Membrane distillation

Lecture 14

Introduction

- Membrane distillation was introduced commercially on a small scale during the 1980s, but it has had demonstrated no commercial success.

- Different names exist to identify the mass transport, in vapor phase, across porous hydrophobic partitions, e.g.: "**membrane distillation**", **"trans membrane distillation"** or "**thermo-pervaporation"**.

- The most suitable term is "membrane distillation", which cannot be confused with other membrane operations.

Introduction

- The main **reason** for choosing this name, regarding the nature of transport, is because **membrane distillation is a process in which the membrane itself has no influence on the vapor-liquid equilibrium of the liquids to be separated.**
- Membrane distillation (MD) is a thermally driven membrane process in which a **hydrophobic microporous membrane separates a heated feed solution and a cooled receiving phase.**
- The **temperature difference** across the membrane results in a **water vapour pressure gradient**, causing **water vapour transfer** through the pores **from high vapour pressure side to the low one.**

1. Advantages of membrane distillation

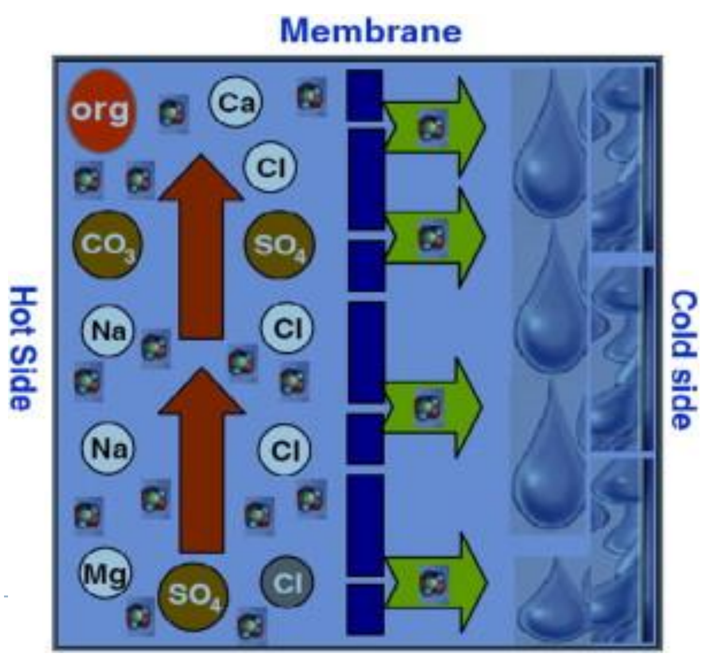
- **Relatively lower energy costs** as compared to distillation, reverse osmosis.
- A considerable **rejection of dissolved, non-volatile** species.
- Much **lower membrane fouling** as compared with microfiltration, ultrafiltration, and reverse osmosis.
- **Reduced vapour space** as compared to conventional distillation.
- **Lower operating pressure** than pressure-driven membrane processes.
- **Lower operating temperature** as compared with conventional evaporation.

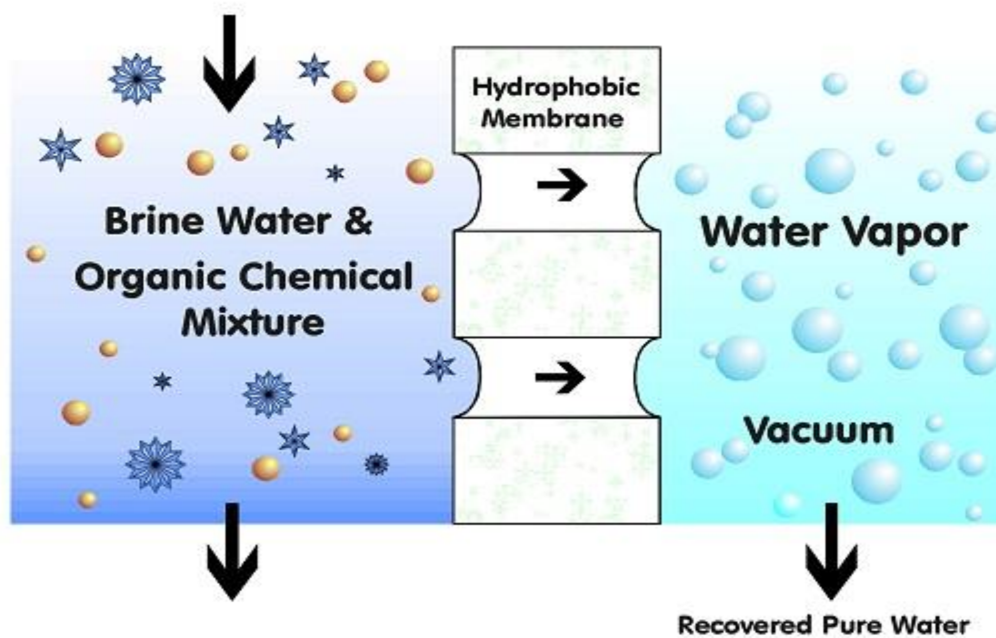
2. Process fundamentals

- As the name implies, the process combines both the use of **distillation and membranes**.
- Both technologies are based on the vapour-liquid equilibrium for separation and both of them require the **latent heat of evaporation** for the **phase change** from liquid to vapour which is achieved by **heating the feed solution.**
- The driving force for MD process is given by the vapour pressure gradient which is generated by a temperature difference across the membrane.

2. Process fundamentals

- The **<u>hydrophobic nature of the membrane prevents penetration of the pores by aqueous solutions.</u>**
- Therefore, liquid/vapour interfaces are formed at the entrances of each pore.

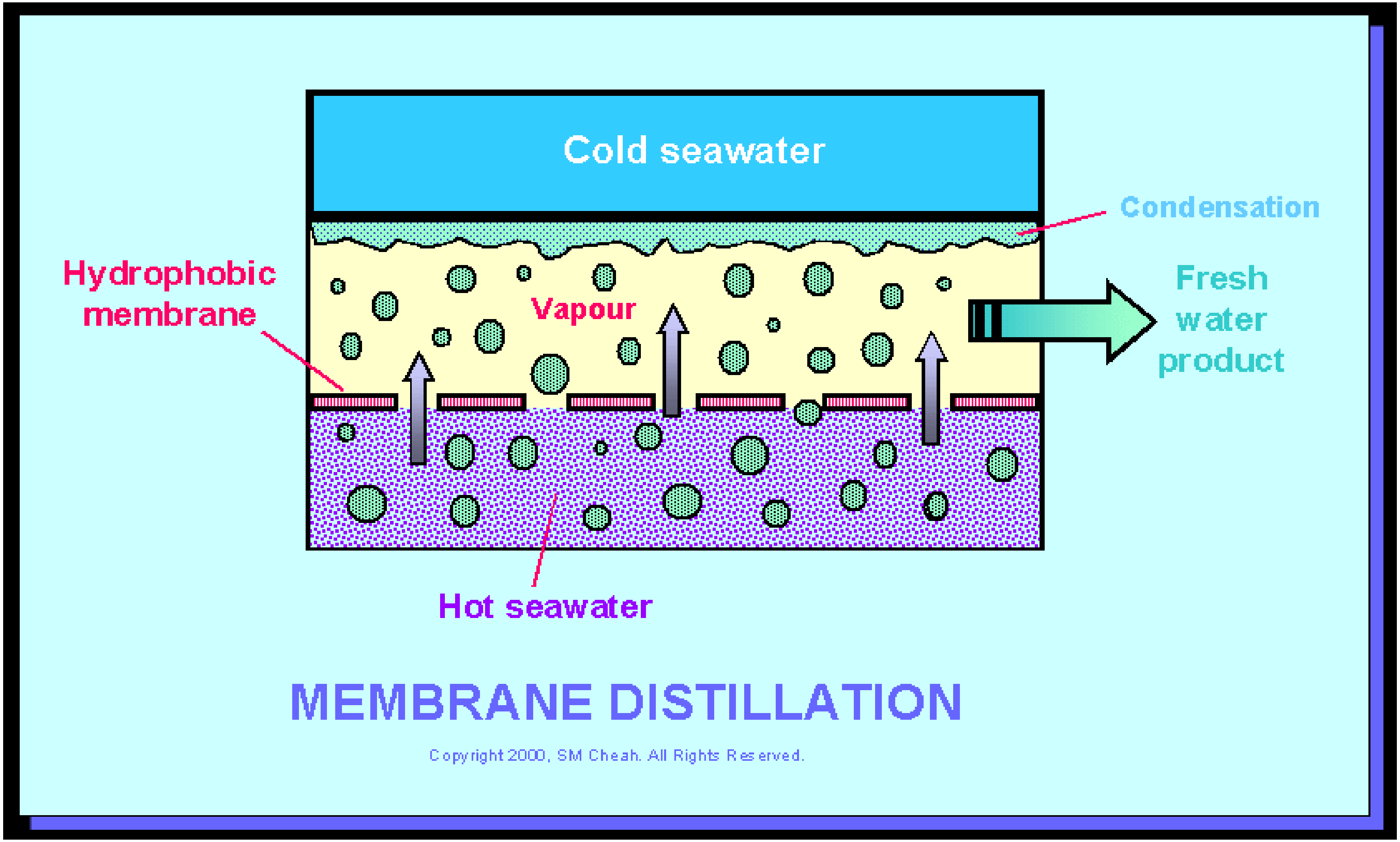




2. Process fundamentals

- The process of water transport through the membrane can be summarized in three steps:
- (1) **Formation of a vapour** gap at the hot feed solution–membrane interface;
- (2) **Transport of the vapour** phase through the microporous system;
- (3) **Condensation of the vapou**r at the cold side membrane–permeate solution interface.

2. Process fundamentals



3. MD configurations

- Various MD configurations can be used to drive flux.
- The difference among these configurations is **the way in which the vapour is condensed in the permeate side**:

1. Direct Contact Membrane Distillation (**DCMD**).
2. Air Gap Membrane Distillation (**AGMD**).
3. Sweeping Gas Membrane Distillation (**SGMD**).
4. Vacuum Membrane Distillation (**VMD**).

3.1. Direct Contact Membrane Distillation (DCMD)

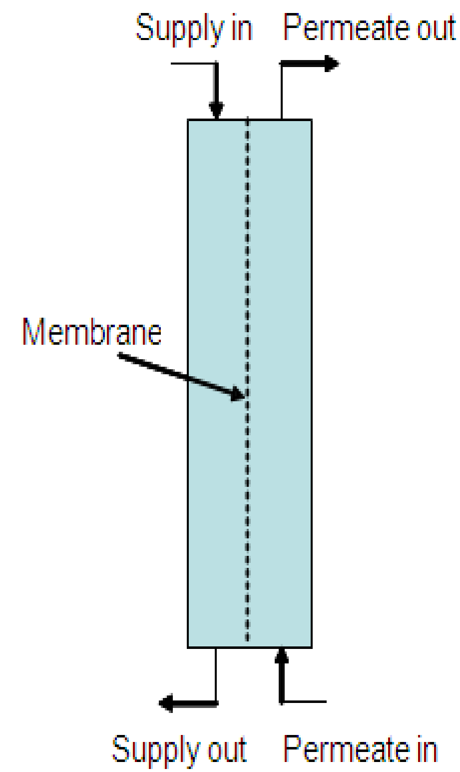
✓ In DCMD, water having lower temperature than liquid in feed side is used as **condensing fluid in permeate side.**

✓In this configuration, the liquid in both sides of the membrane is in **direct contact with the hydrophobic microporous membrane.**

✓DCMD is the **most commonly** used.

✓ However, direct contact of the membrane with the cooling side results in **heat losses** throughout the membrane.

✓Therefore, in DCMD the **thermal efficiency** which is defined as the fraction of heat energy used only for evaporation, is relatively **smaller** than the **other three configurations**.

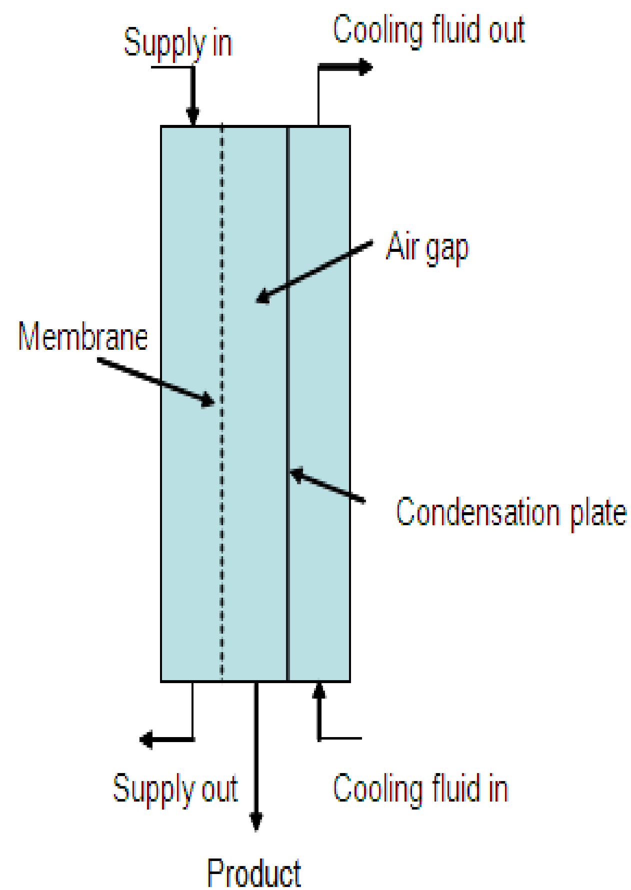


DCMD configuration

3.2. Air Gap Membrane Distillation (AGMD)

- In AGMD, water vapour is condensed on a **cold surface** that has been separated from the membrane via an **air gap**.

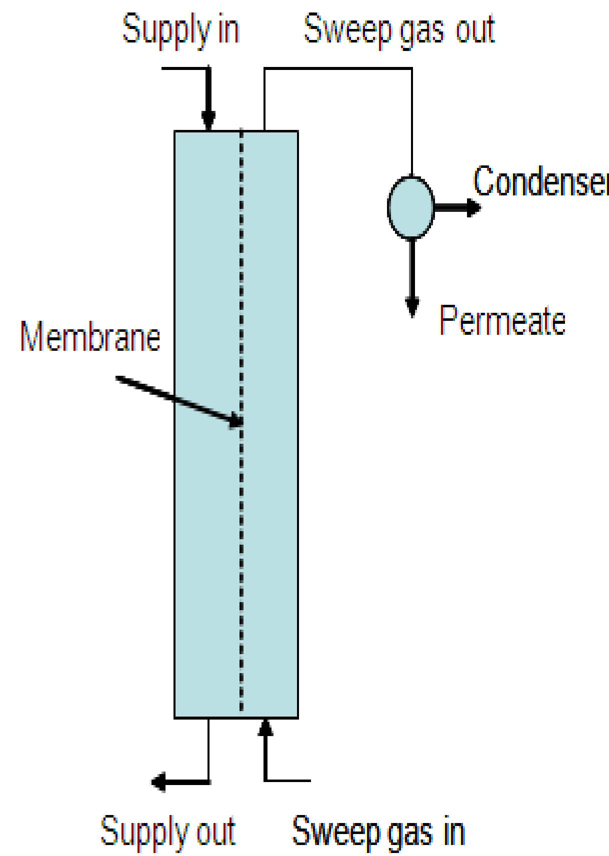
- The **heat losses are reduced** in this configuration by addition of a stagnant air gap between membrane and condensation surface.



AGMD configuration

3.3. Sweeping Gas Membrane Distillation (SGMD)

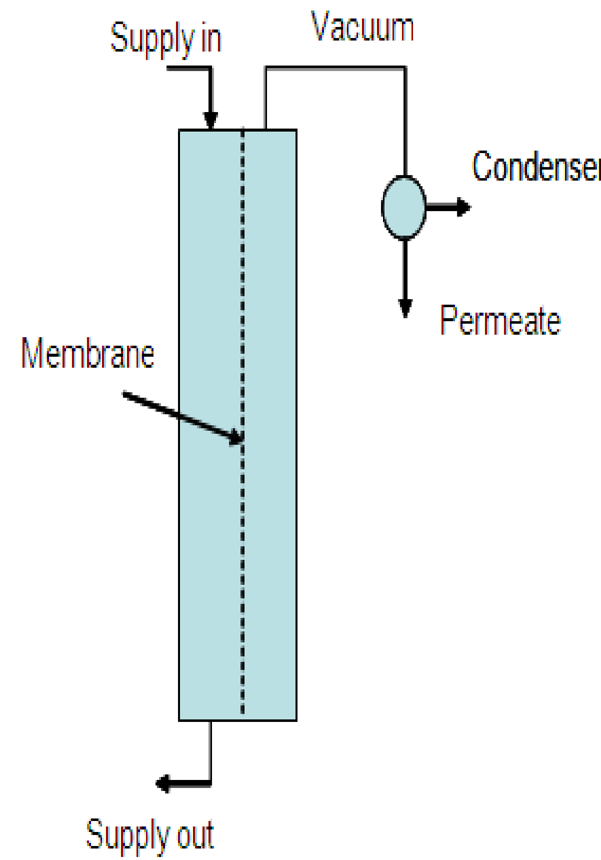
- In SGMD, a **cold inert gas** is used in permeate side for **sweeping and carrying** the vapour molecules to outside the membrane module where the condensation takes place.
- Despite the advantages of a relatively **low conductive heat loss** with a reduced mass transfer resistance, **due to the operational costs of the external condensation system**, SGMD is **the least** used configuration.



SGMD configuration

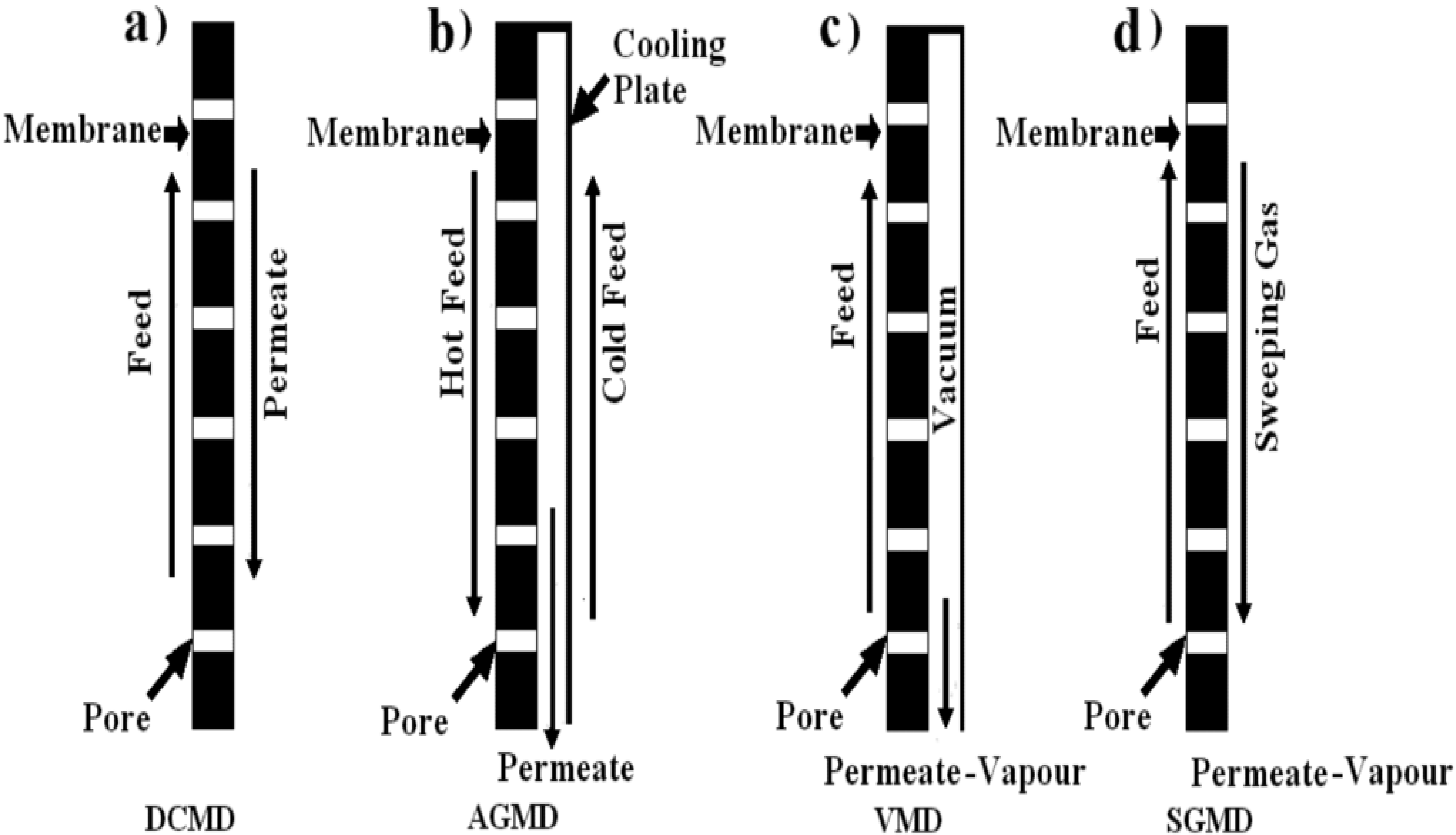
3.4. Vacuum Membrane Distillation (VMD)

- In VMD, the driving force is maintained by **applying vacuum** at the permeate side.
- The applied vacuum pressure is lower than the equilibrium vapour pressure.
- Therefore, condensation takes place outside of the membrane module.



VMD configuration

3. MD configurations



4. Membrane characteristics

- The membrane must be **porous**.
- The membrane must be **not wettable** by the liquids transported.
- **Only vapor** will be transported across membrane matrix.
- There isn't **capillary condensation** inside the pores of membrane.
- The driving force of this membrane operation is a **partial pressure gradient** in the vapor phase for each component.

4.1. Membrane materials

- A large variety of membranes including both **polymeric and inorganic membranes of hydrophobic nature** can be used in MD process; however polymeric membranes have attracted much more attention.
- Polytetrafluoroethylene (PTFE), polypropylene (PP) and polyvinylidenefluoride (PVDF) are the most commonly used polymeric membranes due to their low surface tension values.

4.1. Membrane materials

- Among them, **PTFE** membranes are the most hydrophobic ones showing **outstanding thermal stability** and **chemical resistance** properties.

- **PP** exhibits **excellent solvent resistant** properties and **high crystallinity**.

- **PVDF** membranes exhibit **good thermal and chemical resistances**

4.1. Membrane materials

- There are some **additional criteria** that should be taken into consideration for selection of the appropriate membrane for a given MD application such as
- Pore size,
- Tortuosity,
- Porosity,
- Membrane thickness, and
- Thermal conductivity.

4.1. Membrane materials

Membrane pore size:

- Membranes with pore sizes ranging from **10 nm to 1 μm** can be used in MD.
- The permeate **flux increases** with the **increase in pore size.**
- However, in order to **avoid wettability**, **small pore size** should be chosen.
- Thus, an **optimum value for pore size** has to be determined for each MD application depending on the type of the feed solution.

4.1. Membrane materials

- ***Membrane porosity:***
- Membrane porosity is determined as the **ratio between the volume of the pores and the total volume of the membrane.**
- Evaporation surface area increases with the increase in porosity level of the membrane, resulting in higher permeate fluxes.
- **Membrane porosity** also **affects the amount of heat loss by conduction.**
- In general, the **porosity** of the membranes used in MD operations lies in the range of **65%-85%.**

4.1. Membrane materials

- ***Pore tortuosity:***
- Tortuosity is the **average length of the pores** compared to membrane thickness.
- The membrane pores do not go straight across the membrane and the diffusing molecules must move along tortuous paths, leading a **decrease in MD flux**.
- Therefore, **permeate flux increases with the decrease in tortuosity.**
- This value is frequently used as a **correction factor** for prediction of membrane **flux**.
- In general, a **value of 2** is frequently assumed for tortuosity factor.

4.1. Membrane materials

- ***Membrane thickness:***
- Permeate **flux is inversely proportional to the membrane thickness in MD.**
- Therefore, membrane must be **as thin as** possible to achieve high permeate flux.
- Thickness also plays an important role in the amount of **conductive heat loss** though the membrane.
- **In order to reduce heat resistances, it should be as thick as possible** leading to a **conflict** with the requirement of higher permeate flux.
- Hence membrane thickness should be **optimized** in order to **obtain optimum permeate flux and heat efficiency.**
- The optimum thickness for MD has been estimated within the range of **30–60 μm**.

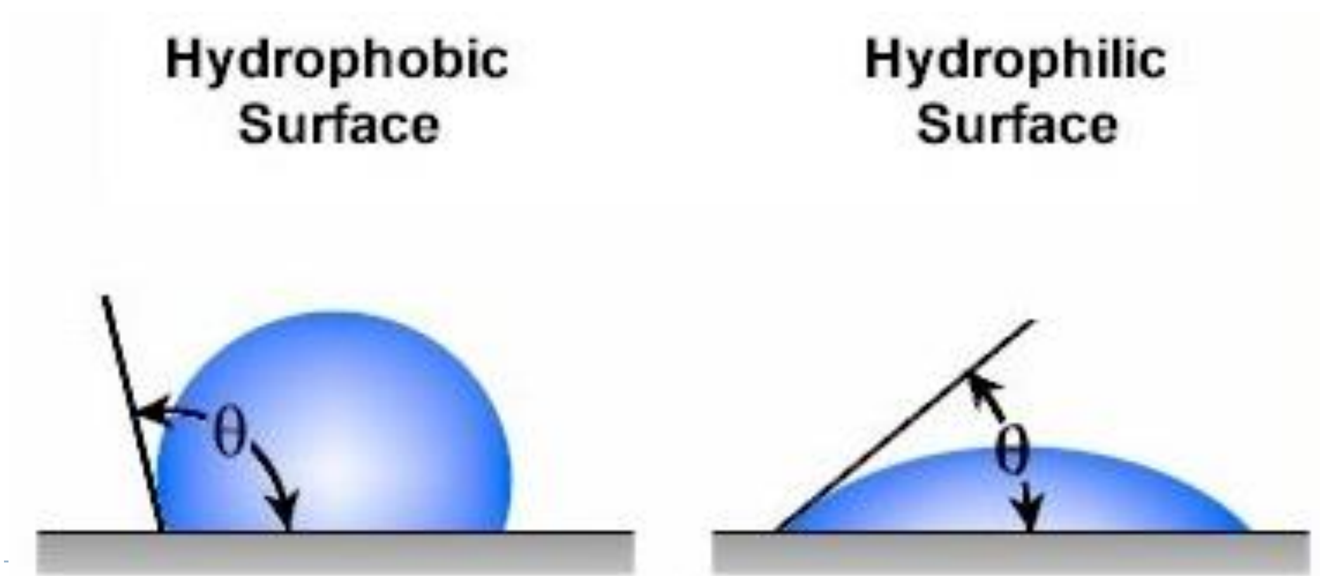
4.1. Membrane materials

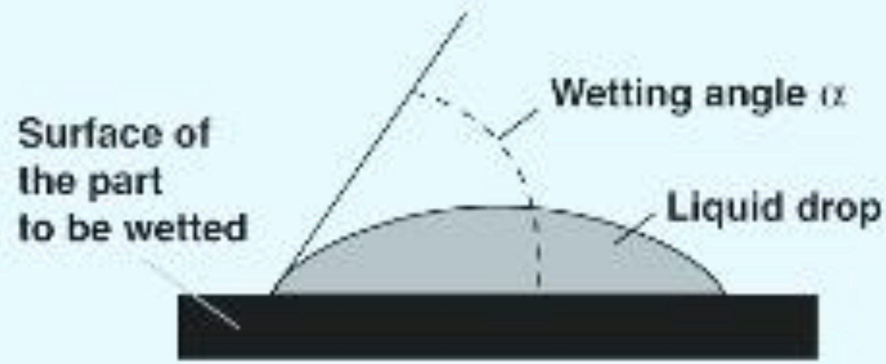
- ***Pore size distribution:***
- Pore size distribution affects uniformity of vapour permeation mechanism.
- In general, **uniform pore** size is preferable rather **than distributed pore size.**
- ***Thermal conductivity:***
- Thermal conductivity of the membrane **should be small** in order to **reduce the heat loss** through the membrane from feed to the permeate side.
- **Conductive heat loss is inversely proportional to the membrane thickness.**

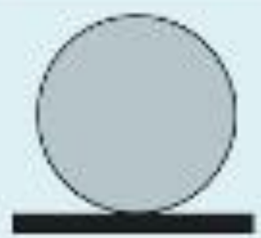
5. Contact angle

- The contact angle is a common measurement of the **hydrophobic or hydrophilic** behavior of a material.
- It provides information about relative wettability of membranes.
- The contact angle is determined as the **angle between the surface of the wetted solid and a line tangent to the curved surface of the drop** at the point of three-phase contact.
- The value of contact angle is **greater than 90°** when there is **low affinity between liquid and solid**; in case of water, the material is considered hydrophobic, and is **less than 90°** in the case of **high affinity**.
- Wetting occurs at 0°, when the liquid spreads onto the surface.
- **The wettability of a solid surface by a liquid decreases as the contact angle increases.**

5. Contact angle





α = 0°		Spreading
α < 90°		Good wetting
α = 90°		Incomplete wetting
α > 90°		Incomplete wetting
α > 180°		No wetting

6. Transport mechanisms

- **6.1. Theory of heat transfer:**
- Heat transfer in the MD includes three main steps:

1. Heat transfer through the **feed side boundary layer**.
2. Heat transfer through the **membrane.**
3. Heat transfer through the **permeate side boundary layer.**

6. Transport mechanisms

- ***Heat transfer through the feed side boundary layer:***
- Heat transfer from the feed solution to the membrane surface across the boundary layer (in the feed side of the membrane module) imposes a **resistance to mass transfer** since a large quantity of heat must be supplied to the surface of the membrane to vaporize the liquid.
- **The temperature at the membrane surface is lower than the corresponding value at the bulk phase.**
- This affects negatively the driving force for mass transfer. This phenomenon is called **temperature polarization**.
- Temperature polarization becomes more significant at higher feed temperatures.

6. Transport mechanisms

- ***Heat transfer through the membrane:***
- Heat transfer through the membrane appears as a combination of **latent heat of vaporization and conductive heat transfer** across both the membrane matrix and the gas filled membrane pores.

6. Transport mechanisms

- ***Heat transfer through the permeate side boundary layer:***
- Heat transfer from the membrane surface to the bulk permeate side across the boundary layer is also related with the **temperature polarization** phenomenon.
- **The temperature of membrane surface at the permeate side is higher than that of bulk permeate due to the temperature polarization effect.**

6. Transport mechanisms

- **6.2.Theory of mass transfer**
- Mass transfer in membrane distillation consists of three consecutive steps:

1. **Evaporation of water** at the **liquid/gas** interface on the membrane surface of the feed side.
2. **Water vapour transfer** through the membrane pores.
3. **Condensation of water vapour** at the **gas/liquid** interface on the membrane surface of the permeate side.

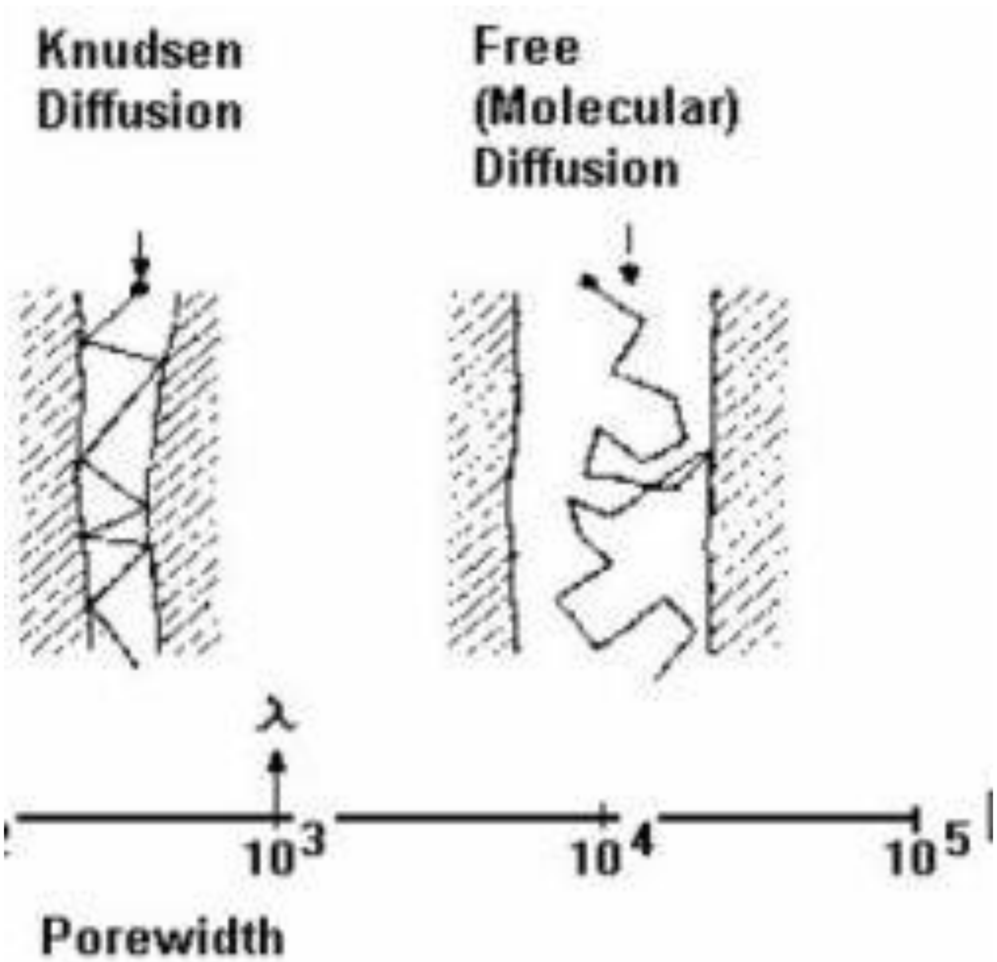
6. Transport mechanisms

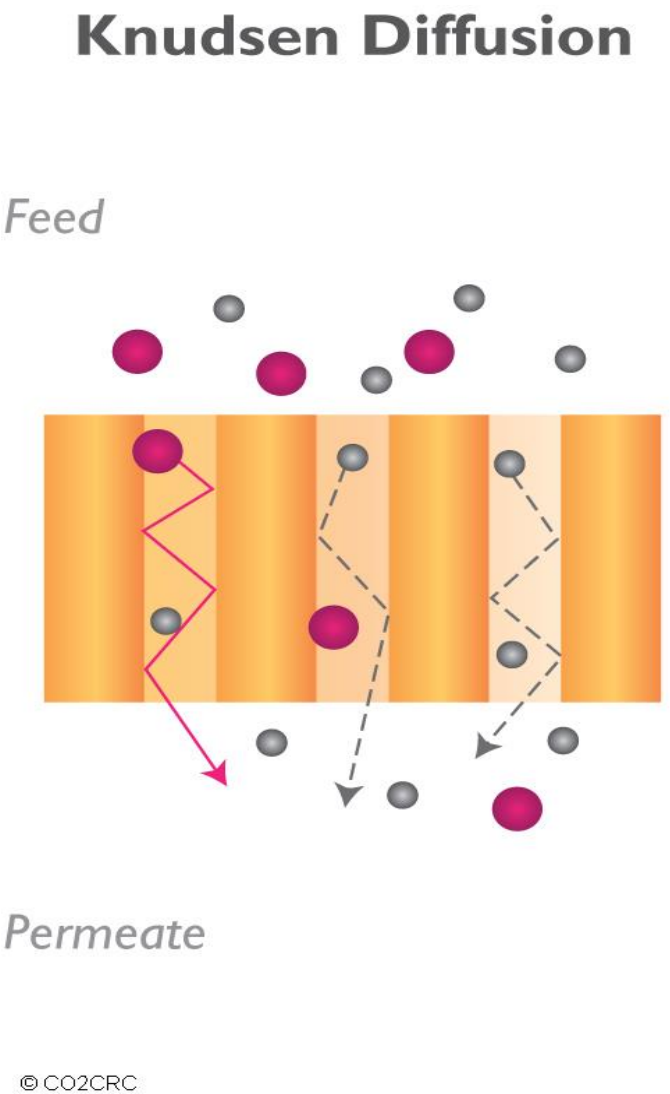
- ***Mass transfer trough feed side boundary layer:***
- In membrane distillation, **only water vapour** transport is allowed due to the **hydrophobic** character of the membrane.
- Therefore the concentration of solute(s) in feed solution becomes higher at the liquid/gas interface than that at the bulk feed as mass transfer proceeds.
- This phenomenon is called **concentration polarization** and results in **reduction of the flux** by depressing the driving force for water transport.

6. Transport mechanisms

- ***Mass transfer through the membrane pores:***
- The main mass transfer mechanisms through the membrane in MD are **Knudsen diffusion and molecular diffusion.**
- **Knudsen diffusion** model is responsible for mass transfer through the membrane pore if the pore size of the membrane is small, and hence, **the molecules tend to collide more frequently with the pore wall**.
- On the other hand, **when the pore size is relatively large**, the molecule–molecule collisions are more frequent and **molecular diffusion** is responsible for mass transfer through the membrane pores.

6. Transport mechanisms





7. Process parameters

- ***Feed concentration***
- **Permeate flux decreases with an increase in feed concentration.**
- This phenomenon can be attributed to the reduction of the driving force due to **decrease of the vapour pressure** of the feed solution and exponential **increase of viscosity** of the feed with **increasing concentration**.
- The contribution of **concentration polarization** effects is also known, however, this is very small in comparison with **temperature polarization effects**.

7. Process parameters

- ***Feed temperature:***
- There is an **exponential increase of the MD flux with the increase of the feed temperature.**
- As the driving force for membrane distillation is the difference in vapour pressure across the membrane, the **increase in temperature increases the vapour pressure of the feed solution**.
- Temperature polarization effect also increases with the increase in feed temperature.

7. Process parameters

- ***Feed flow rate & turbulence:***
- In MD, the increase in flow and/or turbulence rate of feed increases the permeate flux.
- The **shearing forces** generated at high flow rate and/or **turbulence reduces the boundary layer thickness and thus reduce polarization effects.**
- Therefore, the temperature and concentration at the liquid-vapour interface becomes closer to the corresponding values at the bulk feed solution .
- **Consequently, higher productivity can be achieved by the operation under a turbulent flow regime.**

7. Process parameters

- ***Permeate temperature***
- **The increase in permeate temperature** results in **lower MD flux** due to the **decrease** of the membrane **vapour pressure difference** as soon as the feed temperature kept constant.
- However, the temperature of cold water on the permeate side has smaller effect on the flux than that of the feed solution for the same temperature difference.
- This is because the vapour pressure increases exponentially with feed temperature.

7. Process parameters

- ***Permeate flow rate***
- The **increase** in permeate flow and/or turbulence rate **reduces the temperature polarization effect**.
- Consequently, the temperature at the gas/liquid interface approaches to the bulk temperature at the permeate side.
- This will tend to **increase driving force** across the membrane; resulting an increase in MD flux.
- It is important to note that as the permeate used in the MD is distilled water.

Comparison between MD and RO

	MD	RO
Driving force	Temperature difference	Pressure difference
Membrane pore size	Microporous membranes Very large pore diameters (0.1-5µm) and may reach 500µm	Dense membranes of small pore size
Energy	Do not consume much energy	Do not consume much energy
Concentration level	Concentrations up to saturation can be achieved	Concentrations are limited due to high osmotic pressures
Nature of membrane	Symmetric, porous and hydrophobic	Asymmetric and hydrophilic
uses	In demineralization purposes	In demineralization purposes

Questions

- **Answer with Yes or No, and Correct the false ones:**

1. MD is a thermally driven membrane process in which a hydrophilic microporous membrane separates a heated feed solution and a cooled receiving phase.
2. MD is much higher membrane fouling as compared with microfiltration, ultrafiltration, and reverse osmosis.
3. In DCMD the thermal efficiency, is relatively higher than the other three configurations.
4. In SGMD, a hot inert gas is used in permeate side for sweeping and carrying the vapour molecules to outside the membrane module where the condensation takes place.

Question

5. In MD, Only vapor will be transported across membrane matrix.

6. PVDF membranes exhibit bad thermal and chemical resistances.

7. The permeate flux increases with the increase in pore size.

8. Membrane porosity does not affects the amount of heat loss by conduction.

9. Permeate flux decreases with the decrease in tortuosity.

10. Permeate flux is directly proportional to the membrane thickness in MD.

Questions

- **Answer the following questions:**

1. The contact angle is a common measurement of the hydrophobic or hydrophilic behavior of a material. Discuss this statement illustrating your answer with drawings.

2. Compare between RO and MD from the different aspects.