

## Chapter 2

### Literature Review

Membranes are primarily used for the separation process. Over the last 15 years, such processes have been widely adopted by different industries. Large-scale commercial usage of membrane separation have been displacing the conventional separation process. Pervaporation is a membrane process which differed from all other membrane process because of the permeate phase change from liquid to vapor.

#### 2.1 History

Heisler, Binning and James [1] had been the first to study the pervaporation process scientifically, after Kober researched the phenomena of "pervaporation" in 1917 by describing experiments with water selective permeation from an albumin/toluene solution through colloidal containers. This process attracted interest of a number of scientists and during the 1960's many research laboratories were involved with pervaporation test programs.[2]

In the last 10 years, there has been many interests in the pervaporation process which probably due to the advancement of membrane technology. Although pervaporation is expensive owing to the phase change, it is of interest in case when conventional separation processes either fail or result in a higher specific energy consumption, and/or high investment cost.

## 2.2 Solvents Production by Fermentation Process. [3]

Solvent productions by the fermentation process are one of the effective solvent production, such as acetone-butanol fermentation which utilizes microorganisms for substrate inversion. This procedure produce solvent by the selective bacterial fermentation of carbohydrate-containing material such as molasses. Substrate are sterilize, diluted to a concentration of 5%wt. sugar and then cooled down to 30<sup>o</sup>C. A bacterial culture, such as Clostridium acetobutylicum is added to start the fermentation process. After fermentation has proceeded for 36-38 hours, the fermentation broth containing 1.5 to 2.5%wt. mixed solvents are pumped to a column for solid-liquid separation. The vapor from the solid-liquid separation are led to a batch fractionation column from which three fractions (acetone, butanol and ethanol) are obtained. The yield of mixed solvents is approximately 30%wt. base on the sugar charged. Solvent yield ratios are 60-65%wt. butanol, 30-35%wt. acetone, and 5-10%wt. Figure 2.1 are shown the biochemical pathway of acetone-butanol production by the fermentation process.

However, the limitation of the acetone-butanol fermentation process is the product feedback inhibition of accumulated butanol.[4]

## 2.3 Physical Properties of Main Products from Acetone-butanol

### Fermentation broth.

Main products of acetone-butanol fermentation broth are acetone, ethanol, butanol, acetic acid and butyric acid. Physical properties of these products are shown in table 2.1.

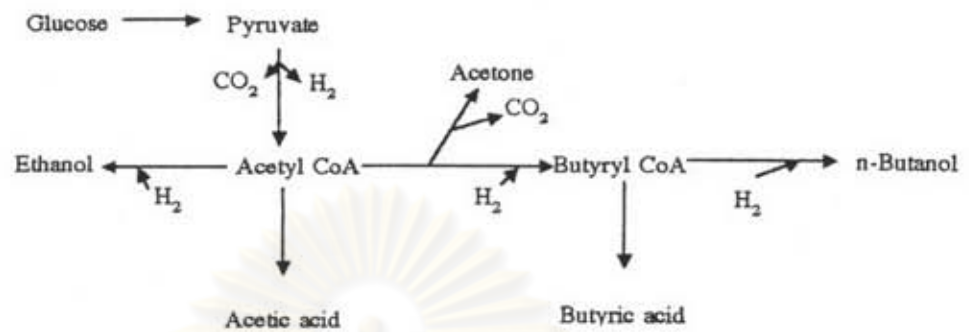


Figure 2.1 The biochemical pathway of acetone-butanol fermentation.[3]

Table 2.1 Physical properties of main products from acetone-butanol fermentation broth.[4]

Product	Acetone	Butanol	Ethanol	Acetic Acid	Butyric Acid
Formula	CH <sub>3</sub> COCH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> OH	CH <sub>3</sub> CH <sub>2</sub> OH	CH <sub>3</sub> CO <sub>2</sub> H	C <sub>2</sub> H <sub>5</sub> CH <sub>2</sub> CO <sub>2</sub> H
Formula Wt.	58.08	74.12	46.07	60.05	88.10
Color and Form	Colorless- Liquid	Colorless- Liquid	Colorless- Liquid	Colorless- Liquid	Colorless- Liquid
Melting point (°c)	-94.6	-79.9	-11.2	-4.7	16.7
Boiling point (°c)	56.5	117	78.4	163.3	118.1

## 2.4 Industrial Application of The Pervaporation Process.

Over the past few years, the number of industrial pervaporation plant has increased. At least 20 to 50 plants around the world have been developed for high productivity and cost effectiveness. For example there have been the reduction in energy and overall system capital costs, improvement to pollution free and compact unit operations.

### 2.4.1 Ethanol Dehydration. [2]

Dehydration of fermentation products either by direct methods or following primary distillation, has become the classic examples of the membrane pervaporation. A typical ethanol dehydration process is shown in Figure 2.2. The feed is run in a one-pass mode through a preheater, into a membrane module. The permeate composed of water with small amount of ethanol is condensed, and either recycled and disposed. A vacuum pump is situated at the downstream of the condenser for any noncondensables and for starting the system. The condenser continue to pull vacuum and maintains steady-state operation.

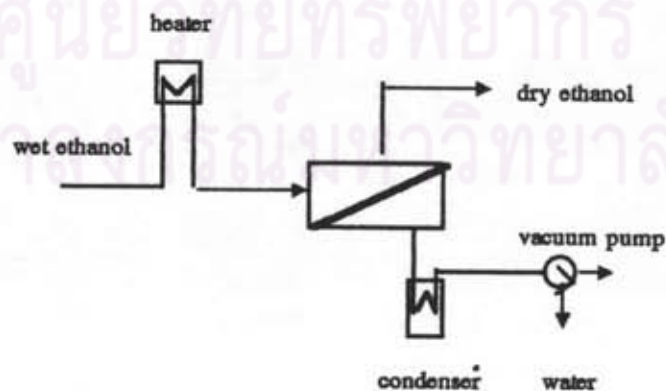


Figure 2.2 Ethanol dehydration.[2]



#### 2.4.2 Dehydration of Organics.[5]

The removal of water from liquid-organic mixtures accounts for the largest segment of new industrial pervaporation plants. The degree of water removal depends on the desired economics. A list of organic solvent which are currently dehydrate and recovered pervaporation process using is given in Table 2.2., and a different form of dehydration of several organic solvents was given in Table 2.3.

Table 2.2 Industrial example of solvents dehydration.

Solvent	Water Content	
	Feed (%)	Product (ppm.)
1-Butanol	8.4	135
n-Butanol	5.4	800
t-Butanol	10.4	581
THF	0.4	220
Xylene	0.1	140
Methanol	7.1	1650
Methanol/IPA	0.21	300
Carpolactam	10.3	671
Ethanol/IPA	0.6	610
Ethanol/Methanol	2.9	780
Ethanol/Benzene	14.1	320
Allyl alcohol	4.85	620
Trichelene	0.01	8
MEK	3.8	220
Methyl Chloride	0.20	140
Ethyl Chloride	0.22	10
Chloroethane	0.0617	12

Table 2.3 Selected water permeable organics/water pervaporation membranes.

Organics	Water Feed Concentration (wt. %)	Selectivity $\alpha$	Water Flux ( $\text{g}/\text{m}^2 \cdot \text{hr}$ )
i-Butanol	8.4	1201	1920
THF/Benzene	0.225	805	82
Xylene	0.04	5799	25
Methanol	5.1	58	229
Methanol/BTX	1.1	1823	258
PFP	4.2	22787	1088
Ethanol/Benzene	14.1	142	4220
n-Butanol	0.41	929	107
MBK	4.0	3967	907

BTX stands for benzene, toluene and xylene

The example of industrial pervaporation for dehydration of organic solvents is reported by Texaco[8] for dewatering isopropylalcohol as shown in Figure 2.3. In this process debottlenecks IPA at 85 %wt. up to 95 %wt. prior to feeding to the extractive column. Only a small pervaporation system is necessary because of the large driving force.

#### 2.4.3 Removal organics from water. [2]

This pervaporation process became commercially available in 1989 by improve process and the membrane development. The well known of the commercial process was GFT process for dealcoholization of beers, wines, and liquors. Using polydimethyl silicone type membranes, reduction, or removal of ethanol has been demonstrated. Figure 2.4 shows in the schematic diagram of the pilot-scale of beer industry. Selective permeation

of ethanol is straightforward, with alcohol reduction to 0.7 %wt. for alcohol-free beer. Reduction was limited to around 0.1 %wt. because the membrane selectivity was not as good as the PVA-based water selective material.

The pervaporation process of other organics from water is also commercially viable, such as ethyl acetate recovery.

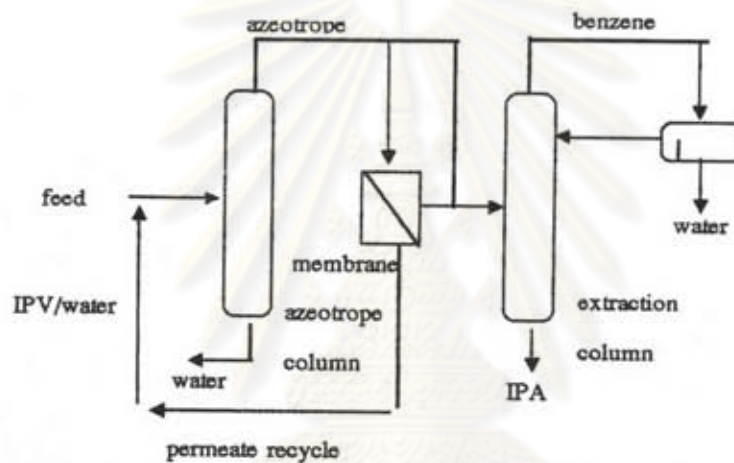


Figure 2.3 Isopropyl alcohol separation process.[5]

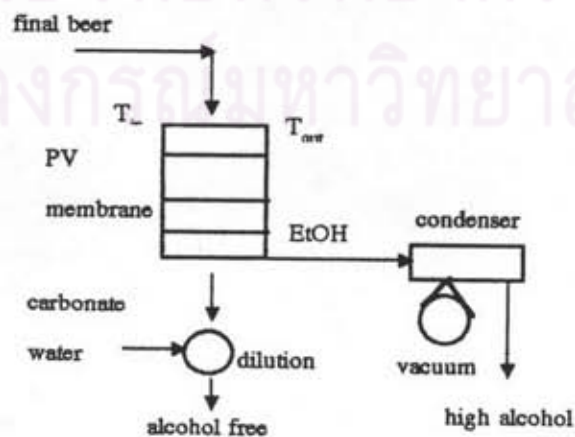


Figure 2.4 Pervaporation process for alcohol reduction in beer.[21]

#### 2.4.4 Organics/Organics Separation. [2,6]

Separation of organics/organics mixture is the least developed, and the largest potential impact for the pervaporation process. Membrane for this process must be designed for the specific process objective.

The example for organics/organics separation by the pervaporation process was the removal methanol from methyl-tert-butyl ether in the production of octane enhancer for fuel blends. This process called TRIM<sup>TM</sup> process and is shown in figure 2.5. The success of this application lies in the high selectivity for the spiral wound cellulose acetate membrane for methanol over MTBE and in its ability to utilize MTBE/C<sub>4</sub> mixtures.

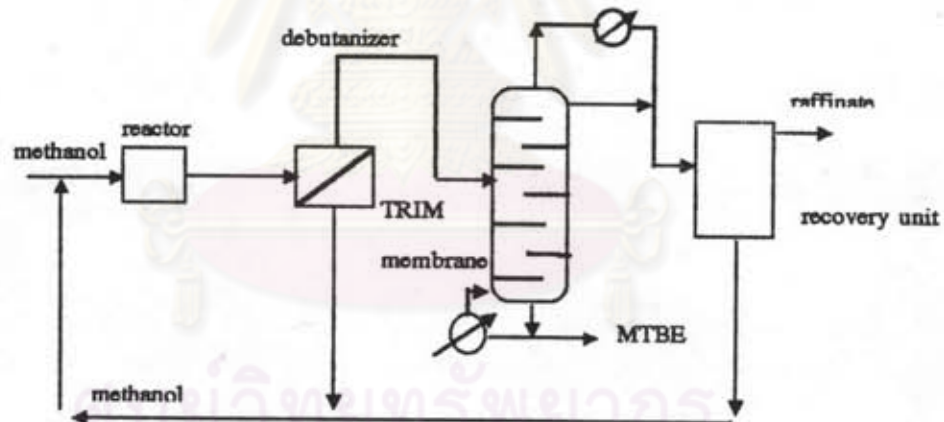


Figure 2.5 TRIM process for methanol/methyl t-butyl ether separation.[6]

#### 2.4.5 Vapor permeation. [7]

This process is one of the membrane pervaporation. The feed stream is a mixture of vapors rather than liquid. The permeate partial pressure is maintained by the use of inert sweep gas, or a vacuum.



Vapor permeation, as a commercial process is only recently being developed. Vapor has other theoretical advantages over the general pervaporation. First, the feed is vapor, so that it would be compatible with fractional distillation. Second, large heat input is not required to vaporized the feed thus the design of complex module and eliminating the need for interstage heating.

### 2.5 Development of The Pervaporation Processes.

In recent years, many scientists have developed and applied the pervaporation processes in various separation process. Main targets of the development and application are to increase productivity and to reduce investment costs.

M.A. Larrayoz and L. Puigjaner[8] studied butanol extraction through pervaporation in acetobutylic fermentation in 1987. The rate of glucose consumption was found to increase when pervaporation was used. In this case, since no product inhibition was present, the microorganisms kept their metabolic activity.

Matsumura et.al.[9] developed liquid membranes for the separation processes in 1987. These processes were the pervaporation through liquid membrane supported with a hydrophobic porous membrane. The liquid membrane prepared with oleyl alcohol was selected as the most suitable for separating volatile products resulting from acetone-butanol fermentation. Using the oleyl alcohol liquid membrane, the dilute aqueous butanol solution of around 4 g/L obtained in acetone-butanol fermentation could be concentrated up to 100 times. The stability of the liquid membrane was also quite good and the separation performance was found after the continuous usage in a long period of 100 hours.

W.J. Groot et.al.[10] integrated pervaporation and continuous butanol fermentation with immobilized cells in 1990. Glucose consumption was found to increase from about 30 to 120 kg/m<sup>3</sup> by pervaporation alcohols. The accumulation of inhibitory acids became substantial.

In 1991, W.J. Groot, T-Barrr et.al.[11] studied mass transfer in silicone rubber membranes for recovery of fermentation products by pervaporation. They was found that existing theories on thermodynamics and diffusion mechanism for dilute liquid were applicable, and correlations were derived to predicted mass transfer of organic solute in silicone rubber membrane on basis of compound properties.

Teruyuki Masawaki, Takahisa Ohno, Masahito Taya, and Setsuji Tone[12] studied separation of butanol from butanol-oleyl alcohol mixture by pervaporation with poly(dimethylsiloxanel) hollow fiber membrane in 1992. Butanol flux was found to increase with temperature and concentration of butanol in feed solution. The separation factors of butanol ranged from 19 to 270 in feed solution in the range of 323-353 K. Afterthat, Michael S.K. Chen et.al.[6] later improved membrane pervaporation for butanol separation from methanol-MTBE-C<sub>4</sub> mixtures. This research described the successful technical development efforts using modified Separex cellulose acetate membrane. In comparison between conventional membrane pervaporation and Separex cellulose acetate, methanol flux rised linearly with the increasing methanol driving force. Total flux remained parallel with methanol flux, indicating that flux of MTBE/C<sub>4</sub> was constant. As methanol driving force increased, the selectivity of methanol also increased.

In 1992, Matsumura and et.al.[13] have been coupled down-flow column reactor with supported liquid-membrane for continuous butanol-isopropanol fermentation. The liquid membrane was prepared with oleyl

alcohol. In comparison with continuous fermentation without product removal, the specific butanol production rate was 2 times higher. The butanol concentration in the permeate was  $230 \text{ kg/m}^3$ , which was 50 times higher than that in the culture broth.

Qinghuang Geng and Chang-Ho Park[14] developed the fermentation process by pervaporation process in 1993. The pervaporation process with  $0.17 \text{ m}^2$  of surface area was made of silicone membrane of  $240 \text{ }\mu\text{m}$  thickness. Silicone tubing was waved through the holes on two flat autoclavable plastic holders horizontally mounten in a fermentor. Butanol and acetone fluxes increased linearly with this concentration in the aqueous phase. During batch and fed-batch fermentation, pervaporation at an air flow rate of  $8 \text{ L/min}$  could removed butanol and acetone efficiently. Glucose consumption rate was found to increase in comparison to the process without pervaporation and up to  $160 \text{ g/l}$  of glucose was consumed during 80 hours. Cell growth was not inhibited by possible salt accumulation or oxygen diffusion through the silicone tubing. The culture volume was maintained relatively constant during fed-batch operation because of an offsetting effect of water and product removal by pervaporation, and addition of nutrient supplements.

In 1994, Chompunut Pipoplapanant[15] studied pervaporation of water-butanol mixtures. The experiments were performed at various temperature ( $30\text{-}60^\circ\text{c}$ ), feed concentration of butanol( $0.5\text{-}4.38 \text{ \%wt.}$ ), and permeate pressure( $20\text{-}50 \text{ mmHg.}$ ). Butanol flux was increased with increasing temperature, feed concentration, and lowering permeation pressure.