

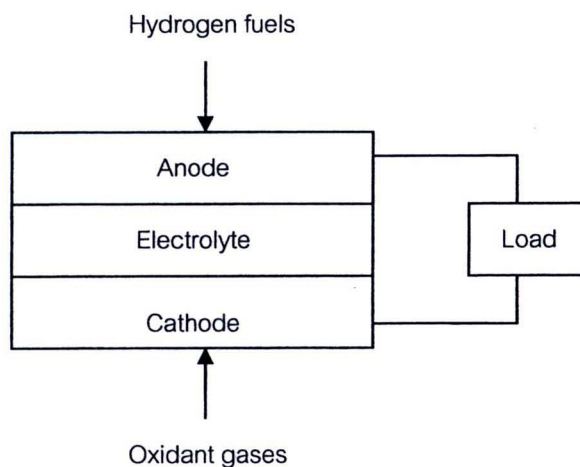
## CHAPTER II

### THEORY

#### 2.1 Fuel Cell

##### 2.1.1 Fundamental Principle

A fuel cell is an electrochemical reactor where the chemical energy of fuel gas is directly converted into electricity (DC), heat and water. It consists of three main parts, a cathode (positive electrode), an anode (negative electrode) separated by an electrolyte. It has a current collector which is connected between two electrodes through an external circuit (load). When connecting the cells together in a stack, interconnect plates are used for separating between a cathode of a cell and an anode of the next cell (Minh, 1993). The diagram of a fuel cell is schematically shown in Figure 2.1. Unlike the conventional batteries, fuel cell does not require recharging and can be operated as long as both fuel and oxidant gases are fed into the electrodes. The oxidant gas is fed to the cathode side while the fuel is fed to the anode side releasing electrons from a hydrogen oxidation reaction. Electrons pass through an external circuit, whilst the ions transfer across the electrolyte. The products from this reaction are water and heat.



**Figure 2.1** The general diagram of a fuel cell

### 2.1.2 Components of Fuel Cell

A fuel cell fundamentally contains major components of electrolyte, cathode and anode as shown in Figure 2.1. When the cells are stacked together, extra components i.e. interconnect and separator plates are required. The required properties for each component are the followings:

#### 2.1.2.1 Electrolyte

Electrolyte, an ion conducting media, performs as a carrier medium of either oxide-ion or proton. The preferred materials for electrolyte are:

- Low electronic conductivity –electrolyte with high electronic conduction can cause higher voltage loss.
- High ion conductivity
- High mechanical and thermal strength.
- Low gas leakage through an electrolyte

#### 2.1.2.2 Anode/Cathode electrode

For an anode electrode, high electronic conductivity is required for transferring electrons because the reaction occurred on the anode side is oxidation which normally releases electrons. The materials must have thermal expansion compatible with electrolyte and interconnector. Tolerance to impurities in fuel gas is needed for anode materials and it also should have a catalytic property which is essential for a fuel oxidation reaction (Fergus, 2006).

The reduction reaction of an oxidant gas occurred on the cathode to complete its mechanism. The required property for the cathode is high electronic conductivity typically in term of electron receptor. The material used in cathode should contain sufficient porosity for gas transport and structural stability during operation. Also, it is less reactive at the vicinity of the electrolyte and interconnector.

### 2.1.2.3 Interconnector

The role of interconnector is to separate between the cells which are stacked together. The required properties are:

- High electronic conductivity
- Structural stability and chemical resistance during operation
- Thermal expansion matching with other components
- Chemically compatible with electrolyte and interconnector at operating conditions

### 2.1.3 Types of Fuel Cells

There are several types of fuel cells categorized by electrolyte materials which are related with anode fuels and operating temperature. The characteristics of these fuel cells are shown in Table 2.1.

**Table 2.1** Characteristics of different types of fuel cells

Fuel Cell Type	Electrolyte	Operating temperature (K)	Fuel	Oxidant	Efficiency (%)
AFC	Potassium hydroxide	323-473	H <sub>2</sub> , Hydrazine	O <sub>2</sub> ,air	50-55
DMFC	Proton-exchange membrane	333-393	CH <sub>3</sub> OH, H <sub>2</sub> O	O <sub>2</sub> ,Humid air	40
PAFC	Phosphoric acid	433-483	H <sub>2</sub>	O <sub>2</sub> ,Air	40-50
MCFC	Molten salts i.e. carbonates, nitrates	903-923	H <sub>2</sub> ,CO, CH <sub>4</sub>	O <sub>2</sub> , CO <sub>2</sub> , Air	50-60
PEFC	Hydrated Polymeric Ion Exchange Membranes	323-353	H <sub>2</sub>	O <sub>2</sub> , Air	40-50
SOFC	Fluorite (Ceramics)	873-1273	H <sub>2</sub> ,CO, CH <sub>4</sub>	O <sub>2</sub> , Air	45-60



Fuel cells have been used for several applications. The appropriate selection of these fuel cells depends on power requirement in each usage, appropriate size for using areas, operating temperature in term of energy supply. Portable fuel cells such as Alkaline Fuel Cell (AFC), Polymer Electrolyte Fuel Cell (PEFC), and Direct Methanol Fuel Cell (DMFC) have been applied for mobile phone, vehicle, laptop, and electronic devices. For stationary fuel cell namely Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC), and Solid Oxide Fuel Cell (SOFC) are suitable for medium-to-large power generation.

#### **2.1.4 Advantages and Disadvantages of Fuel Cell**

Apparently, hydrogen based fuel cell becomes a versatile power generator, releasing both heat and electrical power, that is superior to common power generations. Nonetheless, fuel cells at the present time are still limited in usages due to facing of competitive manufacturing cost and short-life time.

##### **2.1.4.1 Advantages**

- Higher efficiency than conventional combustion heat engines. Because of direct energy conversion and no moving part in the energy converter, so it reduces the energy losses in fuel cells.
- Without burning fuels, fuel cell releases only water and help reduce the emission of  $\text{NO}_x$ ,  $\text{SO}_x$  and particulates to atmosphere.
- Fuel cells can be used in various fuels apart from fossil fuels. The flexibility of fuels takes fuel cells away from limited energy resources.
- Silent operation owing to a lack of moving parts.
- Convenient to supervise since fuel cells mostly consist of stationary parts.
- Able to be an unattended/remote operation.

##### **2.1.4.2 Disadvantages**

- Alternative fuels i.e. methanol, biogas and methane require reforming process. During reforming stages, it is possible that this process can release polluted products via utilizing hydrocarbon feeds.

- Technology is still at a level of development. For example, power density obtained from fuel cell is limited and required further improvements if fuel cell is to compete in portable and automotive applications.
- High market entry cost, less competitive capacity than conventional power generations.
- Operational temperature compatibility, durability under start-stop cycling concerns.
- Almost no infrastructure to support fuel cell technology i.e. fuel storage, transportation.

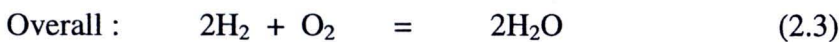
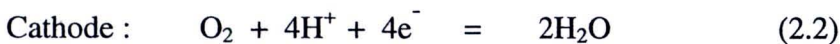
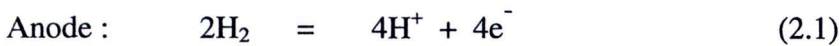
## 2.2 Solid Oxide Fuel Cell

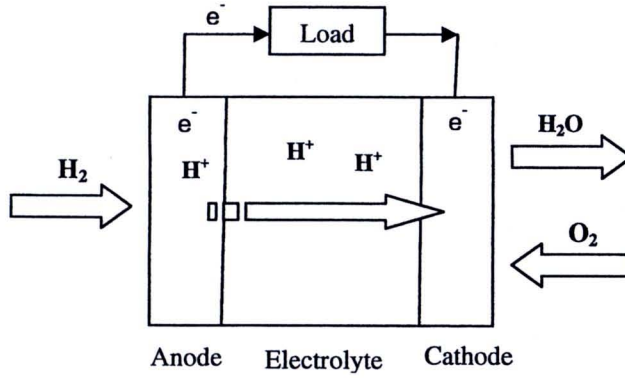
Solid oxide fuel cell is made of rigid ceramics as electrolyte. This material help SOFC alleviate any corrosion problems from poisonous substances usually occurred in the polymer electrolyte. On the other hand, its tolerance benefits various fuels usage. It operates at high temperature about 873-1,273 K. Due to high temperature operation, it is not necessary to use expensive noble metal as a catalyst and also enhance the fuel reforming within the cell at the anode side. This reduces the complexity of system and capital cost for installing an external reformer. However, operating at high temperature leads to slow energy distributed startup and short-life of SOFC structural material.

### 2.2.1 Principle of SOFC operation

Generally, SOFC operation can be divided into two types of electrolyte; namely, Oxygen ion conducting electrolyte and Proton conducting electrolyte. The main difference between these electrolytes is the location of water formation produced from fuel cell occurs in opposite cell sides as shown in Figures 2.2 and 2.3

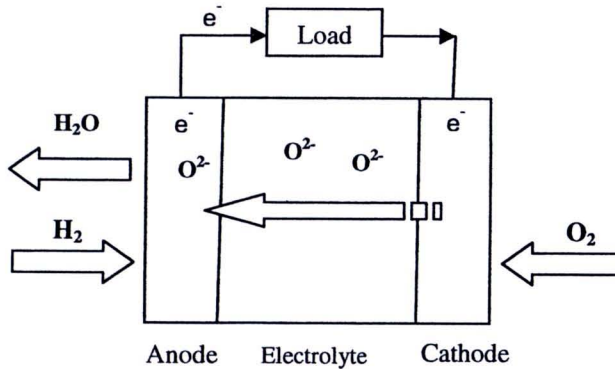
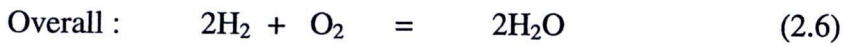
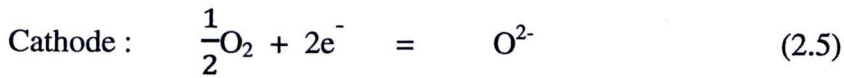
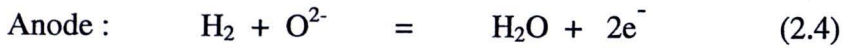
The electrochemical reaction of the SOFC-H<sup>+</sup>





**Figure 2.2** Operational principle of SOFC- $H^+$  operation

The electrochemical reaction of the SOFC- $O^{2-}$



**Figure 2.3** Operational principle of SOFC- $O^{2-}$  operation

## 2.2.2 Characteristics of SOFC

### 2.2.2.1 Open circuit voltage

Open circuit voltage (OCV) is the maximum ideal voltage that can be carried out when operated at a specific condition. Because of different concentration of components between anode and cathode sides, this causes different potential at the anode and cathode and results in OCV of the fuel cell. Electrons were moved from an electrode to another one and the current was generated.



### 2.2.2.2 Polarizations

Although the OCV is the theoretical maximum ideal voltage, the actual voltage of SOFC is less than the theoretical voltage value. Owing to the presence of polarizations, polarizations can be classified into four types as follows:

#### a) Activation Polarization

Activation Polarization is the polarization which occurs from electrochemical reaction at the electrodes. Some energy is required to overcome energy barrier as activation energy for electrochemical reaction, i.e. adsorption of reactant on the electrode surface and desorption of product out of the surface. Normally, activation polarization dominates at low current density regions and the characteristics curve is non-linear. However, at high temperature operation of SOFC, the rate-determining step is very fast resulted in small value of activation polarizations. The linear characteristic curve can be noticed.

#### b) Ohmic Polarization

Ohmic polarization results from the resistance of ions flow within the electrolyte and resistance of electrons flow through the electrodes. Ohmic polarization is a major loss in the SOFC stack when compared to other losses.

#### c) Fuel Crossover or Internal Current Polarization

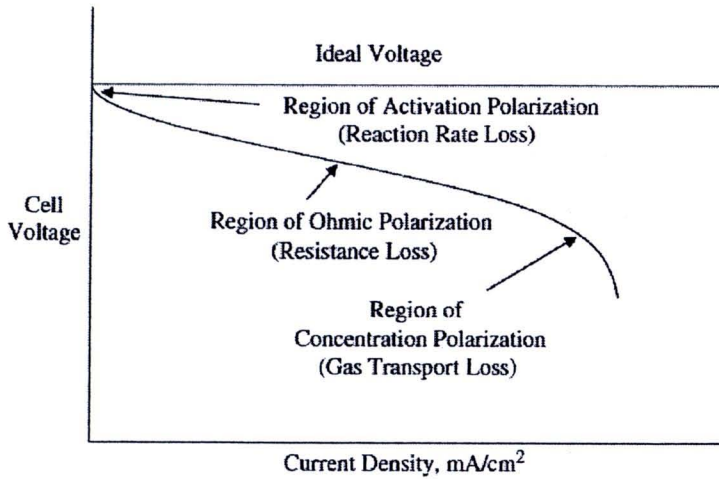
Typically, an electrolyte should permit only ions transported through the cell and no fuel cross over the electrolyte. Although fuel crossing through an electrolyte or electrons leaking to an electrolyte is possible, the fuel crossover loss is very small amount.

#### d) Concentration Polarization

Concentration polarization is caused by concentration in form of partial pressure in porous electrode region reduce more than bulk gas outside this region. This phenomenon occurs when SOFC operates at high temperature or high fuel utilization. The gradient between the concentrations in each region causes this type of

polarization. At lower current densities and fuel utilization. The concentration polarization is very small.

The overall characteristics of SOFC are summarized as shown in Figure 2.4

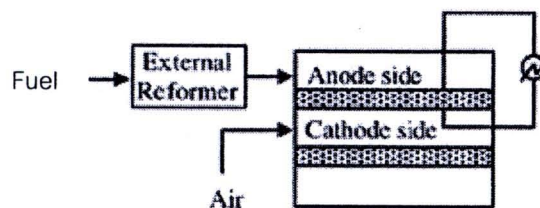


**Figure 2.4** Schematic of ideal and actual voltage in a fuel cell (Kakac et al., 2007)

### 2.2.3 Reforming operation of SOFC

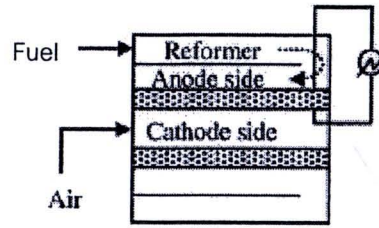
SOFC can be fed with various fuels apart from pure hydrogen i.e. methanol, ethanol, biogas. However, these fuels have to be reformed into hydrogen before being fed to SOFC. There are three modes for SOFC reforming operations; External Reforming (ER), Indirect Internal Reforming (IIR), and Direct Internal Reforming (DIR). Each type of reforming operation is schematically shown in Figure 2.5

a)

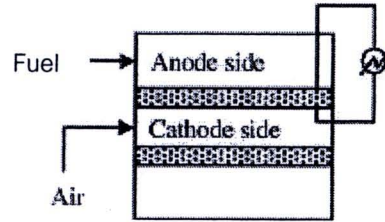




b)



c)



**Figure 2.5** Type of reforming operation of SOFC: a) ER-SOFC, b) IIR-SOFC, c) DIR-SOFC

From these types of reforming, the location of reforming section is significantly different. As the electrochemical reaction is exothermic, releasing steam, while the reforming reaction is endothermic, the reaction can transfer heat and steam each other. For ER in Figure 2.5 a), the reforming section and SOFC are completely separated. Heat and steam from SOFC section do not involve reforming section. For IIR in Figure 2.5 b), the reforming section is located next to the SOFC, this structure makes use of the exothermic heat from SOFC section to reforming section except for steam that could not be involved. For DIR in Figure 2.5 c), the reforming and SOFC sections are located together. Therefore, this system can benefit a full advantage of both heat and steam to interchange each other between these reactions.

#### 2.2.4 SOFC System and Balance of Plant

For SOFC power generation system, by installing only SOFC unit is not enough to improve the process performance. Some extra process equipments are provided to support electricity production. These components are called “Balance of Plant (BoP)”. Generally, the overall SOFC process can be divided into four sections namely; Fuel processing section, Electric generating section, Heat recovery section and electrical power conditioning as follows:



#### 2.2.4.1 Fuel processing section

The role of this section is to modify the incoming reactants to be in proper conditions before being fed into the SOFC. Conventionally, a fuel is reformed into hydrogen in a reformer separated from SOFC to avoid coke formation within the SOFC. The equipments required for bioethanol in a fuel processing section are described below.

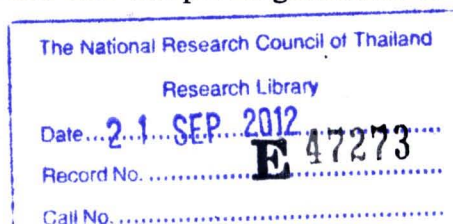
- A pervaporation membrane is used as a separation unit for purifying ethanol to the desired concentration before being fed into the reformer.
- A reformer converts concentration-modified ethanol into hydrogen fuel for the SOFC unit.
- A compressor is used to increase the pressure of the gas stream line to be in a proper condition before being fed into a reformer.
- A vacuum pump is a part of pervaporation unit to create the pressure driving force enhanced separation performance of pervaporation.
- Preheaters are used for modifying temperature of the inlet stream lines of fuel and oxidant feeds to be at a suitable condition.

#### 2.2.4.2 Electrical power generation

This is a major process section in a power generation system. It contains an SOFC unit sequenced after the fuel processing section. The SOFC is fed with bioethanol-derived hydrogen and produces direct current power via electrochemical reaction.

#### 2.2.4.3 Heat recovery section

This section contains heat exchangers and the afterburner to combust residual fuels from electrochemical reaction in SOFC. Thermal power obtained from an afterburner and outlet streams from SOFC is distributed to other equipments requiring some energy supply i.e. reformer, preheaters and other extra power generations in order to reduce the demand of external heat sources and take this power generation to be a worthwhile energy usage.



#### 2.2.4.4 Electrical power conditioning

The electrical power conditioning consists of a unit which converts direct current from SOFC into alternating current for actual usage. In addition, the DC-AC converter is also installed for an added power generation like gas turbine. However, DC-AC inverter is not considered in this study.

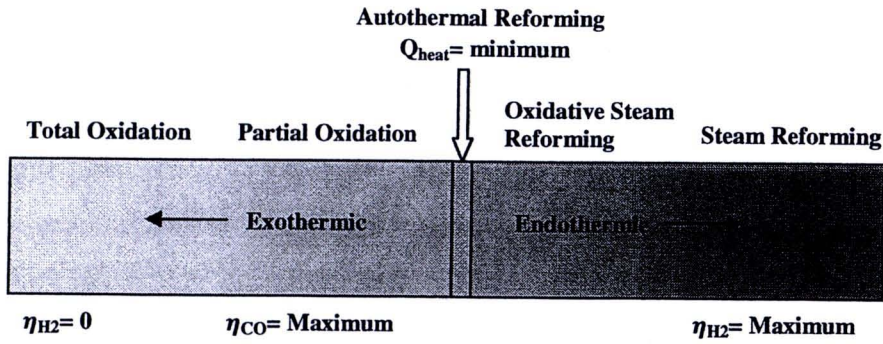
### 2.3 Ethanol reforming reaction

Ethanol as a fuel can be converted into hydrogen. Reforming of ethanol provides a promising method for hydrogen production from renewable sources. Different catalysts such as non-noble metals and noble metals are researched for ethanol reforming. Reforming operation-modes for hydrogen production can be classified into three main types:

- Steam reforming
- Partial oxidation
- Auto-thermal reforming

From these proposed operation modes, selection of each reforming operation is considered from individual objectives. If the main target is to obtain a high yield of hydrogen with low carbon monoxide content, steam reforming operation is a suitable mode but it demands an energy supply due to endothermic reaction. In case of focusing on less system complexity and integration, the exothermic partial oxidation is compatible for these requirements since no external heat source and steam are required (Vourliotakis et al., 2009). However, the hydrogen selectivity of partial oxidation is low. Auto-thermal reforming or oxidative steam reforming is proposed as another choice to improve the hydrogen production. Since it combines steam reforming and ethanol oxidation, its advantages are not only minimum heat input but also high hydrogen production. Characteristics of all reforming modes are summarized in Figure 2.6 (Rabenstein and Hacker, 2008)





**Figure 2.6** Various operating modes of Ethanol reforming

Because ethanol reforming process is considered as a part of fuel processing section and the objective of this research is to obtain hydrogen as high as possible in order to enhance the power generation performance from a fuel cell. The ethanol steam reforming is then selected due to the highest hydrogen yield compared to the other operation modes.

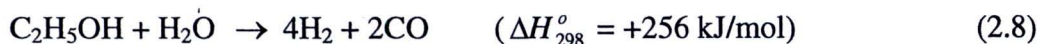
### 2.3.1 Ethanol steam reforming

The studies on steam reforming method are of interest by a number of researchers. Ethanol steam reforming appears at higher temperatures compared to methanol steam reforming and also releases higher carbon monoxide amounts in the outlet stream (Amphlett et al., 1981). Because the target is to maximize hydrogen selectivity and inhibit coke formation, the selection of a suitable catalyst plays a crucial role due to each catalyst induces different pathways. Rh and Ni –noble metal and non-noble metal catalysts- are the best and the most commonly used catalysts for ethanol steam reforming (Meng Ni et al., 2007). In practice, there are a number of possible reaction pathways of ethanol steam reforming to be described as follows:

In case of the process having a sufficient steam supply, the ethanol steam reforming reaction is



The equation (2.7) gives the highest hydrogen production and it is a desired pathway. If the steam is supplied to the process insufficiently, the undesired reactions may occur



These reactions release a lower hydrogen production including byproducts. In addition, the other reactions regarding to ethanol can be occurred namely:

### Dehydrogenation



This is another reaction pathway for hydrogen production in practice. However, acetaldehyde occurred can be further reacted by two reactions:

- Acetaldehyde decomposition



- Acetaldehyde steam reforming



### Dehydration



The dehydration of ethanol is an undesired pathway which is the main source of coke formation according to this reaction:



## Decomposition



Reaction of decomposition products can be converted to methane via the following reactions



The decomposition of ethanol gives a low hydrogen production and may lead to the appearance of coke formation due to carbon monoxide and methane products as following reactions:

- Methane decomposition



- Boudouard reaction



Nonetheless, there are several reactions which obstruct pathways for hydrogen production. The water gas shift reaction can enhance hydrogen production and reduces coke formation.

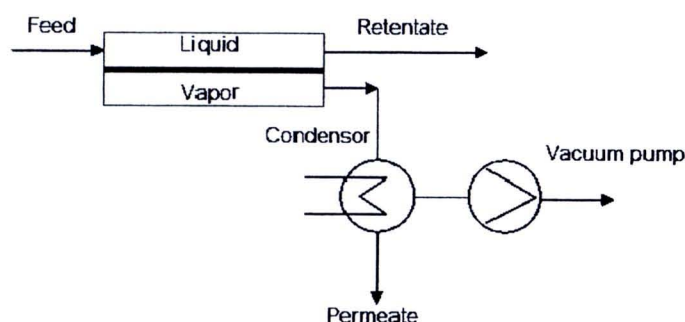




## 2.4 Pervaporation Membrane

### 2.4.1 Fundamental Principle

Pervaporation is a membrane-based separation process to separate liquid mixture using different ability of each liquid which dissolves and diffuses through a dense, non-porous membrane relying on a physical-chemical affinity between the membrane material and the species. As illustrated in Figure 2.7, a liquid feed mixture is in contact with one side of the membrane. In the membrane section, absorbed liquids are under VLE condition and all partial vapor pressure are at saturation. The driving force of pervaporation is the pressure gradient between the feed and the permeate side of the membrane created by vacuum pump or an inert purge stream in order to reduce permeate side partial vapor pressure. The permeate product through the membrane followed by evaporation is removed as a low pressure vapor into another side and then condensed to liquid state.



**Figure 2.7** The schematic diagram of a pervaporation process

### 2.4.2 Characteristics and Important terms of Pervaporation

#### 2.4.2.1 Permeation flux

Permeation flux strongly depends on the feed composition, permeate pressure and temperature of the process (Kujawski, 2000). The permeation involves phase change of the permeating species and can result in significant temperature drop at high

permeation rate. From experimental data, the temperature dependence of the permeation flux is commonly expressed as Arrhenius-type relation.

$$J = J_0 \exp(-E_a/RT) \quad (2.23)$$

where  $E_a$  is defined as an activation energy for permeation. However, this equation is not entirely correct because it does not correspond to any other research dealing with this phenomenon (Feng and Huang, 1997). The flux equation can be derived based on the solution-diffusion model.

$$J_i = \frac{P_i}{l} (p_{io} - p_{ip}) \quad (2.24)$$

where  $p_{io}$  and  $p_{ip}$  are the partial vapor pressures  $i$  on the feed and permeate sides of the membrane, respectively.  $l$  is the membrane thickness, and  $P_i$  is the permeability.  $p_{io}$  can be written in another term dealing with vapor-liquid equilibrium (VLE) condition in a membrane phase as follows:

$$J_i = \frac{P_i}{l} (\gamma_{io}^L x_{io}^L p_{io}^{sat} - p_{ip}) \quad (2.25)$$

where  $\gamma_{io}^L$  is the activity coefficient of component  $i$  on the liquid feed side,  $x_{io}^L$  is liquid mole fraction of component  $i$  in the feed side and  $p_{io}^{sat}$  is the saturated vapor pressure of pure component  $i$ .

#### 2.4.2.2 Membrane separation factor

This parameter is the ratio of the mole fractions of desired component  $A$  and undesired component  $B$  in the permeation and feed sides of membrane.

$$\alpha_{AB} = \frac{y_A / y_B}{x_A / x_B} \quad (2.26)$$

### 2.4.2.3 Membrane permeability

Permeability is the coefficient with respect to the driving force exhibited in terms of partial pressure and is related to the sorption coefficient ( $K_i$ ) and membrane diffusion coefficient ( $D_i$ ):

$$P_i = D_i K_i = J_i \frac{l}{p_{io} - p_{ip}} \quad (2.27)$$

where  $K_i$  and  $D_i$  usually depend on temperature. The relationship of these two parameters and temperature can be expressed as Arrhenius-type relationship. Normally, the permeability is reported as Barrers.

### 2.4.2.4 Membrane permeance

When the membrane thickness is unknown, membrane permeance – a component flux divided by driving force, can be used. Permeance unit is defined as gas permeation unit (gpu)

$$\frac{P_i}{l} = \frac{D_i K_i}{l} = \frac{J_i}{p_{io} - p_{ip}} \quad (2.28)$$

### 2.4.2.5 Membrane selectivity

This parameter is defined as the ratio of the permeabilities or permeances of components  $i$  (desired component) and  $j$  (undesired component) through the membrane:

$$\beta_{ij} = \frac{P_i}{P_j} = \frac{P_i / l}{P_j / l} \quad (2.29)$$

### 2.4.2.6 Recovery

Recovery is defined as the ratio of mass of desired component  $i$  in the permeate stream to that in the feed stream (Mulder, 1996).



$$\text{Recovery} = \frac{m_{i,p}}{m_{i,f}} \quad (2.30)$$

#### 2.4.2.7 Concentration factor

Concentration factor (CF) is defined as the ratio of molar (or mass) fraction of desired component *i* in the permeate stream to that in the feed stream (Soni et al., 2009).

$$\text{CF} = \frac{x_{i,p}}{x_{i,f}} \quad (2.31)$$

### 2.4.3 Practical Applications of Pervaporation

At present, an overview of the potential practical applications of pervaporation is classified into three main areas (Kujawski, 2000):

#### 2.4.3.1 Separation of water from aqueous mixtures

For the removal of water from water/organic liquid, hydrophilic membrane materials have to be selected. The hydrophilic property is caused by groups present in the polymer chain are able to interact with water molecules. Examples of hydrophilic membrane materials are: ionic polymers, polyacrylonitrile (PAN), polyvinylalcohol (PVA) and polyvinylpyrrolidone (PVPD). The industrial dehydration processes that can be separated by pervaporation are:

- Dehydration of water-organic azeotropes such as water-ethanol, water-isopropanol and water-pyridine.
- Dehydration of organic reaction in term of enhancement of the chemical reaction efficiency. There are many organic reactions which can release water as one of the products. Examples of such reactions are: esterification reaction, acetalisation and ketalisation. Removal of water can shift the reaction equilibrium toward and obtain more organic products.

### 2.4.3.2 Removal of organic compounds from aqueous mixtures

For separation of organics from water/organic liquid, hydrophobic polymers are proper membrane property to be chosen. These materials possess no groups that show affinity for water. Examples of these polymers are: polydimethylsiloxane (PDMS), polyethylene (PE), polypropylene (PP), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE). Normally, this process is mostly applied for pollution control such as removal of volatile organic compounds (VOCs) from aqueous because VOCs is a source of air pollution and groundwater pollution. Pervaporation can be used for effectively removing VOCs from water by using specially designed hydrophobic membrane i.e. organophilic membrane. In addition, other applications of pervaporation for removing organics are: separation of bioethanol from fermentation broth, removal of chlorinated hydrocarbons, wine and beer dealcoholization, recovery of high-value aroma compounds (flavors, fragrances, and essential oils) from aqueous or alcohol solutions.

### 2.4.3.3 Separation of Organic-Organic liquid mixtures

For the mixture of two organic liquids, three kinds of mixtures can be differentiated: polar/non-polar, polar/polar and non-polar/non-polar mixtures. Membrane material has to be selected depending on which types of component – polar or non-polar, to remove through the membrane. For the same type mixtures like polar/polar or non-polar/non-polar, it is difficult to separate. The separation has to take place on the criteria of differences in molecular size and shape. Membranes must be custom-designed for specific process objectives. Membrane material such as ceramics has been used as the selective barriers in pervaporation. There are many of organic/organic mixtures which can be separated by pervaporation: Separation of azeotropes (ethanol/cyclohexane, ethanol/ETBE, methanol/MTBE), Separation of isomers (xylenes), aromatics/paraffins (benzene/hexane, isooctane/hexane), olefins/paraffins (pentene/pentane) and purification of dilute streams (isopropyl alcohol from heptane/hexane).