

SPECIFICATION

Thermal distillation apparatus and membranes for use therein

- 5 The present invention relates to thermal distillation apparatus and in particular, to the kind utilizing a lyophobic membrane through which evaporation and condensation takes place.
- 10 The invention also relates to membranes for use in such apparatus.

Known distillation requires heating the distilland to the boiling point of one or more of the constituents of the distilland and then recovering and condensing the resulting vapour to a liquid, the distillate.

Distillation has also been accomplished through the use of a thin, porous, lyophobic membrane separating the distilland, typically an aqueous solution such as salt water, from the distillate, such as pure water.

The terms lyophobic and lyophilic are used herein to describe the wettability of a liquid on a solid surface. Lyophobic describes a non-wetting behaviour of a liquid such that the contact angle between a liquid and a solid is greater than 90° so that the liquid tends to ball up and run off the surface easily. Lyophilic describes a wetting behaviour of a liquid such that the contact angle between a liquid and a solid is less than 90° and the liquid spreads over the solid easily.

The contact angle or wettability depends on the relative attraction between the solid and liquid and between the molecules of the liquid themselves. If the attraction of the liquid for the solid is more than half that for itself, the contact angle is less than 90° and wetting is said to occur and the liquid is said to be lyophilic with respect to the solid. A liquid is lyophobic with respect to a solid when the attraction of the liquid for the solid is less than half that for itself thereby creating a contact angle greater than 90° .

45 When the liquid is water, the terms hydrophobic and hydrophilic are generally substituted for the more inclusive designations.

Due to the properties of the non-wetting lyophobic material at low pressures, liquid is prevented from entering within the pores of the lyophobic membrane. If the distilland has a higher equilibrium vapour pressure than the distillate, evaporation takes place at the hotter distilland side of the lyophobic pores and condensation occurs at the cooler, distillate liquid interface of the lyophobic membrane pores. Thus, in the case of the aqueous solution, in an effort to establish vapour pressure equilibrium, a net flux of water vapour thus passes through the pores of the hydrophobic membrane. One example of such thermal membrane distillation is described in U.S. Patent No: 3,340,186.

This type of distillation process should be contrasted with reverse osmosis processes

which also use porous membranes. Reverse osmosis does not involve an evaporation/condensation process. Thermal membrane distillation is an absolute filtration process where reverse osmosis is a relative filtration process.

Unfortunately, thermal distillation across a hydrophobic membrane has not been a practical approach for separating fresh water from salt water. This is due to a major problem called water-logging. Salt water migrates into the pores of the hydrophobic membrane and causes the fresh water and the salt water to make contact. In other words, the pores fill up with water thereby destroying the vapour barrier needed for the evaporation/condensation process.

The length of time it takes for water-logging to occur depends upon a number of variables. Typically, it only takes a few days for water-logging to occur and for the distillation process to stop completely. Although the membrane's vapour barrier can be re-established by draining the water from the cells and blowing the liquid out of the membrane pores with compressed air, having to do so every four to six days because of water-log greatly decreases the commercial applicability of thermal membrane distillation.

According to the present invention, we have found that by modifying the liquid distilland-vapour interface at the membrane to prevent intrusion of the liquid distilland into the membrane pores, clogging of the pores is substantially avoided. This can be achieved by using a composite membrane having a layer of porous lyophobic material and a layer of lyophilic material. For water distillation, the layers will be hydrophobic and hydrophilic respectively. Use of membranes according to the invention thus render possible distillation processes which may be operative continuously over prolonged periods of time. In apparatus according to the invention for such a process, means are provided for supporting the membrane to define a boundary between a first and a second region for respectively receiving a distilland and a distillate, the hydrophilic layer of the membrane being adjacent the first region.

The proper selection of pore sizes for both the lyophobic and the lyophilic layers is important in maximizing the distillate production rate through the composite membrane for a given temperature and temperature difference. Generally, higher distillate production rates have been observed in composite membranes with the smaller pore sizes in the hydrophilic layer than in the hydrophobic layer, in the case of salt water distillation. Best results have occurred with the hydrophobic layer having a mean pore size of less than $0.5\mu\text{m}$ diameter. The hydrophilic layer, desirably, should also have a mean pore size of less than $0.5\mu\text{m}$ in diameter. It has also been found that the hydrophilic layer can be non-porous. Optimum

pore sizes for systems designed for purposes other than water desalination may differ.

Examples of suitable porous hydrophobic materials for the composite membrane of the present invention include polytetrafluoro-ethylene (PTFE) such as Dupont's "Teflon" (registered Trade Mark) and polyvinylidene fluoride (PVF₂). Suitable hydrophilic materials include cellulose acetate, mixed esters of cellulose, and polysulfone. Other suitable porous hydrophobic and hydrophilic materials can also be used.

PTFE is the most hydrophobic polymeric membrane material known. PVF₂ is somewhat less hydrophobic, but has also been shown to perform well.

Cellulose acetate membranes and membranes of mixed esters of cellulose have water swelling properties, i.e., they expand when wetted with water or other solvents. It is thought that the pores, especially those of small diameter, may completely close on swelling and that the liquid transport through the membrane does not require pores but migrates through the molecular structure. Polysulfone membranes swell very little upon water wetting, therefore, their pore structure remains almost unchanged upon wetting.

Both the water-swelling hydrophilic membrane and the non-water-swelling hydrophilic membrane in combination with a hydrophobic membrane prevent the water-logging phenomenon of prior art systems.

The composite porous membrane can be formed by clamping the hydrophobic/hydrophilic layers closely together to form a cell with a suitable support backing to maintain the integrity of the composite membrane. In accordance with another aspect of the invention, the composite membrane is formed by coating one of the layers on the other. For example, a hydrophobic membrane can be used as a substrate upon which a hydrophilic layer is formed.

In preferred apparatus according to the invention, a plurality of composite porous membranes are arranged in multiple stage cell configurations. A main advantage of multiple stage cell configurations is the conservation of heat energy. In a multiple stage cell, multiple composite membrane system, the heat rejected from one stage is used to provide the temperature gradient across another stage. The optimum number of stages is reached when the operating temperature of any additional stages is so low that the distillate production rate is uneconomically low.

The invention will now be described by way of example and with reference to the accompanying drawings where:-

Figure 1 is an enlarged sectional view of a known single-layer, hydrophobic porous membrane distillation device;

Figure 2 is an enlarged sectional view of a composite hydrophilic/hydrophobic mem-

brane in accordance with the present invention; and

Figure 3 is an exploded sectional view of a multiple-stage-cell, multiple composite membrane distillation system, in accordance with the present invention.

Fig. 1 is a sectional enlargement of a single hydrophobic membrane 10 separating a distilland 12 such as salt water, and a distillate 14 which is fresh water. A pore 16 extends across the hydrophobic membrane 10. Initially, due to the hydrophobic nature of the membrane 10, neither the salt water 12 nor fresh water 14 penetrates within the gaseous region 15 of pore 16. Two convex-shaped liquid-vapour surfaces 18 and 20 are defined at each end of pore 16.

Nonequal equilibrium states exist at the two interfaces 18 and 20 if the distilland 12 has a higher vapour pressure than the distillate 14. As previously explained, pure water evaporates into the capillary pore 16 and the vapour is condensed at the vapour/liquid interface 20 on the distillate side 14 in an effort to establish local vapour pressure equilibrium. The result is the creation of a net flux of water vapour across the pore 16.

In distillation apparatus using the single hydrophobic membrane 10 of Fig. 1, after several days the vapour barrier across the pores is destroyed and hence the distillation process through the membrane, ceases. This is due to water-logging. The distilland liquid-vapour interface 18 migrates in a direction toward the distillate side 14, as indicated by 18' and 18'', until eventually it intersects the liquid-vapour interface 20 on the distillate side of the membrane 10. This destroys the gaseous barrier needed for the distillation process to occur.

It is believed that the reason that water-logging occurs is due to the effect of the dissolved salt in the distilland 12. The saline solution changes the hydrophobic property of the membrane 10. More particularly, it is believed that the saline solution changes the hydrophobic property of the membrane 10 where the liquid-vapour interface 18 contacts the side wall 22 of the pore 16. As a result, the salt water, rather than being prevented from filling the pore, is able to migrate within the pore, eventually completely filling it with liquid.

A possible explanation for the alteration of the normally hydrophobic property of membrane 10 follows.

During distillation, for a given pressure, evaporation takes place at approximately a constant temperature. Addition of heat increases the kinetic energy of some liquid molecules enough to overcome the evaporation energy barrier. This heat is commonly known as the latent heat of evaporation. The latent heat of evaporation is a result of molecular attraction of the molecules which are

tightly packed in the liquid phase. There is an energy barrier at the interface between the vapour and the liquid created by an unbalanced attracting surface force for vapour molecules onto the interface surface. The very short mean free path (average molecular distance) on the liquid side compared with the vapour side creates the unbalanced forces at the interface. This is the phenomenon which creates surface tension.

It is possible to change the evaporation (or condensation) energy barrier by changing the surface curvature at the liquid-vapour interface thereby requiring less kinetic energy by water molecules to escape from the liquid into the vapour. For a convex liquid surface, the greater the convexity, the greater the evaporation rate for a given temperature. Further, a convex liquid surface will have a greater rate of evaporation than a concave liquid surface. Conversely, the rate of condensation is less on a convex liquid surface than on a concave liquid surface.

The effect of the degree of curvature on evaporation rates can be seen in the formation of water droplets at a given temperature. Small drops, having greater curvatures, require higher vapour partial pressure to reach equilibrium with the surrounding gas mixture. As an example, the distribution of different drop sizes existing in a cloud formation or cloud chamber will shift to larger drop sizes with time. The bulk temperature and vapour pressure is the same for all sizes of droplets. Due to the required higher equilibrium vapour partial pressure for small drops, they will evaporate to increase the bulk vapour pressure of the surrounding gas mixture. This, however, causes a condensation to take place on the larger drops since their equilibrium vapour partial pressure is lower, due to their "flatter" outside curvature.

For a period of time the smaller sized drops disappear and the large sized drops become larger. In a rain cloud, as the size of a drop increases, the gravitational force becomes larger than the air current buoyancy forces and rainfall begins.

In an analogous manner, it is believed that the dissolved salt in the distilland 12 can alter the curvature of the liquid-vapour interface 18, thereby altering the evaporation energy barrier. Exactly what the nature of the modification is, is uncertain, but that it does appear to take place is suggested by another well known phenomenon, that of a drying salt water puddle.

In the drying process crystals or solids periodically precipitate at the perimeter to form concentric drying rings around the edge of the puddle. Usually the centre of a drying puddle has a lower solids concentration than at the edge. A close examination of the edge of a puddle indicates that the curvature of the liquid surface at the edge of the puddle con-

taining dissolved salts is considerably modified from a pure water puddle surface contacting edge. The evaporation energy barrier and the salt concentration distribution at the edge of the liquid puddle are also considerably changed from those of the homogeneous solution.

Since the surface tension is a function of the salt concentration, the salt concentration in turn modifies the surface curvature. For example, increasing sodium chloride content increases the surface tension of water. The increased surface tension due to increased curvature at the edge creates two effects. First it increases the rate of evaporation of water at the edge of the puddle. Secondly, it produces a higher salt concentration at the edge while the centre is left with the lower concentration of the homogeneous solution. The evaporation of the puddle increases the burden of the surface tension as it attempts to hold to the original boundary. Eventually, the original boundary cannot maintain its position and recesses to a new equilibrium position. When the boundary recesses, the salt precipitates at the boundary leaving behind a salt ring. The process repeats itself, forming multiple rings until the water is completely dried.

An analogous situation may be responsible for water-logging in the hydrophobic membrane pores. Salt concentration increases at the edge of the liquid-vapour interface 18 adjacent the pore wall 2 due to local surface tension alterations caused by the effects of the hydrophobic material on the salt water. This condition modifies the surface tension there, which in turn modifies the liquid-vapour interface curvature and increases the rate of evaporation of water and causes salt precipitation to occur along the edge 22 of the liquid-vapour interface rendering the hydrophobic wall of the membrane hydrophilic. The original boundary is therefore not maintained, and the liquid-vapour interface 18 migrates to position 18'. Eventually, migration causes the salt water interface to collide with the fresh water interface, and water-logging occurs.

Fig. 2 is an enlarged sectional view of a composite porous membrane 24 for thermal membrane distillation, in accordance with the present invention. The composite membrane 24 comprises a hydrophobic layer 26 to which is closely joined a hydrophilic layer 28. The membranes must be pressed together closely enough to alter the surface tension effect at the salt water/water vapour interface and, therefore, prevent salt precipitation at the edge as will be explained subsequently. The hydrophilic layer 28 is adjacent the distilland 12 and the hydrophobic layer is adjacent the distillate 14. In the embodiment described, the distilland is salt water and the distillate is fresh water.

As with the single hydrophobic distillation membrane 10 of Fig. 1, evaporation and

condensation take place within micropores 29. The hydrophilic layer 28 can also be micro-porous, but because of the affinity of water to the hydrophilic material of layer 28, the pores 30 of the hydrophilic layer 28 fill by capillary action with salt water. With a vapour pressure gradient across the composite membrane 24 a net evaporation takes place at the salt water/vapour interface 32 and a net condensation occurs at the fresh water/vapour interface 34. However, unlike the case of the single hydrophobic distillation membrane, water-logging does not occur within the composite membrane 24. It has been found, as explained previously, that the hydrophilic layer need not be porous. Nor is there a requirement that where the hydrophilic layer is porous, that the pores be aligned with the hydrophobic pores, as shown in Fig. 2.

The vapour transport rate across the pores 29 is dependent on the vapour pressure gradient across the pore cavity, i.e., on the vapour pressure difference at the evaporating liquid/vapour interface 32 and the condensing vapour/liquid interface 34. The vapour pressure is a function of the temperature, salt concentration, and surface curvature. Therefore, all three properties must be considered in creating the desired vapour pressure gradient across the composite membrane 24.

The reason that the composite hydrophilic/hydrophobic membrane does not exhibit water-logging is not known for certain. However, it is believed that the hydrophilic layer adjacent the hydrophobic layer alters the liquid/vapour interface 32 in such a way that salt water 12 does not intrude within the pores 29. The hydrophilic layer 28 may interact with the hydrophobic layer 26 to change the surface curvature of the liquid/vapour interface so that the salt concentration does not increase at the edge of the pore. Both the hydrophilic and hydrophobic layers are needed to accomplish continuous water distillation by a thermal membrane distillation process and to overcome the water log problem.

The proper selection of pore sizes for both the hydrophobic and hydrophilic layers of the composite membrane is important for maximizing distillate production and ensuring uninterrupted flow. The pore sizes of the hydrophobic layer should be chosen to withstand at least the hydraulic pressure exerted by the liquids on either side of the membrane. That is, the bubble pressure across the hydrophobic layer must exceed, at a minimum, the absolute hydraulic pressure. The vapour pressure in the pore may be much lower than atmospheric pressure, therefore the bubble pressure must exceed the absolute hydraulic pressure rather than simply the gauge hydraulic pressure.

Bubble pressure is defined as the required pressure to overcome the capillary surface tension. This is directly related to pore dia-

meter. Since the porous hydrophobic material has a distribution of pore diameters, the maximum absolute pressure on either side of the hydrophobic membrane must not exceed the bubble pressure for the largest pores. Because capillary forces are greater for smaller pores, bubble pressure increases as pore size decreases.

Best results have been obtained with mean pore size for the hydrophobic layer of less than $0.5\mu\text{m}$ for PTFE for desalination of salt water. Preferably, the mean pore size of the hydrophilic layer 28 is smaller than the mean pore size of the hydrophobic layer 26. Generally, best results have been obtained with mean pore size less than $0.5\mu\text{m}$ for the hydrophilic layer as well. The important objective of selecting the hydrophilic layer pore size is to alter the liquid-gas interface 32 at the pores 29 of the hydrophobic layer to prevent migration of the distillate into the hydrophobic pores to prevent water-logging. It has also been found that non-porous hydrophilic materials can also be used in the composite membranes of the present invention.

The composite membrane should be made as thin as possible so that the vapour transport distance across the membrane is as short as possible. A practical limitation on thinness is that it must be sufficiently strong that it does not tear or rupture. Typical thicknesses for the hydrophobic layer are about 1.5 mils for PTFE and about 2 to 6 mils for PVF₂.

Composite hydrophilic/hydrophobic membranes were tested using a PTFE hydrophobic membrane (Millipore "Fluoropore" filler—type FG) with a mean pore diameter of $0.2\mu\text{m}$. Composite hydrophilic/hydrophobic membranes, were tested with hydrophilic mean pore sizes of $0.2\mu\text{m}$, $0.1\mu\text{m}$, $0.5\mu\text{m}$, and $0.025\mu\text{m}$ (Millipore "MF" filter, types GS, VC, VM, and VS, respectively, which are made of a mixture of cellulose acetate and cellulose nitrate).

The large mean pore diameters of $0.2\mu\text{m}$ and $0.1\mu\text{m}$ used for the hydrophilic layer used in the composite membrane system did not significantly differ in performance, but the composite membranes with the $0.05\mu\text{m}$ and $0.25\mu\text{m}$ hydrophilic mean pore sizes did show the positive influence of selective pore size diameter.

Experiments were performed to test and compare the performance of a single $0.2\mu\text{m}$ mean pore size PTFE hydrophobic membrane with a composite membrane comprising a cellulose-acetate/cellulose-nitrate hydrophilic membrane, also with a mean pore size of $0.2\mu\text{m}$, laminated with a PTFE membrane with an identical mean pore size. The salt content used in the water in these experiments was at least 30 grams in 1000 grams of water. Tests were conducted with the salt water heated to both 160°F and 130°F for

comparison.

The results show that the single hydrophobic membrane has a rapid distillate production rate drop off in the 160°F case and stopped completely in four days. At the lower temperature of 130°F, the flow through the single membrane stopped in two days. In contrast, the composite membranes ran for twenty days and still showed no signs of stopping, at which time the experiment was discontinued.

The composite membrane of the present invention functions effectively even at very low temperatures as long as the vapour pressure gradient exists from the distilland to the distillate. The concentration of dissolved salts in the distilland increases with time as evaporation/condensation takes place which eventually causes the precipitation of salts, unless some high salt concentration distilland is drained off and replaced with less concentrated distilland. If the composite membrane causes the salt to concentrate in the centre of the liquid/vapour interface 32, or at least not cause salt to precipitate at the edge of the liquid-solid interface, then the salt concentration, although high at the interface, can still be diffused back into the bulk distilland solution rather than precipitate at the interface and cause water-logging.

Most of the trapped gas in the hydrophobic pores may be absorbed by the condensate water, especially at low temperature operation. This creates a partial vacuum such that the equilibrium at the liquid-vapour interface 32 is changed. The partial vacuum increases the vapour diffusion rate but also reduces the condensation rate at the liquid/vapour interface 34 at the distillate side.

One of the essential elements in water desalination is the best utilization of available energy. The cell in a composite thermal osmosis membrane system can be operated at atmospheric or higher water pressures at temperatures as low as 120°F. Consequently, many sources of waste heat from industrial plants and also from home uses, for example, may be used as energy for creating the necessary temperature differential for thermal distillation to occur across the composite membrane.

In any distillation process, enough energy must be supplied to overcome the latent heat of evaporation, which for water is about 900 Btu/lb. However, some of the heat used for evaporation of the water on the distilland side of the composite membrane can be recovered upon condensation of the distillate. In a thermal membrane distillation system, the temperature drop from the saline water side to the fresh water side desirably exceeds about 2°F.

Fig. 3 is an exploded, sectional view of a multiple stage cell desalination system 50 with three cell stages 52, 54 and 56. Additionally, there is a pre-heat cell stage 58. Each cell stage, 52, 54, and 56 includes two ring members 59 and 60, which sandwich and

support a composite membrane 61 comprising a hydrophilic membrane 62, a hydrophobic membrane 64, and a support screen 66. Individual cell stages are separated by stainless steel plates 67 which pass waste heat to the adjacent, lower temperature cell stages.

Support screen 66 is made of a material, such as stainless steel, which is chemically inert to salt water. It is necessary to support the thin composite membrane 61 to be able to hold the hydrophobic membrane against the hydrophilic membrane and also to prevent rupturing. The screen is attached along its periphery by a stainless steel loop 68 which fits into a recess 70 of ring member 60.

An end cap 72 completes one end of the multiple stage cell system 50. Another end cap 74 seals the other end by engagement with another ring member 76. End cap 74, ring member 76, and stainless steel plate 67 define the preheat cell stage 58. O-rings 78 are provided to maintain the integrity of the pre-heat cell 58, as well as the membrane cell stages 52, 54 and 56. The cell stages 52, 54 and 56 as well as the pre-heat cell 58, and end plates 72 and 74 are clamped together by suitable means, not shown for clarity.

For sake of clarity, the fresh and salt water sides of each of the cell stages 52, 54 and 56 are designated with the letters "F" and "S", respectively. Thus, cell stage 52 has a fresh water side F1 and a salt water side S1, cell stage 54 has sides F2 and S2, and cell stage 56 has sides F3 and S3. Conduits 82, 84 and 86 are provided from the fresh water side of cell stages 52, 54 and 56, respectively, for recovering the condensed distilled water.

A source of salt water to be desalinated is shown at 88. It should be understood that while salt water is the distilland in this particular embodiment, any aqueous solution containing dissolved minerals or particles can be distilled using the multiple-stage-cell apparatus 50. This includes, for example, muddy water, sewage, and aqueous solutions of industrial wastes.

A heat source is provided at 90. Desirably, waste heat is used, but a heater can be used if waste heat is not available. In the multiple-stage-cell system 50, each successive cell stage is cooler than the preceding cell stage, with cell stage 52 being the hottest. The remaining distillation cell stages 54 and 56, and preheat cell stage 58 are each successively cooler. Of course, for each composite membrane 61 within each cell stage, there is a temperature difference maintained across it.

The flow of salt water being distilled will now be explained. Salt water enters the pre-heat cell 58 through conduit 92. The salt water is elevated in temperature by heat transmitted through stainless steel plate 67 from the fresh water side F3 of cell stage 56.

Some of the salt water passing through pre-heat cell stage 58 is passed by pump 94

through an outlet conduit 96, through a heat exchanger 98 where waste heat is dispelled, to maintain the end of the system 50 as cool as possible. The remainder of the salt water passes out of pre-heat cell stage 58 through conduit 100 to the salt water side S3 of distillation cell stage 56. Additional salt water is added to pre-heat cell stage 58 as required.

Salt water entering the S3 side of cell stage 56 is heated by the fresh water side F2 of cell stage 54 through stainless steel plate 67. Desalinated fresh water passes out from the fresh water side F3 of cell stage 56 through conduit 86.

Partially distilled salt water from the S3 side passes through conduit 102 to side S2 of cell stage 54, where it is further heated by the fresh water side F1 of cell stage 52 through stainless steel plate 67. Distilled fresh water passes out of F2 through conduit 84 after passing through the composite membrane.

The partially distilled salt water, now having a higher salinity content, then passes out of side S2 of cell stage 54 through conduit 104 to heat source 90. There it is further heated and is pumped to the salt water side S1 of cell stage 52 through conduit 106 by pump 108. Salt water flowing to cell stage 52 passes through a filter 110 and a flow meter 112.

Distilled water from side F1 of cell stage 52 flows out of the cell through conduit 82. Remaining salt water from side S1 passes out of conduit 114 where it is reheated and mixed with salt water from S2. Some highly concentrated salt water is drained at conduit 115 to maintain the salt concentration at a desired level. Of course, salt water can be drained at any cell stage to adjust the salt concentration as desired.

It can be seen that each cell stage is "driven" by heat from the preceding cell stage. Additionally, since the fresh water sides F1-F3 give off heat to the salt water side, the vapour pressure of the fresh water side is maintained below the vapour pressure of the salt water side of that cell stage by maintaining a sufficient temperature difference. Thus, a vapour pressure gradient is established across each of the composite membranes 61 which is required for distillation to take place.

In an actual embodiment each of the ring members 59 and 60 and the end plates 72 and 74 are made of a polycarbonate plastic. Of course, of primary importance in the selection of this material, is the ability to withstand the corrosive effects of warm salt water solutions.

The hydrophilic membranes 62 in distillation system 50 are made typically of cellulose acetate/cellulose nitrate mixture such as type No: MF-VM made by Millipore. The mean pore diameter for this membrane is .05 μ m. The hydrophobic membranes 64 are PTFE, such as Millipore's "Fluoropore" filter, Type

FG, which has a mean pore diameter of 0.2 μ m.

Once the system reached a steady state condition, the output of pure water from distillation system 50 was 10 pounds of water per square foot of composite membrane 61 per day for cell stage 56; 12 pounds for cell stage 54; and 7 pounds for cell stage 52. Salt water was drained at 6.6 pounds of water per square foot per day of membrane area.

Representative temperatures within each cell stage are:-

Preheat	75°F
80 F3	95°F
S3	115°F
F2	126°F
S2	144°F
F1	158°F
85 S1	171°F

To clamp the hydrophobic membrane 64 against the hydrophilic membrane 62 and also to protect against contamination in the event of rupture of a composite membrane 61, the fresh water sides F1-F3 are maintained at a higher pressure than the respective salt water sides S1-S3 of each of the cell stages.

It is preferable in case of the multiple stage cell configuration of Fig. 3 to have higher concentration saline solutions in the higher temperature cells. It was found that higher temperatures are required to maintain acceptable distillate production rates from the more concentrated distilland solutions. This is determined by the thermodynamic stages of the solution. In general, it is preferred to arrange brine feed so that the salt concentration increases with cell temperature. Thus, the salt concentration is greatest at S1 and lowest in S3.

In multiple stage cell systems, the energy used for fresh water production is reduced approximately as the inverse of the number of cells. For example, a three-stage cell system uses about one-third of the energy required to produce fresh water in a single-stage cell system. Typically, in a multiple stage cell system with salt water temperature of 180°F in the hottest cell, the required energy to produce pure water will be as low as 180 Btu/lb., which is one-fifth the energy necessary to evaporate water.

Commercial stills also use multiple stage evaporation techniques, but limiting consideration for the optimum number of conventional evaporation stages is the pressure difference between evaporator stages, the pressure difference becoming smaller with the addition of stages. On the other hand, with the multiple-stage composite membrane cell system, such as shown in Fig. 3, the limiting consideration is the temperature difference across the cell stages.

When brine attains a sufficient concentration, it has a commercial value as feedstocks to other process industries. High concentration saline solutions may be taken out of the system and reused. Salt brine concentrations as high as 25% have been achieved utilizing the composite membrane cells of the present invention.

10 CLAIMS

1. Thermal distillation apparatus having a composite membrane comprising a layer of porous lyophobic material and a layer of lyophilic material; and means for supporting the membrane to define a boundary between a first and a second region for respectively receiving a distilland and a distillate, the hydrophilic layer of the membrane being adjacent the first region.
2. Apparatus according to Claim 1 wherein the lyophilic material of the membrane is non-porous.
3. Apparatus according to Claim 1 wherein the lyophilic layer of the membrane is porous.
4. Apparatus according to Claim 3 wherein the mean pore diameter of the lyophilic layer is less than $0.5\mu\text{m}$.
5. Apparatus according to Claim 3 or Claim 4 wherein the average pore size of the lyophilic layer is less than the average pore size of the lyophobic layer of the membrane.
6. Apparatus according to any of Claims 3 to 5 wherein the lyophilic layer of the membrane is a mixture of cellulose acetate and cellulose nitrate.
7. Apparatus according to any of Claims 3 to 5 wherein the lyophilic layer of the membrane is cellulose acetate.
8. Apparatus according to any preceding Claim wherein the lyophilic layer of the membrane is polysulfone.
9. Apparatus according to any preceding Claim wherein the mean pore diameter of the lyophobic layer of the membrane is less than $0.5\mu\text{m}$.
10. Apparatus according to Claim 8 or Claim 9 wherein the hydrophobic layer of the membrane is polytetrafluoro-ethylene.
11. Apparatus according to Claim 8 or Claim 9 wherein the hydrophobic layer of the membrane is polyvinylidene fluoride.
12. Apparatus according to any preceding Claim for thermal distillation of aqueous solutions wherein the lyophobic layer of the membrane is hydrophobic and the lyophilic layer is hydrophilic.
13. Apparatus according to Claim 12 including means for providing a temperature differential between the first and second regions and across the membrane such that aqueous solution in the first region has a higher vapour pressure than does pure water in the second region.
14. Thermal distillation apparatus substan-

tially as described herein with reference to Fig. 3 of the accompanying drawings.

15. A composite membrane comprising a layer of porous hydrophobic material and a layer of hydrophilic material.
16. A composite membrane according to Claim 15 wherein the lyophilic layer is porous.
17. A composite membrane according to Claim 16 wherein the mean pore diameter of the lyophilic layer is less than $0.5\mu\text{m}$.
18. A composite membrane according to Claim 15 or Claim 16 wherein the average pore size of the lyophilic layer is less than the average pore size of the lyophobic layer.
19. A composite membrane according to any of Claims 15 to 18 wherein the lyophilic layer is a mixture of cellulose acetate and cellulose nitrate.
20. A composite membrane according to any of Claims 15 to 18 wherein the lyophilic layer is cellulose acetate.
21. A composite membrane according to any of Claims 15 to 18 wherein the lyophilic layer is polysulfone.
22. A composite membrane according to any preceding Claim wherein the mean pore diameter of the hydrophobic layer is less than $0.5\mu\text{m}$.
23. A composite membrane according to Claim 21 or Claim 22 wherein the hydrophobic layer is polytetrafluoro-ethylene.
24. A composite membrane according to Claim 21 or Claim 22 wherein the hydrophobic layer is polyvinylidene fluoride.
25. A composite membrane according to Claim 1 wherein the hydrophilic material is non-porous.
26. Composite membranes substantially as described herein with reference to Fig. 2 of the accompanying drawings.

Printed for Her Majesty's Stationery Office
by Burgess & Son (Abingdon) Ltd.—1982.
Published at The Patent Office, 25 Southampton Buildings,
London, WC2A 1AY, from which copies may be obtained.



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10 CLAIMS

1. Thermal distillation apparatus having a composite membrane comprising a layer of porous lyophobic material and a layer of lyophilic material; and means for supporting the membrane to define a boundary between a first and a second region for respectively receiving a distilland and a distillate, the hydrophilic layer of the membrane being adjacent the first region.

2. Apparatus according to Claim 1 wherein the lyophilic material of the membrane is non-porous.

3. Apparatus according to Claim 1 wherein the lyophilic layer of the membrane is porous.

4. Apparatus according to Claim 3 wherein the mean pore diameter of the lyophilic layer is less than $0.5\mu\text{m}$.

5. Apparatus according to Claim 3 or Claim 4 wherein the average pore size of the lyophilic layer is less than the average pore size of the lyophobic layer of the membrane.

6. Apparatus according to any of Claims 3 to 5 wherein the lyophilic layer of the membrane is a mixture of cellulose acetate and cellulose nitrate.

7. Apparatus according to any of Claims 3 to 5 wherein the lyophilic layer of the membrane is cellulose acetate.

8. Apparatus according to any preceding Claim wherein the lyophilic layer of the membrane is polysulfone.

9. Apparatus according to any preceding Claim wherein the mean pore diameter of the lyophobic layer of the membrane is less than $0.5\mu\text{m}$.

10. Apparatus according to Claim 8 or Claim 9 wherein the hydrophobic layer of the membrane is polytetrafluoro-ethylene.

11. Apparatus according to Claim 8 or Claim 9 wherein the hydrophobic layer of the membrane is polyvinylidene fluoride.

12. Apparatus according to any preceding Claim for thermal distillation of aqueous solutions wherein the lyophobic layer of the membrane is hydrophobic and the lyophilic layer is hydrophilic.

13. Apparatus according to Claim 12 including means for providing a temperature differential between the first and second regions and across the membrane such that aqueous solution in the first region has a higher vapour pressure than does pure water in the second region.

14. Thermal distillation apparatus substan-

tially as described herein with reference to Fig. 3 of the accompanying drawings.

15. A composite membrane comprising a layer of porous hydrophobic material and a layer of hydrophilic material.

16. A composite membrane according to Claim 15 wherein the lyophilic layer is porous.

17. A composite membrane according to Claim 16 wherein the mean pore diameter of the lyophilic layer is less than $0.5\mu\text{m}$.

18. A composite membrane according to Claim 15 or Claim 16 wherein the average pore size of the lyophilic layer is less than the average pore size of the lyophobic layer.

19. A composite membrane according to any of Claims 15 to 18 wherein the lyophilic layer is a mixture of cellulose acetate and cellulose nitrate.

20. A composite membrane according to any of Claims 15 to 18 wherein the lyophilic layer is cellulose acetate.

21. A composite membrane according to any of Claims 15 to 18 wherein the lyophilic layer is polysulfone.

22. A composite membrane according to any preceding Claim wherein the mean pore diameter of the hydrophobic layer is less than $0.5\mu\text{m}$.

23. A composite membrane according to Claim 21 or Claim 22 wherein the hydrophobic layer is polytetrafluoro-ethylene.

24. A composite membrane according to Claim 21 or Claim 22 wherein the hydrophobic layer is polyvinylidene fluoride.

25. A composite membrane according to Claim 1 wherein the hydrophilic material is non-porous.

26. Composite membranes substantially as described herein with reference to Fig. 2 of the accompanying drawings.