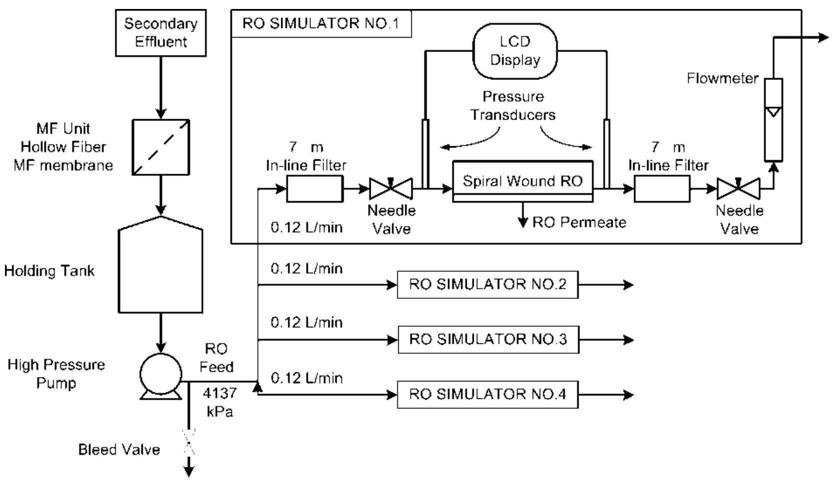

Figure 20. Piping and instrument diagram for RO simulators.0.12 L/min of MF secondary effluent passed through each module, with a recovery of approximately 1.7% (23).

Ray et al. (24) designed and studied a PV-RO hybrid process that has benefits over the conventional technologies such as biological treatment, solvent extraction, and carbon adsorption. In this hybrid system, a solute-removal unit operation (PV) was "balanced" with a solvent-removal unit operation (RO) to enable each unit to operate under conditions as close to optimal as possible; thus, the unit operations worked synergistically as an efficient system. The effect of the hybrid system on the economics of phenol removal was illustrated by comparing the economics of the hybrid system shown in Fig. 21-(b) with those of the pervaporation system shown in Fig. 21-(a). It was concluded that the advantages of this scheme are as follows:

1. The separation was effected over a broader range of feed concentrations than was possible with the component unit operations.
2. The flow rate to each unit was independently adjusted through recycle, to maintain conditions optimum for each unit.
3. The system was adjusted to accommodate fluctuations in membranes in the unit operation.
4. The overall production cost of the separation was lower than that of simple hybrid schemes (those without recycle) or that of a single unit operation.

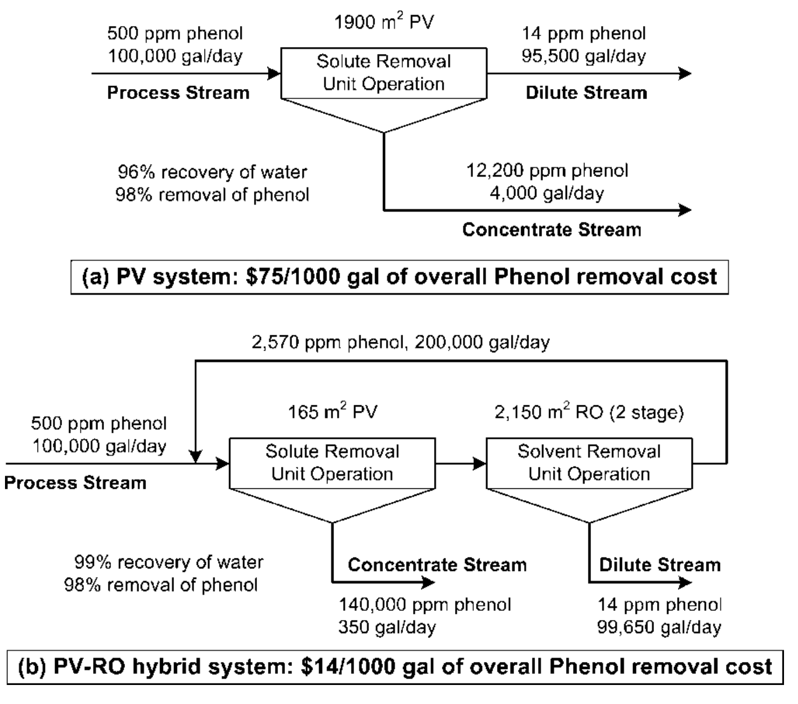

Figure 21. PV only system and PV-RO hybrid system for economic analysis (24).

UF-MD Hybrid Process

Oily wastewater generated by various industries and subsequently discharged into the natural environment creates a major ecological problem throughout the world. The traditional methods for the separation of oil emulsion can be classified as chemical, mechanical, and thermal. The chemical methods based on the neutralization of detergents need further purification in order to meet today's effluent standard for the sewage systems. The mechanical methods based on the phenomenon of gravitational emulsion breaking require heating step that may increase the size of oil droplet significantly. The thermal process requires a large amount of energy, and therefore this process is not cost effective. One of the recently utilized solutions in the treatment of oily wastewater is the biological method. However, this method has disadvantages such as low efficiency, operational difficulties, and high operational costs.

Investigation on the treatment of oily wastewater by a combination of UF and MD as a final purification method was performed by Gryta et al. (25). A tubular UF module equipped with polyvinyliden fluoride (PVDF) membranes and a capillary MD module with polypropylene (PP) membranes were tested using a typical bilge water collected from a harbor without pretreatment. The permeate obtained from the UF process generally contains less than 5 ppm of oil. A further purification of the UF permeate by MD results in a complete removal of oil from wastewater and a very high reduction of the total organic carbon (99.5%) and total dissolved solids (99.9%). Figure 22 is a schematic diagram of a hybrid UF-MD process for treatment of oily wastewater.

UF-NF-RO-MD Hybrid Process

Tap water is often used as a water source for different industries, however, the water repurification is required to meet the specifics of some technologies. The effect of application of UF, NF, RO, and MD processes on the quality of treated water was investigated by Karakulski et al. (26). Portable water used in the study contained significant amounts of solutes and suspended solids, which prevented it from direct use in the technological processes.

The UF process was efficient only in the removal of suspended solid and colloids, which allowed to reduce SDI (Silt Density Index) from 7–10 of tap water to 2. Hence the product water from UF unit could be directly used in RO process. The quality of produced water from UF-RO integrated membrane system (UF-RO hybrid process) corresponds to the quality of distilled water.

The NF process was found to be very efficient in the rejection of organic matter from water (0.8–2.1 TOC/dm^3). The integration of UF with NF

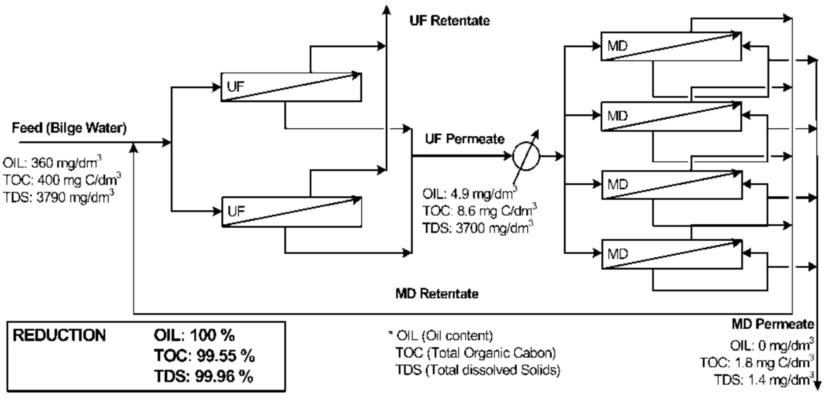

Figure 22. A schematic diagram of a UF-MD hybrid process for treatment of oily wastewater (25).

process (UF-NF hybrid process) increased the effectiveness of removal of organic compounds.

High purity water was produced in the MD process. However, direct purification of potable water by MD resulted in deposition of a significant amount of $CaCO_3$ on the membrane surface. Therefore preliminary softening of water was needed to decrease fouling. The best results were obtained in the RO-MD hybrid process.

PV-MF-MD Hybrid Process

E. purpurea, the purple coneflower, has been widely used as an herbal medicine because of its perceived properties as an immunostimulant when ingested. The major compounds for immunostimulatory acitivity are polysaccharides, caffeic acid and alkyl amides. The most commonly used form of Echinacea herbal medicine is the tincture, which is a liquid ethanol-water extract from *E. purpurea*. The ethanol should be totally or partially removed from the tincture to satisfy Government regulations. In the case of tincture preparation, the extraction has typically been carried out using finely chopped plant and solvent (e.g. 45% ethanol-55%water by volume) over a period of several days at ambient temperature. Following extraction of the active components, ethanol removal has traditionally been carried out by thermal evaporation under reduced pressure. However, the latter step has provided the opportunity for degradation of thermally labile components and evaporation of volatile components.

Johnson et al. (27) investigated a three-stage hybrid membrane process for the concentration of ethanol-water extracts of the *Echinacea* plant. Their preliminary experiments using MD in a single-stage process resulted in severe membrane wet-out by the compounds soluble in ethanol.

In order to avoid the membrane wet-out the following three stage process was proposed. In Stage 1 of the hybrid process, ethanol removal from the neat extract was achieved by PV. This gave an ethanol-free aqueous product containing suspended alkyl amides that was suitable for marketing in tincture form. In Stage 2, the precipitated alkyl amides were removed from the Stage 1 product by MF. In Stage 3, the MF permeate was concentrated several-fold by MD, followed by adding-back of the MF retentate containing the precipitated alkyl amides to the MD retentate. This gave a highly concentrated product suitable for marketing in capsule form (Figure 23). PV was carried out using a Nagayanagi Ind. Co. Ltd., poly(dimethylsiloxane) M60-A hollow fiber module with a membrane area of $0.34\,m^2$. MF of PV retentate was carried out using an Osmonics Sepra CF flat sheet module with an effective membrane area of $0.0155\,m^2$. And MD of the MF permeate was carried out using the same Osmonics module that was used in the MF step and a Hoechst Celanese Celgard 2500 polypropylene flat sheet membrane.

NF-ED Hybrid Process

In the pulp and paper industry the alkaline bleaching streams are produced in large volumes and become a source of severe environmental problems. Besides the inorganic load resulting from the addition of chemicals, there is a wide range of organic solutes resulting from the lignin dissolution and from total organochlorinated compounds (TOCl) formed by chlorination of different fractions of lignin. Most of the TOCl and color produced in the pulp mill is discharged in the first alkaline extraction (E1) effluent. Biological treatment removes only 50% of the produced TOCl and the rest is discharged into the environment. Color, due to lignin compounds, is not removed by

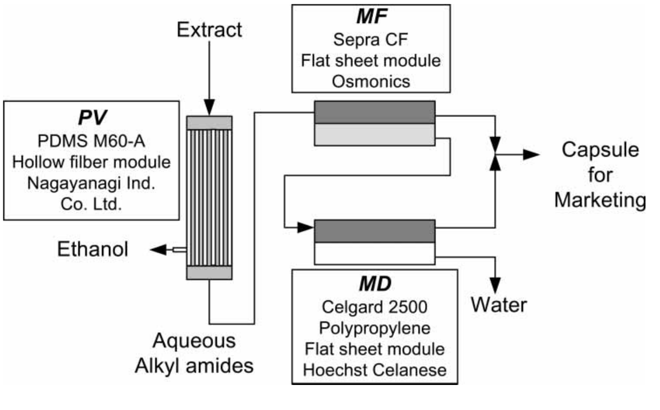

Figure 23. A schematic diagram of PV-MF-MD hybrid process.

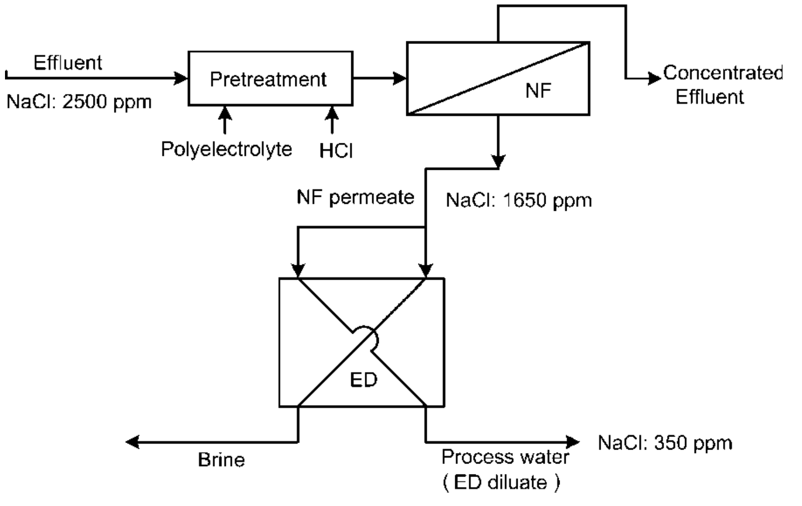

Figure 24. A schematic diagram of NF-ED hybrid process (28).

biological treatment and, besides the aesthetic problem, can affect aquatic life because of UV light absorption.

Geraldes and Pinho (28) proposed a nanofiltration (NF)-eletrodialysis (ED) hybrid process to recover water from the E1 alkaline pulp bleaching effluent. NF was selected to remove organic compounds and undertake partial desalination. A high degree of water purity was further achieved using ED to reduce sodium chloride concentration to a level of 350 ppm (Fig. 24).

CONCLUSIONS

The process design, applications, and economics of membrane based hybrid processes were reviewed. All the hybrid processes were divided into two categories; Membrane-conventional hybrid (MCH) and Membrane-membrane hybrid (MMH) processes. The MCH and MMH processes showed many advantages over a conventional process and a membrane process operated alone respectively. Many of the reviewed papers are still at a theoretical or laboratory level and, consequently, still under optimization. Therefore, the following further work would be required in the future.

1. Hybrid process design including configuration, operating conditions, membrane area, etc. should be optimized.
2. More advanced membrane process should be researched regarding membrane materials, membrane modules, etc.
3. More industrial applicable area should be researched.

In this way, an increasing number of membrane hybrid processes would be appeared in the market to make the chemical processes economically more feasible with more advanced waste-stream treatment processes.

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