

Curricular Innovation in the Chemical Engineering Separation Process Course – Membrane Distillation Module – Materials and Processes

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Introduction:

Membrane distillation (MD) is a novel process that is being investigated as a low cost, energy saving alternative as compared to conventional separation processes like distillation & reverse osmosis. It is believed that this process offers an educational opportunity for the undergraduate chemical engineering curriculum. MD is a thermally driven process in which a microporous hydrophobic membrane separates a warm solution from a cooler chamber containing either liquid or gas. The separation mechanism is based on vapor-liquid equilibrium. Since this is one of the newest membrane processes it has not yet been introduced into the undergraduate/graduate curriculum. No mention of membrane distillation appears in separations textbooks such as “Separation Process Principles” by Seader and Henley, “Transport Processes and Unit Operations” by C J Geankoplis, “Separation Processes” by C. Judson King, “Unit Operations in Chemical Engineering” by McCabe, W. L. Smith and P. Harriott and “Equilibrium Staged Separations” by Philip C Wankat.

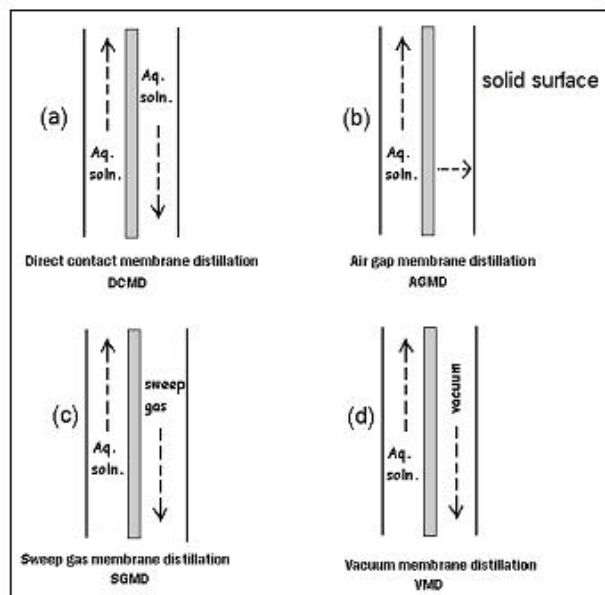


Figure 1. Various models of membrane distillation.

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The solutions used in MD are preferably aqueous and sufficiently dilute to prevent wetting of the hydrophobic membrane. In the literature, effects such as the use of various solvent and non-solvent

combinations, solute concentration and precipitation temperature are known to determine the morphology. The surface characterizations are done using Scanning Electron Microscope and Atomic Force Microscope imaging.

MD is found to be very effective at rejecting macromolecules, colloids and other non-volatiles. Operating temperatures and pressures are lower than conventional distillation making it reliable and cost-effective. This paper connects concepts in traditional chemical engineering separation processes to non-traditional chemical engineering concepts such as membrane materials and polymer science and engineering. It therefore has great pedagogical value as a new part of the chemical engineering separations processes class.

New Concepts in the Chemical Engineering Separations Class

1) Membrane Distillation:

Membrane Distillation, as a new unit operation, complements the concepts of traditional distillation very well. Issues such as flow rate of the feed and yield of the distillate permeated through the membrane are some of the starting parameters for distillation process. The vapor liquid equilibrium curves also play an important role in estimating the physical state of the fluid in the feed reservoir. A hot feed is contacted with one side of a hydrophobic microporous membrane. A variety of methods are employed to impose the vapor pressure difference across the membrane to promote the mass transfer. Figure 1 illustrates various common modules of MD process. In direct contact membrane distillation (DCMD), part (a), the liquid or sweep gas comes in direct contact with the membrane. The major disadvantage of this process is that most of the heat supplied to the feed is lost by conduction through the membrane surface. In air gap membrane distillation (AGMD), part (b), the condensing surface is separated from the membrane by an air gap. The heat lost in this case is less than the previous case. This is because the gap is filled with air, which has increased conductive heat transfer resistance, but there is appreciable drop in mass flux. This is mostly preferred for purifying non-volatile species. In this model, increasing the air-gap width between the membrane and the condensation surface is expected to increase selectivity but reduce permeate flux. In sweeping gas membrane distillation (SGMD), part(c), air is blown over the membrane and the permeate is condensed in an external condenser. Due to the sweeping gas velocity, pressure drop is high. In vacuum membrane distillation (VMD), part (d), low pressure or complete vacuum is maintained on the permeate side. The conductive heat loss through the membrane is negligible. The process is generally used to remove volatile components from dilute aqueous solutions. Care should be taken to prevent membrane wetting in this type.

2) Membrane Processing Concepts in Chemical Engineering:

Formation of polymer membranes is an area, which is certainly not covered in the traditional chemical engineering curriculum. However, an understanding of the membrane formation process is based on the chemical engineering concepts of thermodynamics and mass transport. The connection to these traditional chemical engineering concepts can be presented in this new module. Polyvinylidene fluoride (PVDF) membranes have been explored in MD as microporous hydrophobic flat sheet membranes. The thermodynamics of the precipitation process and membrane solutions can be investigated through and understanding of the phase equilibria of the casting solution. The membranes are prepared by dissolving the polyvinylidene fluoride in any one of the several solvents. The solvent can be selected from any of the following: acetone, N-methyl-2-pyrrolidone,

dimethylformamide, dimethylacetamide, tetramethylurea and dimethyl sulfoxide. Then a non-solvent, selected from: propylene glycol, butanol, methanol, isopropanol, glycerol is added. After some time the liquid layer is plunged into a precipitation bath. The precipitation bath usually consists of ice + water. This precipitates the final membrane from the mixture. The non-solvent plays a key role in the formation of desired pore size. The membrane obtained is then further processed by heat treatment, to remove any residual solvent/non-solvent. With varying solvent-non-solvent combination used in the preparation of the PVDF membrane, the permeability also varies significantly. At higher temperatures (~85°C), cellular asymmetric morphologies are produced. This is because of the domination of liquid-liquid de-mixing over the crystallization. The average pore size is higher in this case. At lower temperature (~25°C), crystallization dominates liquid-liquid de-mixing and so the membrane is formed into a uniform particulate structure and the average pore size is smaller. The usual temperatures during the dissolution step are maintained around 50°C, so that most of the polymer is dissolved and 0-10°C during the precipitation step. The major advantage of using microporous PVDF membranes is that they can filter particulate and colloidal components of a solution very effectively. The membrane is inert to many chemical substances. The cellular morphologies are observed using SEM and AFM imaging. Studies of the phase equilibria and the related concepts play an important role in estimating temperature and pressure conditions during the synthesis of the membrane. Polyvinylidene fluoride (KYNAR Vinylidene fluoride, Elf Atochem North America, Inc.) is the polymeric material used. Acetone (Dow Chemical Co) and glycerol (J.T.Baker Chemical Co.) are the corresponding solvent and non-solvent used for dissolving the polymer. Depending upon the concentration of the solvent used, the porosity of the membrane finally formed alters. The polymer solvent mixture consisting of about 15% by weight of polymer in acetone is heated slowly so that most of the polymer is dissolved and a homogenous solution is formed. Care is taken that the temperature does not exceed 50°C, such that the flash point of acetone is not reached. The precipitation bath consists of ice + water mixture maintained between 0 °C and 10 °C. All the above conditions maintained during the preparation of the membrane are related to the thermodynamics. Since glycerol is soluble in both solvent and in the precipitation bath it is used as non-solvent. The precipitation bath removes all the excess solvent and non-solvent on the membrane formed.

3) Membrane Characterization

Several non-traditional chemical engineering concepts, such as instrumentation for the characterization of the membranes are presented as part of this section.

a) Scanning electron microscope (SEM): The understanding of the SEM involves concepts of fundamental physics and chemistry. This is a commonly used method for membrane characterization and is complementary to the chemical engineering curriculum. The SEM provides information relating to topographical features, morphology, phase distribution, compositional differences, crystal orientation and the presence and

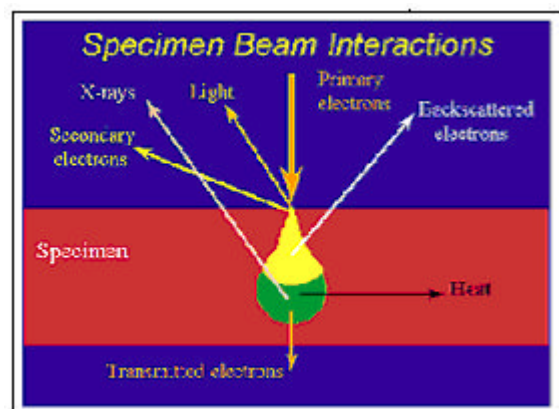


Figure 2. Specimen beam interactions with signal generation.

location of electrical defects. SEM is also capable of determining elemental composition of micro-volumes with the addition of x-ray or electron spectrometer and phase identification through analysis of electron diffraction patterns. The two major benefits of the SEM are its magnification and depth of field in the image. There are different spatial resolutions for the various types of signals generated in the SEM as shown in Figure 2. The electrons and photons released will each have different depths within the sample from which they can escape due to their unique physical properties and energies. Boundary secondary electrons (BSE) are electrons from the incident probe that undergo elastic interactions with the sample and then change trajectory and escape the sample. Secondary electrons (SE) are formed due to inelastic interactions. They are of low energy than BSE's. A SE is emitted from an outer shell of a specimen atom upon impact of the incident electron beam. The intensity of SE's is a function of the surface orientation with respect to the beam and the SE detector. Figure 3 shows the working of SEM instrument. Electron diffraction techniques in the SEM can be used to identify phases, determine their orientation, and study crystal damages and defects (Dingley, 1981). Interpretation of SEM images is dependent upon the geometry of the probe, specimen and detector. The general imaging mode utilizes SE for information on the surface morphology. Surfaces at different angles to the probe produce different brightness levels. The final image generally looks like a black and white optical view of the surface.

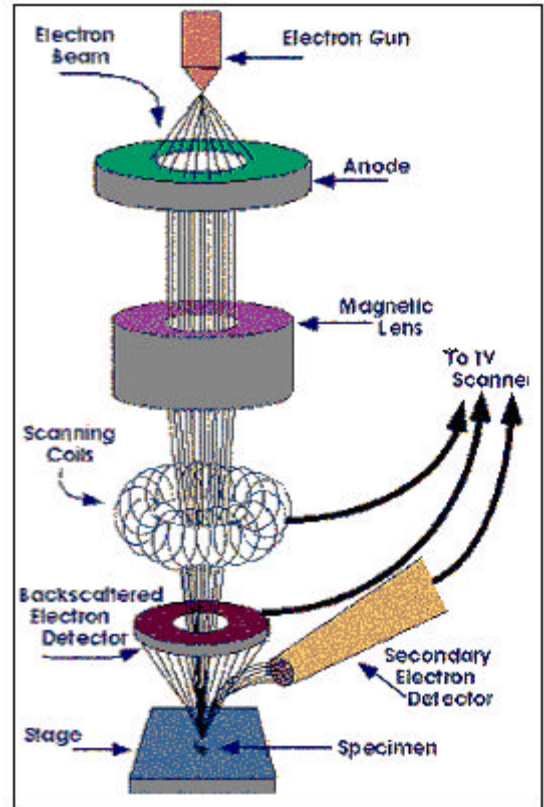


Figure 3. Schematic of SEM with signal generation.

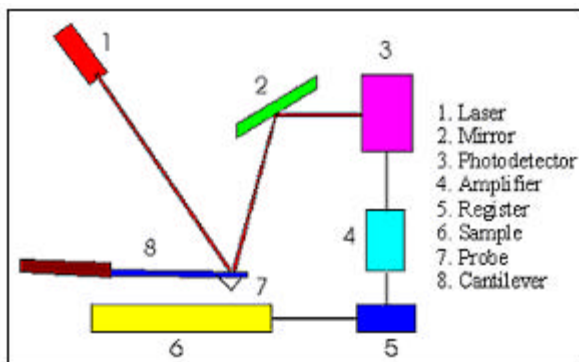


Figure 4. Schematic of AFM instrument.

b) Atomic Force Microscopy (AFM):

Atomic force microscopy is a relatively new characterization and is based on concepts of physics, chemistry and surface science. These concepts also fit well in the chemical engineering curriculum. AFM is a three-dimensional imaging technique. It achieves high resolution without inducing any destructive frictional forces both in air and liquid. One can not only image the surface in atomic resolution but also measure a force at nano-newton scale. An atomically sharp tip is scanned over a surface with feedback mechanisms that enable the piezo-electric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface. The AFM head employs an optical detection system in which the tip is attached to the underside of a reflective cantilever. A diode laser is focused onto the back of a reflective cantilever. The tip scans the surface deflecting the laser beam and finally passes the signals to a photo detector (3) as shown in Figure 4, which measures the difference in light

intensities between the upper and lower photo detectors, and then converts to voltage. Feedback from the photodiode difference signal, through software control from the computer, enables the tip to maintain either a constant force or constant height above the sample. Three dimensional topographical maps of the surface are constructed by plotting the local sample height versus horizontal probe tip position.

c) MD Equipment:

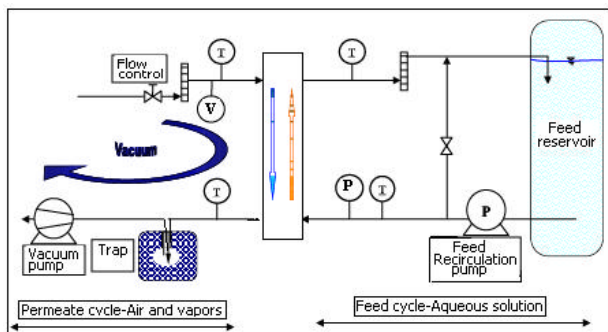


Figure 5. Schematic diagram showing combined vacuum & sweep gas MD

The performance of the MD system is based on an understanding of the heat transfer concepts. This is a good fit with the traditional heat transport part of the chemical engineering curriculum. The amount of vapor permeated entirely depends on the amount of heat it gathers from the surroundings. Experiments are carried out in batch mode. The membranes used are polytetrafluoroethylene (PTFE) and polypropylene. The feed flow rate through the membrane module was monitored using a rotameter with a pressure valve for manual regulation of the flow rate. The influence of the various colloids/precipitates and their effect on the nature of the flow are all related to the fluid mechanics. The

nature of the flow over the membrane judges the permeation rate across the membrane. Permeate was removed from the shell side of the membrane module by the combined action of the suction of a vacuum pump and by the sweep gas flow. A pressure meter connected to the shell side of the module was used to measure the pressure at the permeate side of the membrane. The temperature of the feed was monitored at the inlet and outlet ports of the membrane unit using two thermocouples. The effect of pressure and temperature variations on the permeate flow are also studied.

4) Membrane Distillation Performance Results:

In this experiment an aqueous solution of propylamine is treated by membrane distillation. It is

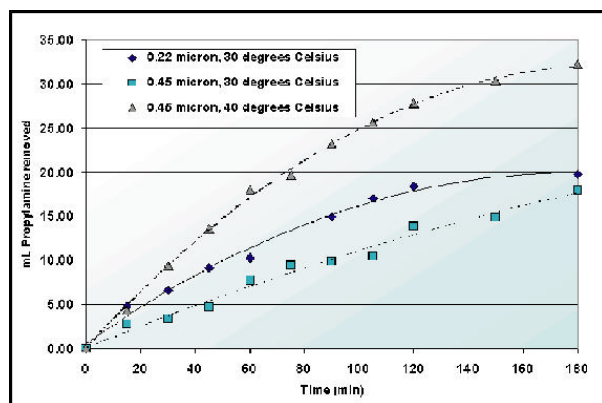


Figure 6. MD results with propylamine at various temperatures and pore size.

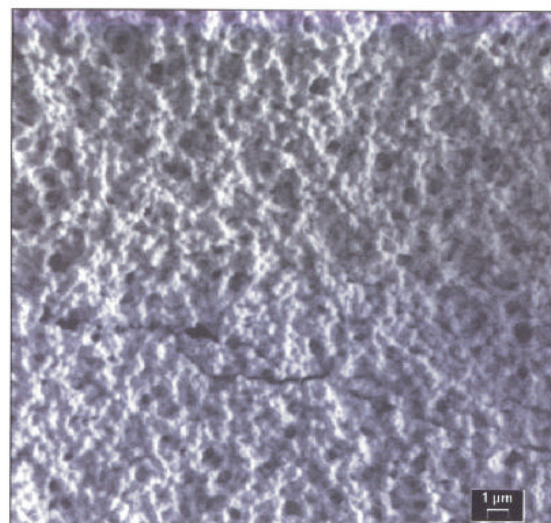


Figure 7. SEM of PVDF membrane.

demonstrated that the removal rate of propylamine is dependant on the membrane pore size and temperature of the solution. The pore size of a membrane must be large enough to facilitate the required flux and small enough to prevent liquid from penetrating. This explains the importance of mass transfer operations in the working of MD system. With increasing temperature, the flux of the amine in the vapor phase also increases, this is because the diffusion coefficient and equilibrium concentration of propylamine in the vapor phase at the liquid-vapor interface increases along with temperature. The range of average pore size of the membrane tested is large, from $0.22\mu\text{m}$ to $0.45\mu\text{m}$. From the graph it is seen that more amine is removed in a membrane with pore size $0.22\mu\text{m}$ rather than $0.45\mu\text{m}$, with both operating at the same temperature. This can be attributed to the differences in the pore density. The membrane with $0.22\mu\text{m}$ pores presumably has higher pore density and hence more amine is removed. The novel approach of combined sweeping gas and vacuum action on the permeate side has many advantages over the conventional individual sweep gas and vacuum processes. The vacuum suction allows the membrane to maintain the negligible conductive heat loss through the membrane while at the same time the sweeping gas increases the transportation of the permeate formed, thus making use of both techniques.

The membranes are characterized using SEM and AFM. The SEM result of the PVDF membrane is shown in Figure 7. The darker portions represent pores, while the brighter portions represent surface. The surfaces at different angles to the probe produce different brightness levels and edges appear brighter. The pore size is typically around $0.4\text{-}0.6\mu\text{m}$. Uniform distribution of the pores can be seen.

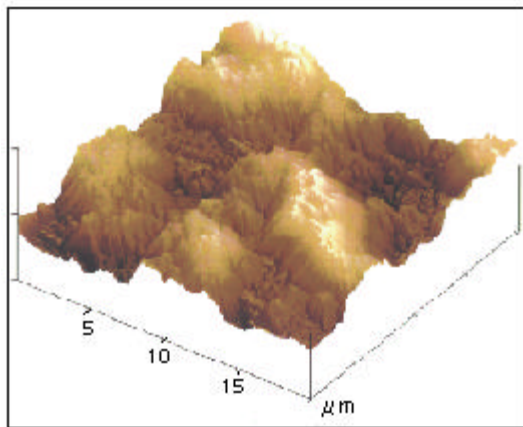


Figure 8. AFM Image of PTMSP

AFM was used to investigate surface properties of a poly(1-trimethylsilyl-1-propyne) (PTMSP) membrane. The surface of the membrane was scanned by AFM using tapping mode. The results of the AFM are shown in Figure 8. The figure illustrates the relatively large-scale order (5 micrometer) present in the material. This AFM image gives a rough estimate of the pore size. This structure takes the form of clearly observable peaks. This result indicates that other membranes could also be characterized in a similar way.

Conclusions:

Membrane distillation is a novel membrane process and is considered to be an exciting addition to the chemical engineering undergraduate curriculum. It provides an interesting contrast to the traditional distillation portion of the separations processes class. In addition to traditional chemical engineering concepts such as thermodynamics and heat and mass transport, non-traditional chemical engineering concepts such as polymer science and engineering, membrane processing and characterization methods are included.

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