CHAPTER III

THEORY

3.1 Membrane

Nowadays, many membranes types are produced for use in many industries. But these membranes have only 2 structures: symmetric and asymmetric. The difference between symmetric and asymmetric membranes is shown in Figure 3.1.

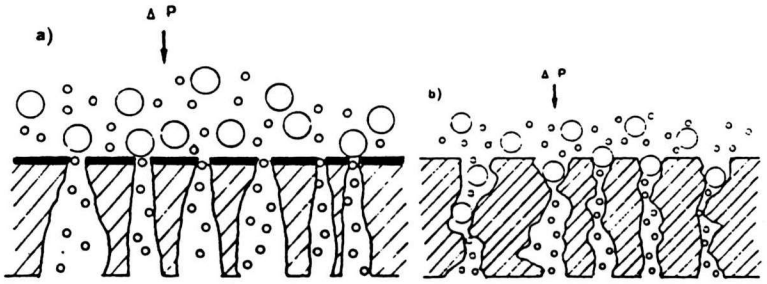


Figure 3.1 Schematic Representation of an Asymmetric Membrane (a) and a Symmetric Membrane (b) [14]

The top of an asymmetric membrane contains only relatively small pores only whereas in a symmetric membrane, these small pores are distributed randomly over the membrane cross section. The advantages of symmetric

membranes are that higher fluxes can be obtained and that membrane fouling is restricted to the top of the membrane.

3.1.1 Types of Membrane

Membranes which use in industrial processes can be classified into 3 types:

1 *Polymeric Membrane* is made from polymer: such as Polyvinyl Alcohol, Polypropylene, Polysulfone, Cellulose Acetate, and etc. This type of membranes is cheaper than the others, but it can be used only in the low temperature range and not be stable with chemical substances.

2 *Metallic Membrane* is made from metal fiber: such as stainless steel. The advantages of this membrane are its strength, and durability.

3 *Ceramic Membrane* is made from ceramic substances: such as Alumina, Silica, Titania, Zirconia, Silica Carbide, and etc. Ceramic membrane is of more favorable properties than polymeric membrane.

3.1.2 Properties of Ceramic Membrane [14]

The followings are favorable properties of ceramic membrane show some advantage over polymeric membrane.

1 *Chemical stability*

Especially organic solvents, chlorine and extremes of pH often pose limits to the applicability of polymeric membrane, whereas no problems are expected for ceramic membrane.

2 *Applicability in high temperature separation process*

Ceramic membrane is stable at very high temperatures, thus allowing more efficient sterilization of process equipment than polymeric membrane.

3 *Stability to microbiological degradation.*

Ceramic membrane is generally quite resistant to microbial or biological degradation while certain polymeric membrane (like cellulose acetate) suffers from this.

4 *Mechanical stability*

Polymeric membrane compacts under high pressure, leading to lower permeabilities. This is expected to play no significant role for ceramic membrane.

5 *Cleaning conditions*

Better cleaning conditions can be chosen for ceramic membrane: such as steaming.

While these characteristics seem to favor ceramic membrane, it has not been used to any significant extent in commercial applications because of the

difficulty in producing crack-free membrane having ultrafine pores and narrow pore size distributions.

3.2 Membrane Processing

There are many interesting membrane processes which can be classified by driving force of preferentially permeating component: such as liquid membrane which concentration difference is a driving force. However, we are interested in "pressure-driven processes".

1 *Reverse Osmosis* always use the membranes which have the range of pore sizes from 0.0001 to 0.01 μm that are permeable to water but not to salts and most larger molecular-weight species. The term "reverse osmosis" refers to the fact that applied pressures must exceed the osmotic pressure of the feed before water is forced through the membrane, this pressure can be up to 80 bars.

2 *Ultrafiltration* is a process consist of an asymmetric membrane with pore sizes in the range of 0.001 to 0.1 μm and are capable of retaining species in the molecular weight range of 300 to 500,000 daltons. Ultrafiltration processes operate up to 10 bars and separate or concentrate the macromolecular solutions: such as protein, enzyme, polysaccharide, and etc.

3 *Microfiltration* is an extension of Ultrafiltration, but the membranes have a large pore size in the range of 0.02 to 10 μm. These sizes can separate

the suspensions: such as cells, bacteria, yeast, and etc. The pressure which drives the microfiltration process is up to 5 bars.

3.3 Preparation of Membrane Over Support

There are two methods which can produce thin porous membrane: one is a suspended powder technique and the other is sol-gel technique.

For suspended powder technique, the size of the pores is dictated by the size of the particles in the sol from which the membrane is produced. Hence, if one wishes to produce membranes whose pores are characterized by very small diameters, it is necessary to employ a sol which contains very small particles. Smaller particles produce smaller pores. This technique is difficult to produce very small pores, so none of these membranes is currently available commercially. [15]

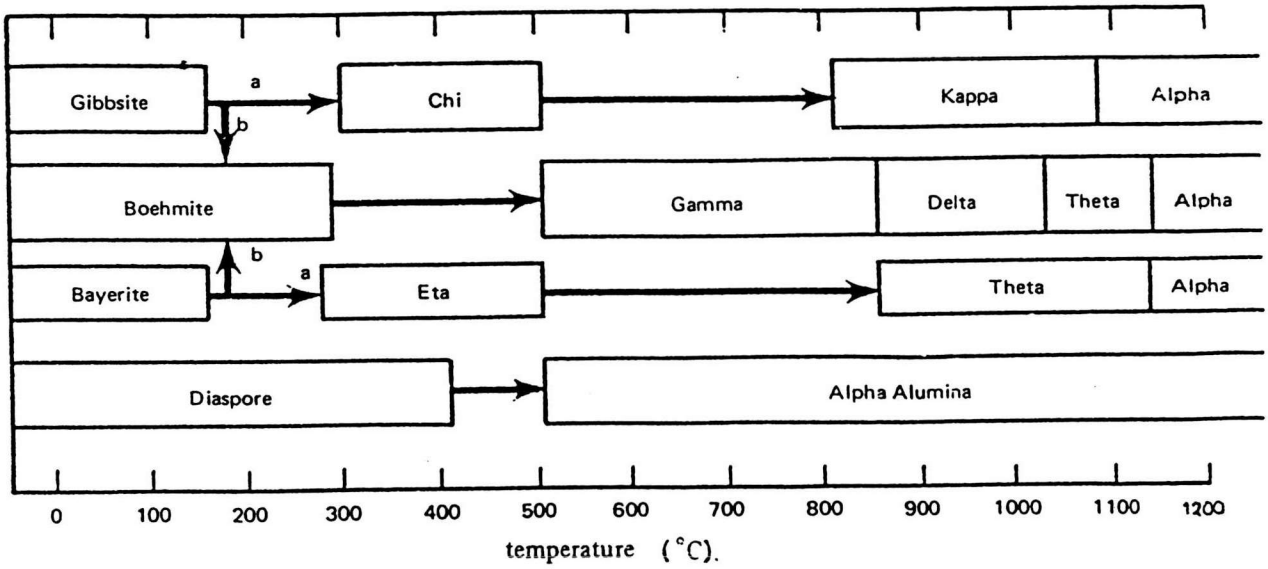
Sol-gel technique is interesting because it can be obtained at a relatively low sintering temperature, the particle size is very homogeneous and thus, the cut-off is very narrow.

So, the best membrane preparation is obtained by coating the sol of boehmite, prepared from sol-gel method, on the support. After heat treatment,

boehmite gel which is converted to γ-Al_2O_3 at 300°C will be used as a membrane.

3.3.1 Boehmite [16]

Xerogels are composed of boehmite (γ-AlOOH) or pseudo-boehmite which is a less crystallized boehmite containing 1.7 H_2O/Al. Both kinds of boehmites can be transformed by heating which causes dehydration and rearrangement of their molecules to α-Al_2O_3 at 1200 °C as shown in Figure 3.2.



Note: Enclosed area indicates range of stability. Open area indicates range of transition. Path b is favored by moisture, alkalinity, and coarse particle size (100 microns); path a by fine crystal size (below 10 microns).

Figure 3.2 Dehydration Sequence of Alumina Hydrates in Air [17]

In boehmite, the oxygens are arranged in a distorted octahedral configuration around aluminum and are organized in parallel layers linked by hydrogen bonds, each layer of octahedral comprising two sublayers as shown in Figure 3.3.

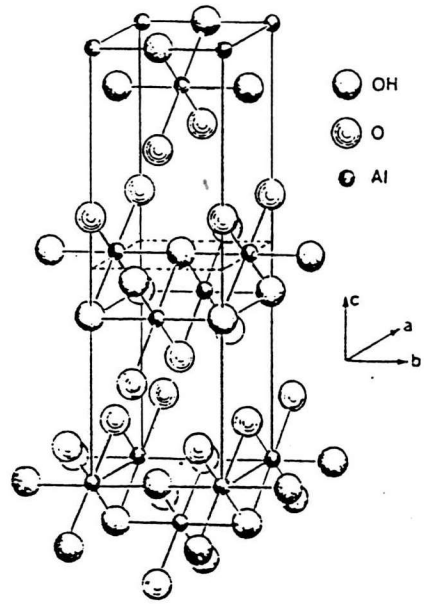


Figure 3.3 Structure of Boehmite [18]

3.3.2 Synthesis of Sols

Sol-gel can be classified into two kinds of techniques, polymerization of molecular units (PMU) and destabilization of colloidal solutions (DCS) (Figure 3.4).

The DCS process uses peptization of metal alkoxides with an electrolyte that beginning with a solution of a metal alkoxide dissolved in alcohol. The

alkoxide is then hydrolyzed with water. This hydrolysis reaction is followed by a condensation reaction. The relative rates of the hydrolysis and condensation reactions will determine the size of the particles which are produced. If the hydrolysis reaction is fast relative to the condensation reaction, then the final particle size will be large. On the other hand, when the rate of the hydrolysis reaction is slow relative to that of the condensation reaction, the final particles are small. [15]

The PMU process is based on controlled hydrolysis of alkoxide and condensation-polymerization reactions. In polymeric system, a true oxide network is formed by chemical bonds in the solution. Hydrolysis and polymerization reactions are very important for the properties of the gel. Water molecules can be added directly (drop by drop as a mixture of water and alcohol) or produced in situ by an esterification reaction. Hydrolysis reaction must be controlled to avoid precipitation of hydrous metal oxide.

These two techniques are different in the first step, a physical gel of DCS is formed by peptization reaction but a chemical gel of PMU results from polymerization and controlled hydrolysis reactions. [19]

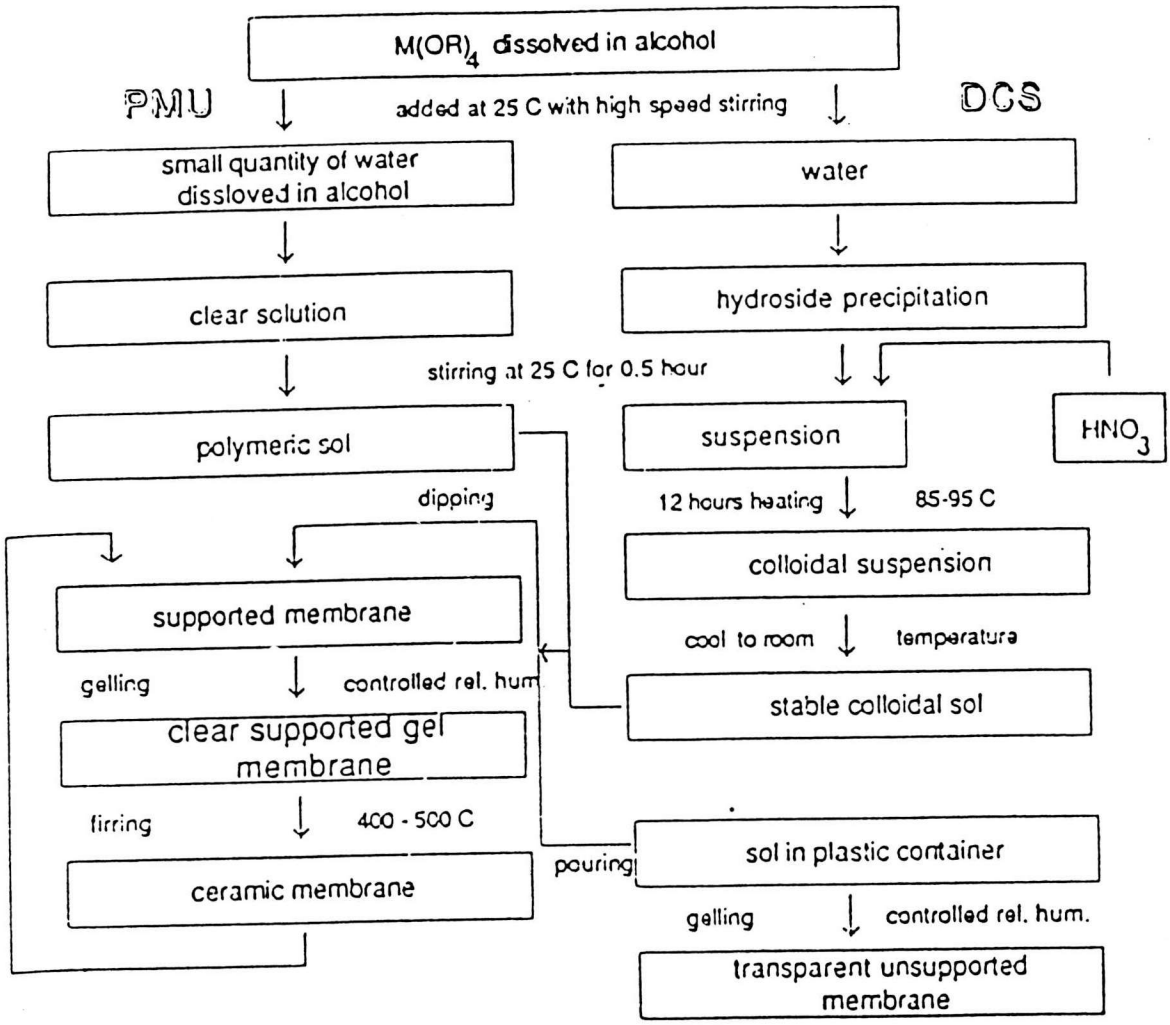


Figure 3.4 Preparation Scheme for DCS and PMU

3.3.3 Placement of Sols [15]

The placement of sols on support is the technique to form a membrane with the mechanical strength. There are many methods which can place the sol on the support, as follows:

1. *Slip casting*

Slip casting involves placing a dry support into sol. The suspension is then absorbed into the pores of the support by the capillary forces. As the suspension is drawn into the support, the concentration of the sol particles at the surface of the support increases. When this concentration increases to a sufficient degree, the sol then transforms into a porous gel layer. In this process, it is essential to control the viscosity of sol. If the viscosity is greater than 1 poise, the thickness of the cast layer will vary from the top to the bottom of the support. If it is less than 0.1 poise, the sol particles is absorbed into the pores along with the solvent. These membranes are frequently defected by cracking while sintering, so they must be repaired by repeated casting.

2. *Filtration*

In this method, a pressure difference is imposed across the support material. As in the slip casting process, the sol particles are largely excluded from entering the support. When the concentration of sol particles becomes sufficiently large, a gel layer is formed. The advantage of this method is that the forces arising from the pressure applied to bring the sol particles into contact with the support material are larger than that used in slip casting.

3. *Coating*

In this approach, the support is dipped into solvent before into sol. This technique effectively inhibits capillary action. Hence, the sol is retained on the external surface of the support by viscous forces and surface tension effects. The support is then removed from the sol at constant rate. If the removable rate

is constant, the thickness of the fluid adhering to the support can be related to the velocity of removal, the radius of the cylindrical, the viscosity and surface tension of fluid, and the gravitation constant. By appropriate choice of the experimental conditions, one can increase or decrease membrane thickness.

3.4 Influential Factors of Ceramic Membrane [19]

1. *Addition of acid or base*

Complete hydrolysis of metal alkoxides leads to precipitation of metal hydroxides or hydrous metal oxides, so it is necessary to add a quantity of acid or base for peptization the precipitate and for obtaining a colloidal solution. The peptization phenomenon is based on electrostatic interactions. Repulsion which depends on size and concentration of particles is caused by the electric double layer around the colloidal particles. We can determine the stability range of colloidal particles by measuring their mobility in an electric field as a function of pH and electrolyte concentration. If the pH value is near the zero point charge (ZPC), the sol is not very stable, then the gel is not very dense.

2. *Addition of organic binders*

The addition of a polymer has an important influence, because it avoids particle aggregation, permits adjusting the sol viscosity, increases the strength of the unfired material and prevents crack formation. It burns gradually without leaving ashes or tar. Generally, 2-5% of binders are sufficient to avoid cracks in the gel layer.

3. *Sol viscosity*

The sol containing is obtained by coating the sol on the support. The solvent is absorbed by the porous structure of the microfiltration support. The rate of solvent absorption is a function of sol viscosity (sol viscosity should be 0.1-1 Poise). If the viscosity is more than 1 Poise, the layer thickness is not regular from the bottom to the top of the support. If viscosity is less than 0.1 Poise, all the sol will be absorbed by the support.

4. *Coating time*

The gel layer thickness is the function of rheologic parameters of the sol and of absorption by colloidal particles forming the first layer; the coating time being the only varying parameter, as the equation:

$$x = Kt^{1/2} \qquad (3.1)$$

where x is the thickness of membrane ; μm

t is the coating time ; sec

K is a constant

3.5 Sol-Gel Theory [16]

Sol-gel processing is a process which produces ceramic membrane. Starting from preparation a colloidal suspension of solid particles (~1-1000 nm) in a liquid which is called *Sol*. So the processes of colloid preparation consist of

a metal or metalloid element surrounded by various ligands which are necessary for gel formation. The common precursors for metal oxide include inorganic (containing no carbon) salts and organic compounds. When the sol loses its fluidity, many cluster will be present in the sol phase until the clusters collide, then link forms between the clusters to produce a single giant cluster that is called a *Gel*. The dried gel must be calcined to obtain ceramic membrane.

In sol-gel process, metal alkoxides react with water-forming oxide and hydroxide, as follow:

$$M(OR)_v + vH_2O \Rightarrow M(OH)_v + vROH \qquad (3.2)$$

$$M(OH)_v \Rightarrow MO_{v/2} + v/2H_2O \qquad (3.3)$$

where M is a metal with valence v

R is an alkyl C_nH_{2n+1}

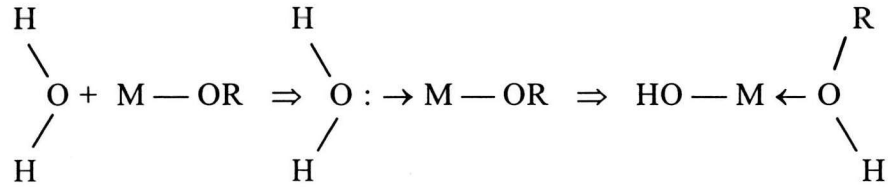
(n often used for valence)

Equation (3.2) and (3.3) are overly simplified and there are two simultaneous reactions in these processes, as a following:

3.5.1 Hydrolysis Reaction

$$HOH + \equiv M\text{-}OR \Rightarrow \equiv M\text{-}OH + ROH \qquad (3.4)$$

Mechanism of Hydrolysis Reaction



$$\Rightarrow \quad M - OH + ROH$$

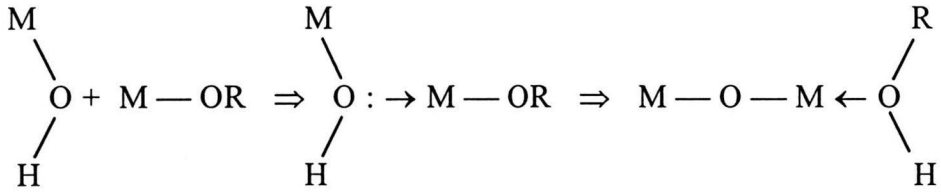
3.5.2 *Condensation Reaction*

$$\equiv M\text{-}OH + \equiv M\text{-}OR \Rightarrow \equiv M\text{-}O\text{-}M\equiv + ROH \qquad (3.5)$$

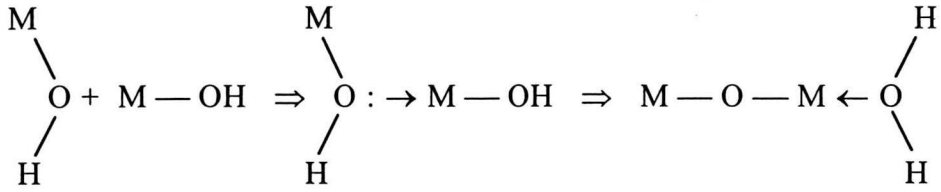
$$\equiv M\text{-}OH + \equiv M\text{-}OH \Rightarrow \equiv M\text{-}O\text{-}M\equiv + HOH \qquad (3.6)$$

where M has a valence of four

Mechanism of Condensation Reaction



$$\Rightarrow \quad M - O - M + ROH$$



$$\Rightarrow \quad M - O - M + H_2O$$

Both reactions occur between "OR" and "OH" groups by nucleophilic substitution (S_N) mechanisms involving nucleophilic addition (A_N) followed by proton transfer from the attacking molecule to an alkoxide ($-OC_nH_{2n+1}$) or hydroxo-ligand (-OH) within the transition state and removal of the protonated species as either alcohol or water.

Hydrolysis and condensation reactions of metal alkoxides are affected by three external parameters. The parameters affecting the kinetics of these reactions are the water/alkoxide ratio, which determines the degree of hydrolysis and nature of initial species formed, dilution of the reacting species with a neutral solvent which affects the reaction rates and ensures uniformity of the hydrolysis and condensation throughout the system, and temperature. [4]

3.6 Enzymes [20],[21]

Enzymes have been used since early human history without knowledge of what they were or how they worked. They were used for such things as making sweets from starch, clotting milk to make cheese, and brewing soy sauce. Enzymes have been utilized commercially since the 1890s, when fungal cell extracts were first added to brewing vats to facilitate the breakdown of starch into sugar (Eveleigh, 1981). The fungal amylase takadiastase was employed as a digestive aid in the United States as early as 1894.

Because enzymes are biological catalysts that are protein molecules in nature, they are produced by living cells and are absolutely essential as catalysts in biochemical reactions. Almost every reaction in a cell requires the presence of a specific enzyme. A major function of enzymes in a living system is to catalyze the making and breaking of chemical bonds. Therefore, like any other catalysts, they increase the rate of reaction without themselves undergoing permanent chemical changes.

The catalytic ability of enzymes is due to its particular protein structure. A specific chemical reaction is catalyzed at a small portion of the surface of an enzyme, which is known as the active site. Some physical and chemical interactions occur at this site to catalyze a certain chemical reaction for a certain enzyme.

Enzyme reactions are different from chemical reactions, as follows:

1. An enzyme catalyst is highly specific, and catalyzes only one or a small number of chemical reactions. A great variety of enzymes exist, which can catalyze a very wide range of reactions.

2. The rate of an enzyme-catalyzed reaction is usually much faster than that of the same reaction when directed by nonbiological catalysts. Only a small amount of enzyme is required to produce a desired effect.

3. The reaction conditions (temperature, pressure, pH, and so on) for the enzyme reactions are very mild.

4. Enzymes are comparatively sensitive or unstable molecules and require care in their use.

Nowadays, there are production and employment of enzymes in many industries. These enzymes are produced by plant, animal, or microorganism but an interesting source of enzymes is microorganism, since it can produce high amount of enzymes due to its rapid growth. These industrial enzymes can be classified into 4 categories:

1. *Digestive Carbohydrate Enzymes* are used for digestion from a large molecule to small and sugar transformation: such as amylase, invertase, gluco isomerase, melibiase, glucose oxidase, β-galactosidase, and etc.

2. *Digestive Protein Enzymes* are used for partial protein digestion or non-complete digestion for increase dissolution. These enzymes are proteinase, renin, and etc.

3. *Enzymes which are used to improve product quality* : such as lipase, pectinase, naringinase, and etc.

4. *Medical and the other enzymes.*

3.7 α-Amylase Enzyme [21]

α-amylase is an extracellular enzyme which hydrolyze starch molecules. This enzyme is produced by animal, plant, and microorganism. Sources of α-amylase enzyme are shown in Table 3.1:

Table 3.1 Sources of α-Amylase Enzyme from Natural

Origin		Main Products from Starch
Plant	Malt	Maltose
Animal	Saliva	Dextrin , Maltose
	Pancreas	Dextrin , Maltose
Microorganism	B.subtilis	Glucose, Maltose, Dextrin
	B.stearothermophilus	Dextrin, Maltose
	Rhizopus sp.	Glucose
	A.oryzae	Glucose
	Endomycopsis sp.	Glucose
	Cospora sp.	Dextrin

3.7.1 Types and Properties of amylase enzymes

amylase enzymes can be classified into 2 categories (see Figure 3.5) by their actions on polysaccharide:

1. *Endoamylase* acts randomly on the α-1,4-glucosidic linkage bond. In non-complete action, glucose, maltose, and dextrin are produced. On other hand,

maltose and glucose are produced in the complete action. This enzyme is "α-amylase or amylo (1-4) dextrinase".

2. *Exoamylase* attacks the polysaccharides only from the non-reducing terminal bond. One type cleaves each bond of α-1,4 and α-1,6 glycosidic linkage to produce solely glucose. This enzyme is called "glucoamylase or γ-amylase or amylo (1-4,1-6) glucosidase". Another type breaks every alternate bond of α-1,4 glycosidic linkage to produce maltose. This enzyme is "β-amylase or amylo (1-4) maltosidase". Both of these enzymes are incapable of acting at branching points, α-D (1-6) linkage bond hence high molecular weight limit dextrins are produced.

Furthermore, there is any amylase which can digest α-1,6 glycosidic linkage bond. It is "isoamylase".

After an enzymatic action, the characteristic starch have been changed: such as the decrease in iodine color reaction showing dextrinization of starch, the increase in reducing sugar as a result of saccharification of starch, and the viscosity reduction resulting from starch liquefaction. So an ability of starch action of amylase enzymes can be examined by these properties.

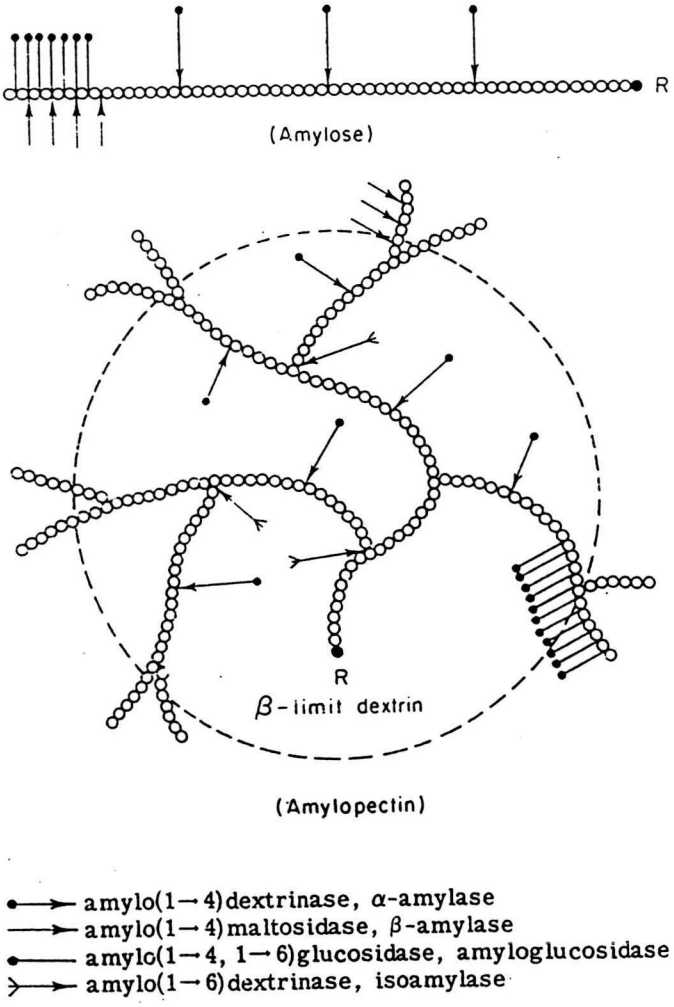


Figure 3.5 Reaction Mechanisms of Various Amylases

3.7.2 The Production of α-Amylase Enzyme [22]

1. *Submerged Culture* is used extensively for the production of bacterial amylase and fungal glucoamylase. Usually, large amount of bacterial or fungal culture were seeded in a large fermentor. A medium is sterilized at 110-115 °C for 15 to 30 minutes. The fermentor is inoculated with 3 to 5 % of seed culture. The rate of aeration and agitation are controlled throughout the fermentation. This culture takes a short period of time to increase product, and it is easy to control various conditions. However, it is possible to massively contaminate the system, and therefore decreases efficient production.

2. *Surface Culture* has many adaptations of the original process, but basically it is as follows: moist wheat bran or other suitable substrate is steamed in a pressurized vessel for a period time, after which it is cooled. When cool, the substrate is inoculated with a heavy suspension of spores. The inoculated substrate is then incubated under controlled conditions of temperature and humidity. After a sufficient period of time the moldy bran (koji) is harvested. There are a number of this culture that make use of this basic scheme in rather ingenious ways: such as Drum method, and Tray-Chamber method. This culture can produce various enzymes, but it requires more labor and massive contamination is easier than submerged culture.

3.7.3 Concentration and Purification of α-Amylase Enzyme [23]

After enzyme production, the crude enzymes will be concentrated and purificated in order to obtain the high qualitative enzyme. These operations can be classified into 5 categories:

1 *Precipitation* can separate by addition the chemical substance: such as inorganic salt, organic solvent, and high molecular weight polymer into the crude enzyme solution. Enzyme will be precipitated after substance addition, and the free enzyme solution will be discarded after centrifugation.

2. *Chromatography* use the different properties: such as charge, affinity, solution property, or molecular size for separation. Chromatography can be classified into 2 parts: stationary phase and mobile phase. The separation could be achieved by passing the mobile phase to the stationary phase to elute the substance to be separated from the stationary phase.

3 *Crystallization* is an operation which use the difference of solution property in the solvent to obtain pure dry enzyme. The pure enzyme can be obtained by adding the reduced solution substance, crystallizing, and separating the pure enzyme crystal from the solution. Generally, crystallization is always chosen as the last unit operation of the whole purification process because it gives high enzyme purity. However, crystallization can't be employed to separate some enzymes which are not crystalizable.

4 *Drying* use hot or cool air with pressure in order to evaporate water or solvent from solution, and obtain dry or concentrate product.

5 *Ultrafiltration* is the filtration operation which based on molecular size. In this operation, pressure which is a driving force for separating crude enzymes pressure is exerted on a solution in contact with the membrane. Substances smaller than the pore size of the filter are driven through while larger are retained.

In this study, we use ultrafiltration for separate α-amylase enzyme from the solution because ultrafiltration can be operated in the low temperature range instead of drying or evaporation which are high temperature operations. Thus, separated enzyme will not be denatured. Advantages of using ultrafiltration are: low energy requirement, no chemical substance needed, easy and clean to operate, and easy to protect the enzyme solution from bacteria by addition stabilizer substance into solution before or after filtration for maintain an enzyme stability.

3.7.4 Industrial Applications of α-Amylase Enzyme [22]

1 *Production of Starch Syrups*

When one attempts to produce a starch syrup with a DE (dextrose equivalent) above 50 by straight acid conversion, the resulting syrup has a bitter taste and objectionable color. Since the introduction of α-amylase enzyme, it is

possible to prepare syrups having DE values well above 60. This is accomplished by a partial acid conversion followed by enzyme treatment.

2 *Use in Baby Food*

α-amylase enzyme finds extensive use in the preparation of dried baby foods and cereal products. The cereal to be treated is heated to a temperature of 150-160 °F and α-amylase enzyme added. The sugars produced during enzyme treatment help impart a malt syrup flavor to the product and also help produce a smoother sheet on the drying rolls. This is a distinct advantage, especially with the barley- and rice-type baby foods.

3 *Desizing of Textiles*

The process of weaving cloth tends to break the threads making up the warps. In order to give greater tensile strength to the yarn, the individual threads are coated with gelatinized starch. In the final stage, woven cloth must be treated by α-amylase enzyme to remove starch from fibers.

4 *Clarification of Fruit Juices for Jelly Manufacture*

Jellies made from juices are hazy in appearance because of the high starch content. Treating the juice with α-amylase and filtering produces a clear juice suitable for making a sparkling jelly.

5 *Production of Chocolate Syrup*

Chocolate syrup made by treating cocoa slurries with α-amylase enzyme, produces a product which does not tend to layer in storage, eliminates appreciable stiffening or setback, and gives rise to a product with an improved flavor and solubility in milk.

6 Miscellaneous Uses

α-amylase enzyme also finds its use in brewing in place of malt, in the preparation of grain alcohol, and in the production of moist cakes and fruit cakes. Its use in the baking field has as additional advantage in that it produces a product with greater resistance to staling. In the pharmaceutical field, α-amylase preparations are sold as digestive aids. Among other industrial applications are the incorporation of α-amylase into mashing in alcoholic beverage production, sugar recovery from scrap candy, treatment of pig starter feedstuffs, liquefying of soups and purees, cold water dispersion of laundry starch, and wallpaper removal.

3.8 Ultrafiltration [24]

Ultrafiltration is a membrane separation technique for dissolved and suspended materials based on molecular size. Ultrafiltration is used for separating particles with molecular weights from 300 to 500,000 daltons (or 10 - 1,000 A). The pressure which is a driving force for exertion solution in contact with membrane is up to 10 bar. [25] This causes a flow of solutes and water toward the ultrafilter.

3.8.1 Mass Transfer and Concentration Polarization

In ultrafiltration, pressure is exerted on a solution in contact with the membrane. Substances smaller than the pore size of the filter are driven through with the solvent while larger solutes are retained, so the concentration of retained macrosolutes will build up at the membrane surface. This phanomenon is the result of concentration gradient.

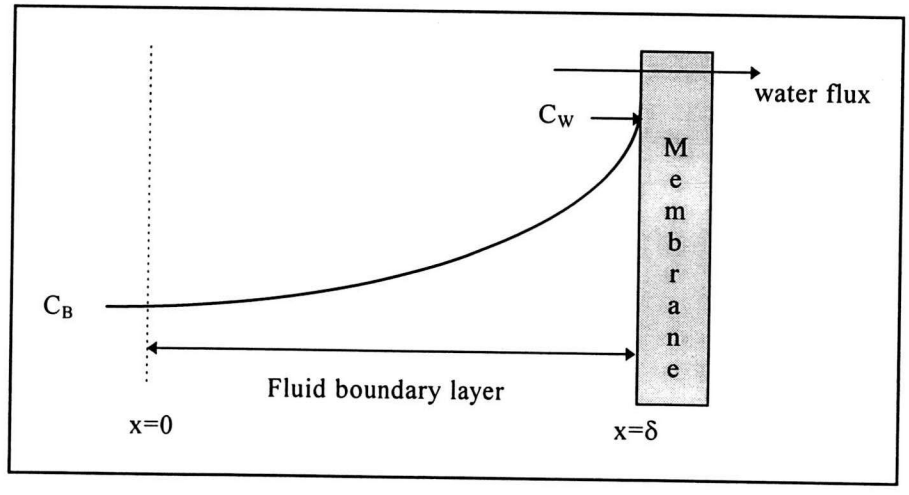


Figure 3.6 Concentration Gradient

The concentration gradient is known as concentration polarization which is the maximum solute concentration at the membrane surface. As a result of the increased concentration at the membrane surface, there is a tendency for solute to diffuse away from this point. Under steady state conditions, the convective mass transfer due to filtration is balanced by the diffusive movement in the opposite direction, as the following:

$$JC - D_V \frac{dC}{dx} = 0 \qquad (3.7)$$

where J is filtration flux rate ; $cm^3/min\text{-}cm^2$

C is the solute concentration at x ; g/l

D_v is the solute diffusivity ; cm^2/min

Equation (3.7) can be integrated across the solute boundary layer from x=0 ,$C=C_B$ to $x=\delta$, $C=C_W$ (see Figure 3.6) to give:

$$J = \frac{D_v}{\delta} \ln \frac{C_W}{C_B} \qquad (3.8)$$

$$J = K \ln \frac{C_W}{C_B} \qquad (3.9)$$

where K is mass transfer coefficient ; cm/min

Under this condition, the mass transfer coefficient is not a function of the solute concentration, but it is dependent on the driving pressure and any fluid flow

across the membrane. These forces affect K by changing the boundary layer thickness, δ.

3.8.2 Gel Polarization

The filtration flux rate may be increased by raising the solute concentration at the membrane,C_W. However, the value of C_W can be increased until a point that the retained solute form a gel layer. This gel concentration,C_G, is the maximum value of C_W and may be substituted into equation (3.9):

$$J = K \ln \frac{C_G}{C_B} \qquad (3.10)$$

The gel concentration will depend on several variables including pressure, temperature, solubility and pH. Ingham et. al. (1980) suggested that C_G is actually the concentration at osmotic back-pressure which is high enough to prevent flux.

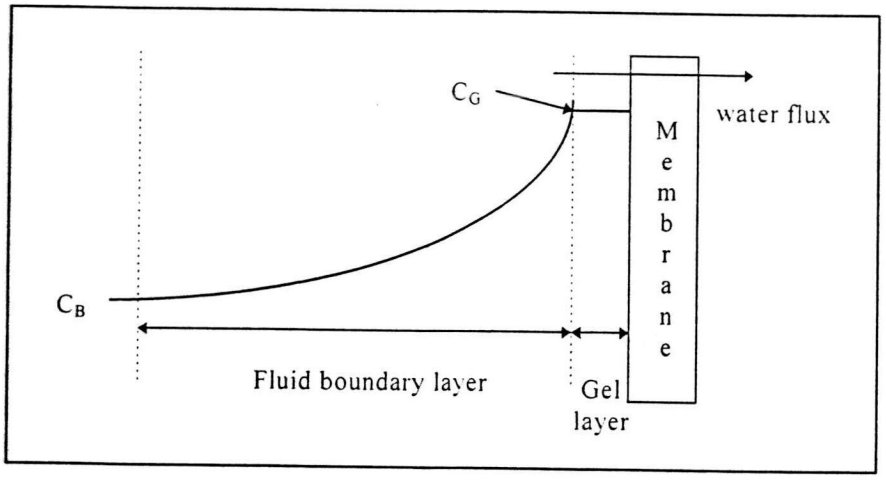


Figure 3.7 Concentration Gradient until Gel Polarization

Blatt et. al. (1970) showed that K is a function of the fluid velocity,v, across the membrane; the following Sherwood number relationship is:

$$Sh = \frac{Kd}{D_V} = A\,Re^B\,Sc^{1/3} \qquad (3.11)$$

where d is the fluid channel height on the top of the membrane ; μm

Re is the Reynolds number = $\rho dV/\mu$

Sc is the Schmidt number = $\mu/\rho D_V$

A,B is the constant values

Theoretically, the value of B is 0.33 in laminar flow and 0.8 in urbulent flow. Constant A is $1.62(\frac{d}{L})^{0.33}$ in laminar flow and 0.023 in turbulent flow. [25]

Gel polarization will actually take place under all but the most dilute solute concentrations, the flux rate at very low concentration is relatively constant. At these level, flux is determined by equation (3.10). When the gel layer forms, flux will decline logarithmically as shown.

3.8.3 Cross-Flow Filtration

The effects of gel polarization can be reduced by making the movement of a solute away from the membrane and reduce the thickness of the gel layer. This is usually accomplished by cross-flow filtration.

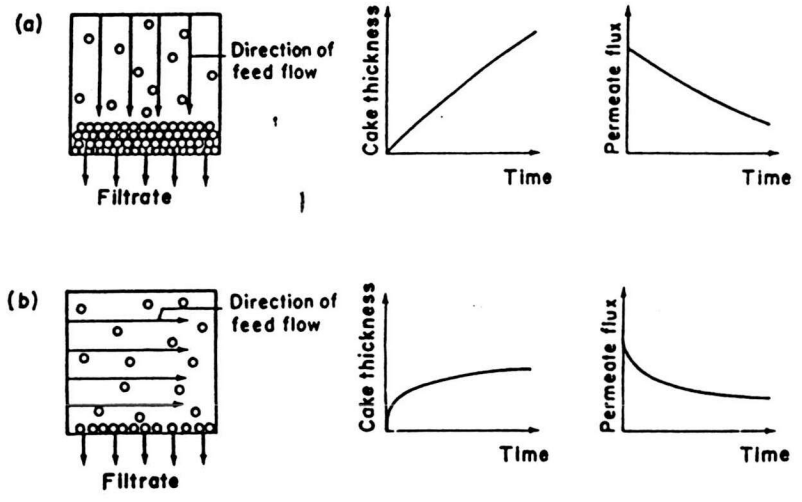


Figure 3.8 The Comparison between Conventional Filtration and Cross-Flow Filtration

The feed stream flows across the ultrafilter and creates a pressure differential from the inlet,P_i, to the outlet,P_o:

$$\Delta P = P_i - P_o \qquad (3.12)$$

where ΔP the pressure drop ; bar

This pressure drop can be related to the flow rate,Q, or velocity across the membrane,V. According to the Poiseuille equation for laminar flow:

$$\Delta P = \frac{c_1 \mu L V}{d^2} = \frac{c_2 \mu L Q}{d^4} \qquad (3.13)$$

where μ is the viscosity ; kg/cm-min

L is the filter length ; cm

c_1, c_2 is the constants dependent on channel geometry

In turbulent flow, based on the Fanning or Darcy equation modified as follows:

$$\Delta P = \frac{c_3 f L V^2}{d} = \frac{c_4 f L Q^2}{d^5} \qquad (3.14)$$

where f is a factor based on the Reynolds number

c_3, c_4 is the constants dependent on channel geometry

The gel concentration is a function of temperature, solubility and pH. The gel concentration can also be dependent on the recirculation flow velocity and flow channel geometry. This fact is important in that velocity changes may affect the gel concentration as well as the mass transfer coefficient.

The driving force through the membrane is also determined by pressure. This transmembrane pressure,ΔPTM, is the difference between the pressure on the feed side and on the filtrate side of the ultrafilter. The differential will be highest at the inlet and reduce to a minimum at the outlet.

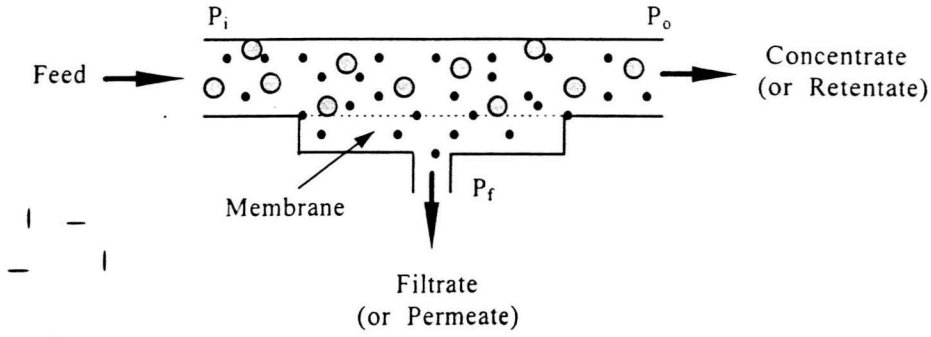


Figure 3.9 Cross-Flow Filtration Pressure Relationship

An average driving force:

$$\Delta PTM = \frac{P_i + P_o}{2} - P_f \qquad (3.15)$$

where P_f is the filtrate pressure ; bar

Generally, the filtrate pressure is negligible and P_f is taken as zero:

$$\Delta PTM = P_i - (\frac{\Delta P}{2}) \qquad (3.16)$$

From equation (3.16), if fixed inlet pressures, a change in the cross-flow velocity as measured by pressure drop will also affect the transmembrane pressure.

The flux will be a function of the transmembrane pressure as defined by:

$$J = \frac{\Delta PTM}{\mu(R_M + R_G)} \qquad (3.17)$$

where R_M is the hydraulic resistances created by the membrane ; cm^{-1}

R_G is the hydraulic resistances created by the gel layer ; cm^{-1}

μ is the viscosity of solution ; kg/cm-min

The membrane resistance is considered to be constant during a situation where no gel polarization occurs, flux will increase linearly with the transmembrane pressure. When gel polarization occurs, the total resistance is increased, so flux will decrease until constant.

From above equations, the permeation flux depends on these parameters.

1 *Pressure*,P_i [equation (3.16),(3.17)]

The permeation flux will increase linearly with the transmembrane pressure until gel formation and increase overall resistance. Further in higher pressure, the thickness and the resistance of the gel layer will increase. So at high transmembrane pressure, flux will reach a maximum and become relatively constant with pressure.

2 *Recirculation Velocity*,V [equation (3.9), (3.11), (3.14), (3.16) and (3.17)]

The mass transfer coefficient will increase with velocity, so the flux rate will increase with velocity according to the mass transfer coefficient. Moreover in higher recirculation velocity, the shear force at membrane surface will increase such that the thickness of gel layer and gel resistance will decrease. Furthermore the mass transfer coefficient will decrease with increase velocity, so the permeation flux will decrease too.

3 *Solute Concentration*,C_B [equation (3.10),(3.17)]

The permeation flux will decrease with higher solute concentration, so the transmembrane pressure will decrease with higher solute concentration too.

3.8.4 Membrane Rejection

The ability of an ultrafiltration membrane to retain a given species is defined by the rejection coefficient,σ:

$$\sigma = 1 - \frac{C_P}{C_B} \qquad (3.18)$$

where C_P is the concentration of the species in the permeate side of the membrane at a given instant of time ; g/l

C_B is the concentration of bulk solution ; g/l

If the membrane completely retains the species, its concentration in the permeate would be zero ($C_P = 0$) and its rejection coefficient would be one ($\sigma = 1$). The rejection can be a function of solute concentration and transmembrane pressure.