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RECOVERY OF FLAVOR COMPOUNDS FROM ORANGE JUICE MODEL SOLUTION BY PERVAPORATION WITH TUBULAR PDMS MEMBRANE

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งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาพฤติกรรมการเคลื่อนที่ของสารกลิ่นรสสำคัญ ได้แก่ เอทิลบิวทิเรต, ทรานส์-2-เฮกเซนาล, 1-เฮกซานอล และ ดีลิโมนีน ซึ่งมีอยู่ในน้ำส้มจำลองที่แยกโดยเมมเบรนพอลิไดเมทิลไซลอกเซนแบบท่อด้วยกระบวนการเพอแวปพอเรชัน โดยศึกษาผลของตัวแปรต่างๆต่อประสิทธิภาพในการแยก ได้แก่ ความเข้มข้นของสายป้อน (ความเข้มข้นของน้ำส้มจริง, น้ำส้มเข้มข้น 75 เท่า และ 150 เท่าของน้ำส้มจริง), อุณหภูมิสายป้อน (30, 40 และ 45 องศาเซลเซียส) และ ความดันด้านเพอร์มิเอท (5, 10 และ 15 มิลลิเมตรปรอท) จากการศึกษาพบว่า การเพิ่มความเข้มข้นในสายป้อนส่งผลให้ค่าฟลักซ์ของสารเพิ่มขึ้น แต่ค่าการเลือกผ่านและค่าร้อยละผลได้ลดลง เมื่อเพิ่มอุณหภูมิสายป้อนทำให้ค่าฟลักซ์และค่าร้อยละผลได้เพิ่มขึ้นแต่ค่าการเลือกผ่านลดลง นอกจากนี้การเพิ่มความดันด้านเพอร์มิเอทส่งผลให้ค่าฟลักซ์ ค่าการเลือกผ่าน และค่าร้อยละผลได้ลดลงเล็กน้อย แต่อย่างไรก็ตามพฤติกรรมของสารกลิ่นรสบางตัวไม่เป็นไปตามที่กล่าวมาข้างต้นในบางการทดลอง ได้แก่ ดีลิโมนีนและทรานส์-2-เฮกเซนาล ซึ่งค่าการเลือกผ่านของดีลิโมนีนเพิ่มเมื่อเพิ่มความเข้มข้นในสายป้อน แต่ค่าการเลือกผ่านของทรานส์-2-เฮกเซนาลเพิ่มขึ้นเล็กน้อยเมื่อเพิ่มความดันด้านเพอร์มิเอท เนื่องจากค่าฟลักซ์และค่าการเลือกผ่านของสารแปรผกผันกัน ดังนั้นจึงใช้ค่าดัชนีการแยกเป็นตัวระบุความเหมาะสมของสภาวะที่ใช้ในกระบวนการแยกด้วยเมมเบรน จากค่าดัชนีการแยกพบว่าการเพิ่มความเข้มข้นและลดอุณหภูมิในสายป้อนส่งผลให้ค่าดัชนีการแยกของ เอทิลบิวทิเรต, ทรานส์-2-เฮกเซนาล และ 1-เฮกซานอล ลดลง แต่ค่าดัชนีการแยกของดีลิโมนีนเพิ่มขึ้น ในขณะที่การเพิ่มความดันด้านเพอร์มิเอทส่งผลให้ดัชนีการแยกของสารกลิ่นรสทุกตัวลดลงยกเว้นทรานส์-2-เฮกเซนาล ทั้งนี้เนื่องจากดีลิโมนีนมีค่าดัชนีการแยกติดลบที่ความเข้มข้นของน้ำส้มจริง ดังนั้นเพื่อให้ดัชนีการแยกของสารกลิ่นรสสำคัญอย่างดีลิโมนีนมีค่าเพิ่มขึ้น การศึกษาที่ความเข้มข้นสายในป้อนสูงจึงมีความเหมาะสมสำหรับการแยกมากกว่าแต่ดัชนีการแยกของสารตัวอื่นจะลดลง เพราะฉะนั้น สภาวะที่เหมาะสมที่สุดสำหรับการแยกดีลิโมนีน คือ ที่ความเข้มข้นในสายป้อน 75 เท่าของน้ำส้มจริง อุณหภูมิขาเข้า 30 องศาเซลเซียส และความด้านดันด้านเพอร์มิเอท 5 มิลลิเมตรปรอท ในขณะที่สภาวะที่เหมาะสมสำหรับการแยก เอทิลบิวทิเรต, ทรานส์-2-เฮกเซนาล และ 1-เฮกซานอล คือ ที่ความเข้มข้นของน้ำส้มจริง อุณหภูมิขาเข้า 45 องศาเซลเซียส และความด้านดันด้านเพอร์มิเอท 5 มิลลิเมตรปรอท

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สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....

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ANONGNART KHAWSANG: RECOVERY OF FLAVOR COMPOUNDS FROM ORANGE JUICE MODEL SOLUTION BY PERVAPORATION WITH TUBULAR PDMS MEMBRANE. ADVISOR: ASSOC. PROF. ARTIWAN SHOTIPRUK, PH.D., 98 pp.

The objective of this work is to investigate the pervaporative transport behavior of orange juice model solution consisting of four key flavor compounds, namely, ethyl butyrate, trans-2-hexenal, 1-hexanol and D-limonene through the tubular polydimethylsiloxane (PDMS) membrane. The effect of variables on the separation performance were investigated such as feed concentration (original orange juice concentration, at 75-fold and at 150-fold of the original orange juice concentration), feed temperature (30, 40 and 45 °C) and permeate pressure (5, 10 and 15 mmHg). The results show that, increase in feed concentration resulted in increase in the partial flux of flavor compounds but decreased selectivity and recovery percentages. The increase in feed temperature leads to higher permeation flux and recovery percentages of each flavor compound but lower selectivity. In addition, increase in permeate pressure slightly reduced the permeation flux, selectivity and recovery percentages. However, the behavior of some flavor compounds did not follow this trend at some experimental conditions such as that of D-limonene and trans-2-hexenal. The selectivity of D-limonene increased as feed concentration increased. But the selectivity of trans-2-hexenal on the other hand increased slightly with the same increase in permeate pressure. As permeation flux of flavor compounds is inversely proportional to the compound selectivity, the pervaporation separation index (PSI) was more often used in membrane separation processes as a criterion for the selection of appropriate conditions. Base on the PSI, it has been found that increase in feed concentration and decrease in feed temperature led to the decrease in the PSI values of ethyl butyrate, trans-2-hexenal and 1-hexanol, and the increase in PSI value of D-limonene. Whereas, increase in permeate pressure decreased the PSI values of all flavor compounds except for trans-2-hexenal. It should be noted that the PSI for D-limonene was negative at low feed concentration, and to increase the PSI value of the key flavor compound like D-limonene, high feed concentration would be more appropriate, however with the expense of lower PSI values for the other compounds. The most suitable conditions for separation of D-limonene are at 75-fold of original orange juice feed concentration, high feed temperature of 45 °C and low permeate pressure of 5 mmHg. Whereas the appropriate conditions to separate ethyl butyrate, trans-2-hexenal and 1-hexnol is operated with real orange juice concentration, feed temperature 45 °C and permeate pressure 5 mmHg.

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CHAPTER I

INTRODUCTION

1.1 Motivation

Flavor is an important sensory quality of food, fruits and beverages which is produced from several volatile compounds. Human senses change of flavor by the taste and the odor. It has been shown that complacent flavors can trigger freshness and appetite for the consumer (ROVNER 2010). In fruits, more than 6,000 flavor compounds have been identified. Of these, a surprising number of 203 flavor compounds can be found in sweet orange (Johnson, Braddock et al. 1996). Juice of oranges is considered the most widespread beverage having high contents of vitamin C and antioxidants (Med-Health.net 2013). While fresh orange juice consists of complex volatile compounds, mainly alcohols (about 22%), hydrocarbon (about 22%), esters (about 20%) and aldehydes (about 18%) in the range of ppm or ppb (Robards and Antolovich 1995), processed orange juice loses its natural flavors as a result of thermal processes such as evaporation, plasticization or sterilization. The loss and/or chemical change due to heat induced oxidation or/and Millard reactions, which lead to quality loss and degradation of products (Martins, Jongen et al. 2000, Kato, Shimoda et al. 2003)

Since the market for commercial orange juice is highly competitive, natural quality and authenticity are the critical factors which determine consumers' satisfaction. This makes pure premium orange juice much more popular than the concentrated juice. Recently, it appeared as shocking news when *Food and Drug Administration* (FDA) of United State found that the premium orange juice from large companies is not all natural. Without labeling, flavor packs made from synthetic flavors or by chemical extraction of orange byproduct are being added back to restore flavor of the heavily processed juice (JAMES 2012).

Therefore, there is a need for orange juice and other juice industries to devise a technique that recovers natural flavors and aroma compounds that can later be added back to the processed product to restore the flavors. Conventional methods such as distillation, solvent extraction, partial condensation, adsorption, gas stripping, supercritical fluid extraction and flash distillation are primary techniques used to recover and concentrate aroma compounds (Schäfer, Bengtson et al. 1999). Unfortunately, these techniques often are complex, and results in chemical contamination, poor aroma recovery and high energy consumption. Recently, it has been reported that pervaporation is a good alternative to these techniques because the process yields good separation, operates under mild conditions the process requires no entraineraddition , no regeneration and is easy to scale up (Karlsson and Trägårdh 1997, Raisi, Aroujalian et al. 2008).

Most of pervaporation researches on flavor compounds recovery were conducted on a system made of polydimethylsiloxane (PDMS) membrane (Pereira, Rufino et al. 2002) using model flavor solutions consisting of only critical elements, called “key components”. Only a few reports employed real solutions because it is difficult to maintain the original concentration of the real flavors (She and Hwang 2006).

The objective of this work was to investigate the behavior transport of orange juice model solution consisting of key flavor components. The effect of operating conditions: operating time, feed concentration, feed temperature and permeate pressure on pervaporation process will be determined. The analysis for the profile of the volatile in the permeate will be carried out with Gas Chromatography-Flame ionized detector (GC-FID).

1.2 Research objectives

To recovery the key flavor compounds from orange juice model solution in three ranges of concentration by pervaporation with tubular polydimethylsiloxane membrane and investigate the effect of operating time, feed concentration, feed temperature and permeate pressure on the transport behaviors, as expressed by permeation flux, selectivity, recovery percentages and pervaporation separation index through the membrane.

1.3 Working scope

1.3.1 Determine the suitable batch operating conditions: operating time (1-10 h), feed concentration (original orange juice concentration and at 75-fold and at 150-fold of the original orange juice concentration), feed temperature (30, 40, 45 °C), permeate pressure (5, 10, 15 mmHg) at fixed feed flow rate (15 L/h) for pervaporation of orange juice model solution through a dense PDMS membrane. The permeation flux, selectivity, recovery percentages and pervaporation separation index through the membrane will be evaluated at the above conditions.

1.3.2 The model solutions of orange juice in aqueous solution including of ethyl butyrate, trans-2-hexenal, 1-hexanol and D-limonene. The analysis of the permeate for the composition of these compounds will be carried out first by extracting the permeate with n-pentane:dichloromethane at 2:1 ratio. The analysis of the extract will then be carried out with GC-FID.

1.4 Expected benefit

The appropriate operating conditions will be determined for pervaporation of orange juice model solution to concentrate the flavor compounds. And the result from this work will suggest the possibility for application of the technique in industrial scale.

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 Orange

Orange is the fruit of the Citrus species and Rutaceae family which is widely grown in the tropical and subtropical climate particular in Brazil, United state of California and Florida (NRCS 2013). There are more than one hundred strains of oranges around the world, and in a tropical country like Thailand, tangerine and honey oranges (Sainumphung) are the most commonly grown and squeezed for the production of orange juice. Fresh oranges have been found to contain a variety of phytonutrients such as vitamin C and antioxidants, as well as complex flavor compounds mainly as alcohols, hydrocarbons, esters and aldehydes (Robards and Antolovich 1995).

2.1.1 Orange juice manufacturing

Orange juice, squeezed from mature oranges, is one of the world most popular juices. As freshly-squeezed orange juice has a short shelf life, commercial orange juice processing was therefore developed to solve this problem. As a result, approximately 80% of all oranges consumed today are processed for commercial juice products of various kinds (Chicago 2012). In a typical orange juice process, oranges are hand-picked or machine-picked, loaded into trailers and delivered to the processing plant. The oranges are dumped from trailers onto conveyers where they are carried through a washing process. They are then graded, and those not acceptable for processing are separated and diverted as the by-products. Oranges are then transported via conveyor to juicing machines (extractors). After juice extraction, the stream of pulpy juice goes through a finisher (screen) where the pulp and seeds are removed. Along with the peel, these were diverted as by-products. At this stage, the juice is made into three types of product forms: frozen concentrated orange juice (FCOJ), not-from-concentrate juice (NFCJ) and unpasteurized orange juice (UPOJ) (Morris 1996).

Frozen concentrated orange juice (FCOJ)

FCOJ is the concentrated orange juice which is to be mixed at home with a part of water to create a potable juice. Nowadays, it accounts for less than 50% of the orange juice market. In processing FCOJ, the orange juice is pasteurized at 92-95 °C and then filtered before being sent to an evaporator where vacuum and heat are used to remove excess water in order to obtain a base concentrate of 65% sugar by weight. The FCOJ is then stored at 10 °F (-12°C) or lower in a tank until packing. As the evaporative process strips off most of the aroma compounds, the juice quality is severely lost. To give it a fresh-squeezed taste and the consistent year-round taste, flavor packs, which contain artificial flavors, are added back into the product before packing (Hamilton 2009). Due to high thermal treatment employed in this process, this FCOJ has very long shelf life of about 6-12 months non-refrigerated, as long as the packing is kept sealed.

Not-from-concentrate juice (NFCJ)

NFCJ is the orange juice that is pasteurized and frozen or aseptically packed for shipment to the consumers without being concentrated. However, in the process in which NFCJ is made, natural flavor aromas were reduced, and therefore flavor packs are again added back into the juice in the final step before packaging. This kind orange juice has a shelf life of up to 30 days and must be kept chilled.

Unpasteurized orange juice (UPOJ)

UPOJ is the closest to freshly squeezed orange juice, which accounts for only two percentages of the market. The juice is squeezed and then bottled without having any additives or flavor packs added. The taste of this juice is naturally fresh but it has a short shelf life of about 12 days and must only be stored in a refrigerator.

As the majority of oranges sold today undergo pasteurization process, adding back the recovered flavor becomes necessary for the orange juice manufacturer to be competitive in the market place. However, the technologies that benignly recover the flavor compounds must be devised.

Of all possible separation techniques, membrane separation is advantageous as the membrane devices are much smaller. Furthermore, the processes can be conducted at lower temperatures, and is therefore suitable for separation of heat sensitive compounds from dilute aqueous solution such as in this case (Oliveira, Scarpello et al. 2002, Ulbricht 2006, Schmeling, Konietzny et al. 2010).

2.2 Membrane separation

Membrane separation is a technology used in laboratory and industry to separate substances from a mixture through a separation barrier called “membrane”, which allows some particles or chemicals to selectively pass through. As schematically shown in Figure 2.1, the stream carrying components which can be transported through the membrane is called “Permeate” and the other stream carrying the components that cannot be transported through the membrane is called “Retentate”.

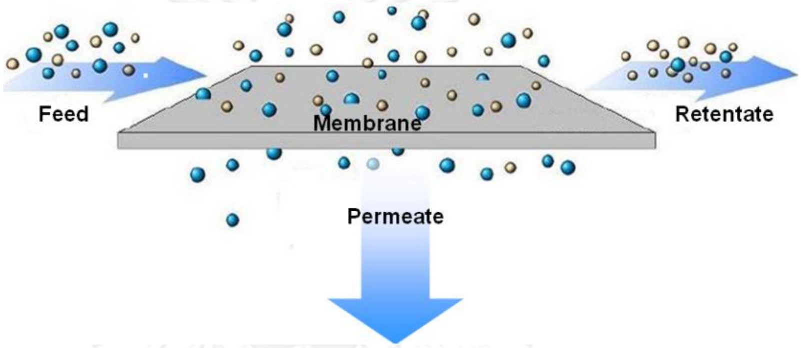


Figure 2. 1 Membrane based separation process (Schmeling, Konietzny et al. 2010)

Effective membranes must exhibit high transmembrane flux (permeability) and high selectively. The factors that have direct effects on transmembrane flux are membrane properties and the driving forces of mass transport of the species of interest through the membrane, as expressed by the following equation.

$$J_i = \left(\frac{P_{M_i}}{l_M}\right)(drivingforce) = \overline{P}_{M_i}\,(drivingforce) \qquad (2.1)$$

where $\overline{P}_{M_i}$ is the permeance

P_{M_i} is the permeability

l_M is the membrane thickness

2.2.1 Membrane properties

Factors that affect membrane properties include the type of material, pore size and structure of the membrane. Initially, membranes for separation process were made from natural polymers like cellulose and rubber. Later, the synthesis membranes were developed for diverse applications (J. D. Seader 2011). For industrial processes, the synthetic polymer membranes are more preferred than natural membranes due to their advantages such as exhibiting better thermal and mechanical properties and thus versatility.

As membrane pore size can greatly affect transmembrane flux and selectivity, membranes may be classified according to their pore size into three major categories: macro-porous, micro-porous and non-porous (dense) membranes. Macro-porous membranes have large pore size than molecular size of the mixture, and all molecules can pass through these membrane. Micro-porous membranes contain interconnected pores, thorough which molecules can be selectively separated by their size differences. Non-porous or dense membranes on the other hand show amorphous structure with their microscopic pores of size less than a few Å in diameter. Due to high selectivity of these dense membranes, they are generally used for separations of small molecules. However in some cases, separation of small molecules through dense membranes presents some problem since a high permeability is not compatible with a high separation factor. As a result, three membrane structures: asymmetric, caulked asymmetric and thin-film composite membranes were developed for solve this problem (J. D. Seader 2011).

As schematically shown in Figure 2.2, asymmetric, caulked asymmetric and thin-film composite membranes differ in forming processes employed to increase flux. Asymmetric membrane consists of a thin dense skin about 0.1–1.0 μm thickness, called the “permselective layer”, which is formed over a micro-porous support layer made of the same material as the dense skin. As a solution to the defect problem generally found in asymmetric membrane, caulked asymmetric membrane (Figure 2.2 (b)) was developed in which the polymer film is pulled from the coating on the skin surface, into the defect by applying a vacuum. The last type of the membrane structure is the thin-film composite membrane, which has dense skin of 250 to 500 Å coated on a thicker micro-porous support made of a different type of polymer. Because thin-film composite membrane has high flux and selectivity, as well as good mechanical strength, it is often used in industrial separation processes such as water purification, water desalination, and in batteries and fuel cell production (wilkipedia 2013).

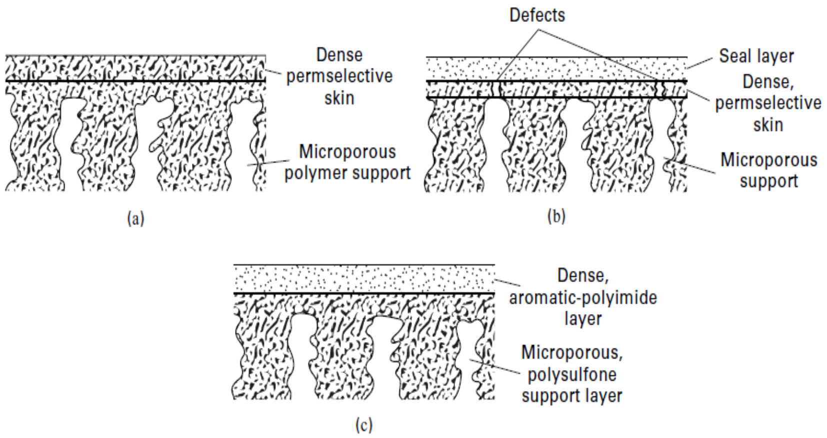


Figure 2. 2 Polymer membranes: (a) asymmetric, (b) caulked asymmetric and (c) typical thin-film composite (J. D. Seader 2011)

2.2.2 Membrane separation techniques

Table 2.1 summarizes various membrane separation techniques including dialysis (D), electrodialysis (ED), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reversed osmosis (RO), gas permeation (GP) and pervaporation (PV). Many of these techniques are driven by pressure difference across the membrane, while dialysis and electrodialysis are driven by concentration difference and electrical potential difference, respectively.

Table 2. 1 Summary of the established membrane separation technologies (Wee, Tye et al. 2008, J. D. Seader 2011)

Process	Principle	Type of membranes	Initial phase	Driving forces	Industrial applications
D	The smaller molecules of solute can pass through membrane from a higher concentrate side to other side	Finely micro porous<10 Å	Liquid	Concentration difference	Purification of blood (artificial kidney)

Process	Principle	Type of membranes	Initial phase	Driving forces	Industrial applications
MF	Separation of organic and polymeric compounds with micro-pore ranges of 0.1–10 µm	Finely micro porous 200-100,000 Å	Liquid or gas	Pressure difference 35–350 kPa	Removal of suspended solids, bacteria and yeast in pharmaceutical and electronics industries
UF	Separation of water and microsolutes from macromolecules and colloids	Finely micro porous 10-200 Å	Liquid	Pressure difference 140–700 kPa	Removal of colloidal material from wastewater and food process streams
NF	It use pressure to separate soluble ions from water through membrane	Finely micro porous 1-10 Å	Liquid	Pressure difference 1000–7000 kPa	Water pre-treatment, treatment, separation of dye and sugar and purification food and dairy sector
RO	Passage of solvents through a dense membrane that is permeable to solvents but not solutes	Dense solution-diffusion	Liquid	Pressure difference 700–7000 kPa	Drinking water from sea, brackish, groundwater, waste water, production of ultra-pure water for electronics

Process	Principle	Type of membranes	Initial phase	Driving forces	Industrial applications
GP	Component of mixture of gaseous is removed through a pressure gradient	Dense solution-diffusion	Vapor of gas	Pressure difference 700–7000 kPa	Removal of nitrogen from air, hydrogen from petrochemical /refinery vents, carbon dioxide from natural gas and VOCs from petrochemical vents
PV	Component of a mixture diffuses through, evaporates under a low pressure and is removed by a vacuum	Dense solution-diffusion	Liquid	Pressure difference 7–70 kPa	Dehydration of solvents, separation of azeotropic mixtures and separation of volatile component from organic or dilute aqueous solution

As shown in Table 2.1, pervaporation is suitable for recovery of thermal sensitive organic compounds from very dilute solution, it is therefore employed in this study for the recovery of flavor compounds from orange juice.

2.2.3 Pervaporation

Pervaporation is a separation technique, which employs a dense membrane to separate a liquid mixture. Some advantages of this technique include high efficiency (selectivity and permeability), compact modular design and high flexibility.

Furthermore, compared with other thermal separation processes, pervaporation requires no need entrainer equipment, gives no contaminates and is energy efficient. Pervaporation is generally suitable for three major areas, which are

- Dehydration of organic-organic mixtures
- Separation of organic-organic solvent mixtures
- Remove or recovery volatile organic compounds (VOCs) and aroma from organic compounds or aqueous solution

Some examples of applications of pervaporation include dehydration of water–organics mixtures, concentration of temperature sensitive biochemical, such as flavors and fragrances from aqueous solution, recovery of chemicals produced from fermentation broth, separation of VOCs from organic or aqueous mixture, determination of organic trace compounds in waste water, as well as in and food and beverage analysis (Huang and Meagher 2001, Liang, Dickson et al. 2004).

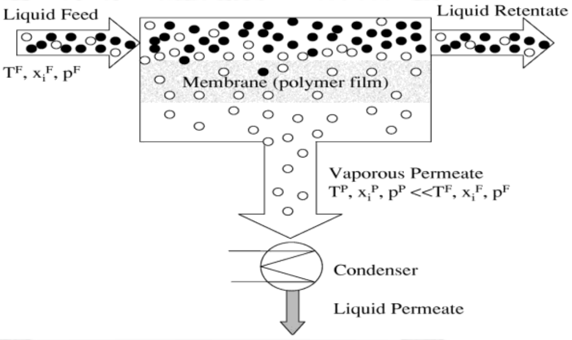


Figure 2. 3 The pervaporation process (Schleiffelder and Staudt-Bickel 2001)

As sown in Figure 2.3, in a pervaporation process, a liquid mixture is placed on one side of a dense membrane, a vacuum is applied on the other side to supply the driving force. Due to the pressure difference between feed side and permeate side, some components in the mixture can differentially permeate through the membrane by sorption, diffusion and then finally desorption as a vapor from the downstream side of the membrane, which is then collected by a condenser (Li, Srivastava et al. 2010).

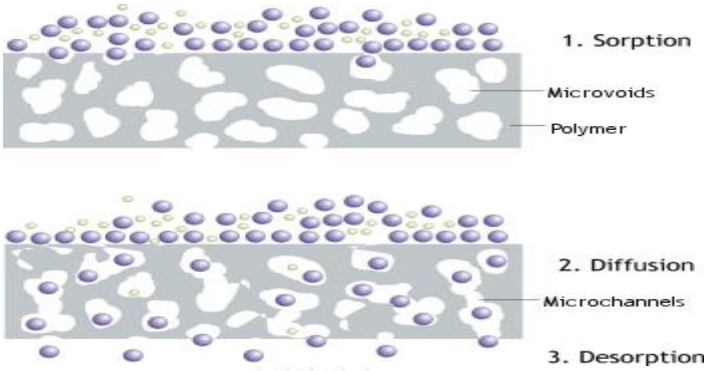


Figure 2. 4 The mechanism of transport through the membrane (Graham 1867)

2.3 Solution-diffusion Model

Solution-diffusion model is the most wildly used model to describe pervaporation transport (sorption and diffusion) in dense membrane such as that used in dialysis, reverse osmosis, gas permeation as well as pervaporation.

Generally, sorption and diffusion of solution through the membrane depend on the interaction between solution and membrane interface. The overall driving force producing the movement for the permeating molecule is the gradient in its chemical potential. Therefore, the flux of the component I can be described by

$$J_i = -L_i \frac{d\mu_i}{dx} \tag{2.2}$$

where L_i is a coefficient of proportionality

$\frac{d\mu_i}{dx}$ is the chemical potential gradient of component i

The chemical potential gradient can be influenced by gradients in concentration, pressure, temperature and electrical potential (Baker 2000). Restricted to driving force generated by pressure and concentration gradients, Equation (2.2) can be rewritten as:

$$d\mu_i = RTd\ln\left(\gamma_i c_i\right) + \nu_i d_p \tag{2.3}$$

where c_i is the molar concentration of component i

ν_i is the molar volume of component i

γ_i is the activity coefficient of component i

p is pressure

For the incompressible phase such as in the liquid or the solid membrane phase, volume does not depend on pressure. In this case, integrating Equation (2.3) with respect to pressure and concentration as

$$\mu_i = \mu_i^0 + RT\ln\left(\gamma_i c_i\right) + \nu_i\left(p - p_{i_{sat}}\right) \tag{2.4}$$

where μ_i^0 is the chemical potential of pure i at saturated vapor pressure

$p_{i_{sat}}$ is the reference pressure at saturation vapor pressure

For the compressible gases: the molar volume change with pressure. So, Equation (2.3) with ideal gas law assumption is written as

$$\mu_i = \mu_i^0 + RT\ln\left(\gamma_i c_i\right) + RT\ln\frac{P}{P_{i_{sat}}} \tag{2.5}$$

Assumptions for permeation model are

- The fluids either side of the membrane are equilibrium with the membrane. This assumption lead to the continuity of chemical potential at the membrane interfaces on both sides.
- Sorption rate is assumed to be much faster than diffusion. Furthermore, desorption at downstream side is assumed to be instantaneous, that is the porous support layer is usually considered negligible. (Trifunović and Trägårdh 2005, Raisi, Aroujalian et al. 2009).

Assumptions for solution-diffusion model are

- Pressure within the dense membrane is uniform at the highest pressure.

- Chemical potential gradient across the membrane is expressed only as a concentration gradient.

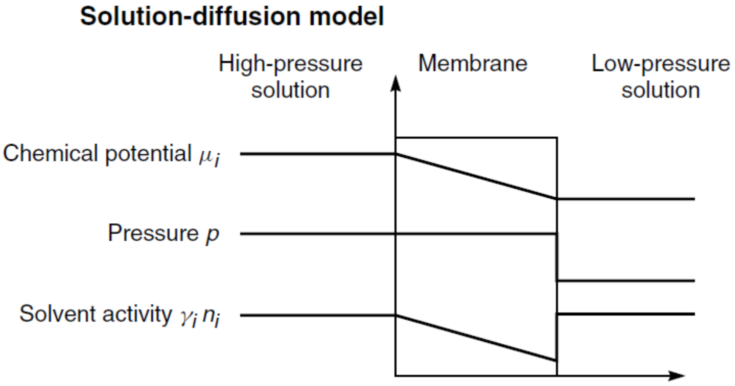


Figure 2. 5 Pressure driven permeation of a one-component solution through a membrane according to the solution-diffusion transport model (Baker 2000)

With these two assumptions of solution-diffusion model, Figure 2.5 therefore illustrates the pressure-driven permeation of a one component as shown in. From this figure, pressure within the membrane is uniform and chemical gradient potential across the membrane is express as a smooth gradient in solvent activity. Thus, the Equation (2.2) and Equation (2.3), can be combined, and after rearrangements assuming activity coefficient is constant, gives

$$J_i = \frac{D_i\left(c_{i_{0(m)}} - c_{i_{l(m)}}\right)}{l_M} \tag{2.6}$$

where D_i is diffusion coefficient

$c_{i_0(m)}$ is solute concentration in the membrane just adjacent to the upstream membrane surface

$c_{i_l(m)}$ is solute concentration in the membrane just adjacent to the downstream membrane surface

l_M is membrane thickness

2.3.1 Solution diffusion model for pervaporation

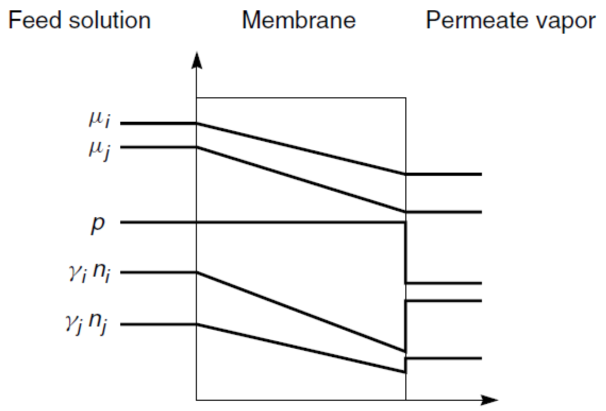


Figure 2. 6 Chemical potential, pressure, and activity profiles through a pervaporation membrane following the solution-diffusion model (Baker 2000)

Pervaporation differs from other nonporous membrane separation techniques such as dialysis, reverse osmosis and gas separation in that the phases on the two sides of the membrane are different. The feed side is liquid whereas the permeate side is vapor. The gradients in chemical potential, pressure, and activity across the membrane are illustrated in Figure 2.6. Therefore, the simple solution-diffusion models for just liquid phase that can be used for dialysis or for just a vapor phase for gas permeation cannot be used here.

For the **liquid-solid membrane interface at feed side** in pervaporation, the chemical potential of liquid solution is in equilibrium with the chemical potential in the membrane at the same pressure. The equilibrium condition based on Equation (2.4) can be written as:

$$\mu_i^0 + RT\ln\left(\gamma^L_{i_0} c_{i_0}\right) + \nu_i\left(p - p_{i_{sat}}\right) = \mu_i^0 + RT\ln\left(\gamma_{i_0} c_{i_{0(m)}}\right) + \nu_i\left(p - p_{i_{sat}}\right) \tag{2.7}$$

Which leads to

$$\begin{aligned} c_{i_0(m)} &= \frac{\gamma^L_{i_0} c_{i_0}}{\gamma_{i_{0(m)}}} \\ &= K_i^L \cdot c_{i_0} \end{aligned} \tag{2.8}$$

where K_i^L is the liquid-phase sorption coefficient

c_{i_0} is solute concentration in the feed liquid just adjacent to the upstream membrane surface

c_{i_l} is solute concentration in the feed liquid just adjacent to the downstream membrane surface

At the **permeate gas/membrane interface**, the equilibrium expression for the chemical potentials in each phase is:

$$\mu_i^0 + RT\ln\left(\gamma_{i_l}^G c_{i_l}\right) + RT\ln\left(\frac{p_l}{p_{i_{sat}}}\right) = \mu_i^0 + RT\ln\left(\gamma_{i_{l(m)}} c_{i_{l(m)}}\right) + \nu_i\left(p - p_{i_{sat}}\right) \tag{2.9}$$

Rearranging Equation (2.9) leads to

$$c_{i_{l(m)}} = \frac{\gamma_{i_l}^G}{\gamma_{i_{l(m)}}} \frac{p_l}{p_{i_{sat}}} c_{i_l} \exp\left(\frac{\nu_i\left(p - p_{i_{sat}}\right)}{RT}\right) \tag{2.10}$$

As before, the exponential term is closed to one, thus the concentration at the permeate side interface is:

$$c_{i_{l(m)}} = \frac{\gamma_{i_l}^G}{\gamma_{i_{l(m)}}} c_{i_l} \frac{p_l}{p_{i_{sat}}} \tag{2.11}$$

The product $c_{i_l} p_l$ can be replaced by the partial pressure, p_{i_l}, thus

$$c_{i_{l(m)}} = \frac{\gamma_{i_l}^G}{\gamma_{i_{l(m)}}} \frac{p_{i_l}}{p_{i_{sat}}} = K_i^G \cdot p_{i_l} \tag{2.12}$$

where K_i^G is the gas-phase sorption coefficient

The concentration terms in Equation (2.8) and Equation (2.12) can be substituted in to Equation (2.6) to obtain an expression for the membrane flux, which leads to

$$J_i = \frac{D_i\left(K^L{}_i c_{i_0} - K^G{}_i p_{i_l}\right)}{l_M} \tag{2.13}$$

However, the sorption coefficient in Equation (2.8) is a liquid-phase coefficient, whereas the sorption coefficient in Equation (2.12) is a gas-phase coefficient. The interconversion of these two coefficients can be handled by considering a hypothetical vapor in equilibrium with a feed solution. This **vapor–liquid equilibrium** can then be written

$$\mu_i^0 + RT\ln\left(\gamma^L_{i_0} c^L_{i_0}\right) + \nu_i\left(p - p_{i_{sat}}\right) = \mu_i^0 + RT\ln\left(\gamma^G_{i_0} c^G_{i_0}\right) + RT\ln\frac{p_0}{p_{i_{sat}}} \tag{2.14}$$

Where the superscripts L and G represent the liquid and gas phase.

Follow the same steps from Equation (2.9) to Equation (2.11), Equation (2.14) becomes

$$C^L_{i_0} = \frac{\gamma^G_{i_0}}{\gamma^L_{i_0}}\frac{p_0}{P_{i_{sat}}}C^G_{i_0} \tag{2.15}$$

where p_{i_0} is the partial pressure of i in equilibrium with feed liquid $\left(P_{i_0} = p_0 C^G_{i_0}\right)$

Also

$$C^L_{i_0} = \frac{K_i^G}{K_i^L} p_{i_0} \tag{2.16}$$

This expression links the concentration of component i in the liquid phase, $C^{L}_{i_0}$, with p_{i_0},the partial vapor pressure of i in equilibrium with the liquid. Substitution of Equation (2.16) into Equation (2.13) yields

$$J_i = \frac{D_i K^{G}_{i}\left(p_{i_0} - p_{i_L}\right)}{l_M} \qquad (2.17)$$

where p_{i_0} and p_{i_L} are the partial vapor pressure of component i on either side of the membrane. This equation explicitly expresses the driving force in pervaporation as the vapor pressure difference across the membrane.

The term $\frac{D_i K_i}{l_M}$ represents mass transfer coefficient through the membrane. The sorption coefficient (K_i), is the term linking the concentration of a component in the liquid phase with its concentration in the membrane polymer phase. And diffusion coefficient (D_i) is the kinetic term that reflects the effect of surrounding environment on the molecular motion of permeating components. Equation (2.17) can also be written as

$$J_i = \frac{P^{G}_{i}\left(p_{i_0} - p_{i_L}\right)}{l_M} \qquad (2.18)$$

where P_{M_i}, permeability coefficient, is generally used to represent the product $D_i K_i$, and is usually treated as a pure materials constant.

Since D_i is generally very small, therefore, to increase the flux, K_i should have a large value and/or membrane with small thickness should be used.

2.4 Evaluation of membrane performance

In order to evaluate the performance of membrane separation experimentally, many parameters have been widely used, namely: permeation flux, separation factor, enrichment factor and pervaporation separation index.

Permeation flux

Permeation flux is defined as the amount of permeate per unit membrane area and unit time at a given membrane thickness. So total permeation flux is according to the following equaiton:

$$J = \frac{W}{At} \tag{2.19}$$

where J is total permeation flux (g/m^2.h)

W is weight of permeate (g)

A is effective membrane area (m^3)

t is permeation time (h)

And the individual flux of each component is called partial flux shows as:

$$J_i = y_i J \tag{2.20}$$

where J_i is partial flux

y_i is mass fraction of component in the permeant

Separation factor and enrichment factor

The selectivity of the membrane can be classified by two alternative dimension ratios: separation factor and enrichment factor.

Separation factor indicates the preferential permeation of the process between component i and component j. It is defined as the ratio of permeate concentration ratio of components i and j to that of the feed concentration ratio, according to the following equation:

$$\alpha = \frac{c_i^P / c_j^P}{c_i^F / c_j^F} \tag{2.21}$$

where α is separation factor

c_i^P, c_j^P is weigh percentage of component i and j in the permeate

c_i^F, c_j^F is weigh percentage of component i and j in the feed solution

Enrichment factor presents the membrane capacity to concentrate component i, and is expressed as:

$$\beta_i = \frac{c_i^P}{c_i^F} \tag{2.22}$$

where β_i is enrichment factor

c_i^P is weigh percentage of component i in the permeate

c_i^F is weigh percentage of component i in the feed solution

In case of very dilute feed concentration, the concentration of solvent in Equation 2.22 and Equation 2.33 will access to 1 in both the feed and permeate. Then, the value of separation factor is closely with the value of enrichment factor.

$$\alpha \approx \beta_i \tag{2.23}$$

Pervaporation separation index (PSI)

Pervaporation separation index is a composite parameter, defined by total flux and separation factor, to characterize the overall performance of the membrane according to PSI value is generally used to design pervaporation process and to represent the efficiency of the membrane.

$$PSI = J(\alpha - 1) \tag{2.24}$$

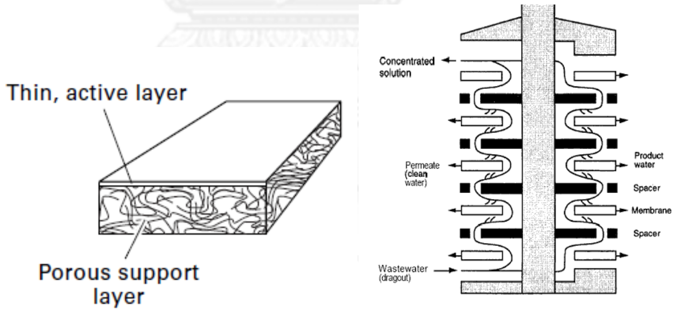
2.5 Membrane modules

In membrane separation processes, membranes are generally contained in a unit called a “module” to achieve the active site as needed. The important aspects to be taken into consideration for module design include packing density, cost effectiveness, ease of manufacturing, cleaning and replacement.

Generally membrane module can be divided into 4 types that suit various applications. These include plate and flame, spiral wound, hollow fiber and tubular modules.

Plate and flame module

Plate and frame modules were among the earliest module type which is formed by flat sheet membranes (Figure 2.7 (a)). As shown in Figure 2.7 (b) taken from waste water treatment process, the module consists of spacers for liquid passage and porous supports are alternated to form a pressed filter element from which permeating water and concentrate is taken. The chief merit of this type of module is easy disassembly for cleaning the membrane.

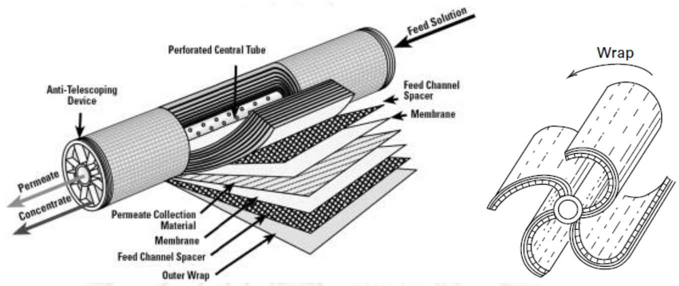


(a) (b)

Figure 2. 7 (a) Flat sheet membrane, (b) Plate and flame module (J. D. Seader 2011)

Spiral wound module

Spiral wound module is fabricated from flat sheets membrane but it has greater packing density. Figure 2.8 (a) shows a laminate, consisting of two membrane sheets separated by spacers for the flow of feed and permeate, which is wound around a central perforated collection tube. In axial direction, feed flows through channels created between the membranes by porous spacers. The permeate travels spirally inward through the membrane to the collection tube. Normally spiral wound module has 0.1–0.3 meter in diameter and 3 meters long (J. D. Seader 2011). As shown in Figure 2.8 (b), spiral wound module can be constructed with four leaves to minimize the permeate pressure drop because the permeate flows less distance for the same membrane area.



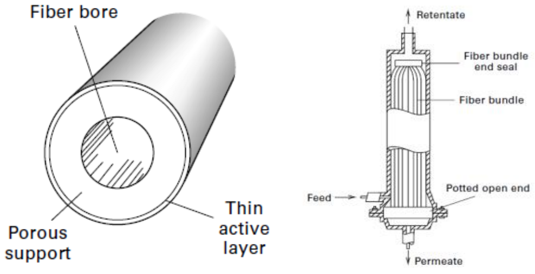
(a) (b)

Figure 2. 8 (a) Spiral wound module, (b) Four-leaf spiral wound module

(J. D. Seader 2011, Yee, Bao et al. 2012)

Hollow fiber module

As shown in Figure 2.9, a hollow fiber membrane module is a shell and tube module, that consists of a bunch of hollow fibers of typically 42 μm i.d. x 85 μm o.d. x 1.2 m. long with a 0.1- to 1.0-μm thick dense skin. This type of module provides a large membrane surface area per unit volume. The pressurized feed solution enters the shell side at one end. While flowing over the fibers toward the other end, permeate passes through the fiber walls into the central fiber channels.



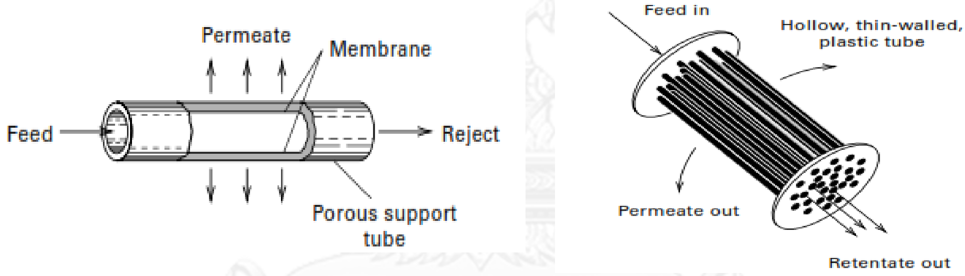
(a) (b)

Figure 2. 9 (a) Hollow fiber membrane, (b) Hollow fiber module (J. D. Seader 2011)

Tubular module

Tubular membrane module is also a shell and tube module containing a number of tubes which are typically 0.5 to 5.0 centimeter in diameter and up to 6 meter long. A thin dense layer is always on the inside tube surface. Since tubular are membranes not self-supporting, therefore the thin dense membrane needs to be supported by special kind non-woven material such as ceramic. Because the location of tubular membranes is inside a tube, the flow in a tubular membrane is usually inside out, and thus the support must be very strong.

Tubular membranes have high durability due to their rugged construction and are extremely foul-resistant. In cross-flow mode, the rugged large-diameter tubes allow for high velocity in the tubes even with very dirty process fluids. This maintains maximum “sweeping” action at the membrane surface and minimizes foul build-up and clogging, even with high suspended solids.



(a) (b)

Figure 2. 10 (a) Tubular membrane, (b) Tubular module (J. D. Seader 2011)

Due to their high durability, good resistance to fouling and very ease of cleaning, tubular membrane modules are attractive to recovery flavor compounds from fruit juice and will be used in this study for pervaration of orange juice.

2.6 Factors affecting membrane performance

There are several factors that affect the performance of pervaporation process. These include feed temperature, permeate pressure, feed concentration, membrane thickness, feed flow rate, membrane material, concentration of polarization, coupling effect and plasticizing effect.

Feed temperature

The feed temperature is an important factor affecting the pervaporation process as it has influences on the solubility and diffusivity of all permeants. So, the solubility and diffusion coefficient are normally relate with Arrhenius type:

$$S_i = S_{0,i} \exp\left[\frac{-\Delta H_{s_i}}{RT}\right] \tag{2.25}$$

$$D_i = D_{0,i} \exp\left[\frac{-E_{D_i}}{RT}\right] \tag{2.26}$$

Thus, the variation of total and individual fluxed are related to the temperature according to Arrhenius type too, as expressions:

$$J = J_0 \exp\left[\frac{-E_a}{RT}\right] \tag{2.27}$$

Where E_0 is apparent activation energy of permeation

R is Universal gas constant (8.314 J/K mole)

J_0 is pre-exponential factor

T is the feed absolute temperature (K)

Permeate pressure

Permeate pressure is the main driving force of pervaporation. The rate of permeation at any feed component increases when partial permeate pressure is lowered or when the pressure difference between inlet and outlet of membrane is high.

Feed concentration

Feed mixture concentration is another interesting factor especially when it refers to the feed concentration of the preferentially permeating components (which is usually minor), because it directly affects to the sorption phenomena (Smitha, Suhanya et al. 2004). Both the activity and solubility of the target components are important aspects to be considered.

Membrane thickness

The resistance to mass transfer can be high for thick membrane. Therefore thin membrane is more favorable in terms of overall permeation flux, however not in terms of selectivity. Membrane thickness can be affected by the degree of swelling. Generally, elastomeric polymer membranes swell more than glassy polymer membranes.

Feed flow rate

Feed flow rate have an effect on the mass transfer in the feed side of membrane as it helps reduce concentration polarization and increase in permeation flux due to a reduction of transport resistance in liquid boundary layer (Xie, Ng et al. 2011).

Reynolds number is used to described feed flow rate as follows;

$$\mathrm{Re} = \frac{\rho \upsilon d_h}{\mu} \qquad (2.28)$$

Where ρ is density of solute

υ is velocity

d_h is hydraulic diameter of pervaporation cell

μ is viscosity of feed

Membrane material

Chemical nature of membrane material has a large effect on permeation rate (Binning, Lee et al. 1961). Good membrane materials should have three important features: high chemical resistance, high sorption capacity and good mechanical strength. Furthermore, the interaction between the membrane and solution would also influence the membrane performance. For example, membranes that contain polar groups tend to flavor permeation of polar feed components (Buckley-Smith 2006) and solutes that have similar solubility parameter to the membrane are preferentially soluble in the membrane (Smitha, Suhanya et al. 2004).

Concentration polarization (CP)

Concentration polarization occurs in the membrane separator when the impermeable molecules are carried by bulk flow and are accumulated at the interface between liquid and membrane at feed side, causing the polarization layer, which lowers the permeation flux (Smitha, Suhanya et al. 2004, J. D. Seader 2011).

Coupling effect

Coupling effect is a result of the interaction force between molecule i and j that may increase or decrease diffusion of component i in mixture. For instance, the permeation of smaller molecules of i (which usually have high permeation rate) may be deterred when the molecules interact with the molecules of j which are larger. On the other hand, by the coupling effect, j may permeate more quickly by the influence of the higher permeating molecules of i (Isci, Sahin et al. 2006).

Plasticizing effect

As shown in Figure 2.11, plasticizing effect is caused by the interaction force between components of liquid mixture and membrane, which leads to an increase in the intermolecular distance and a decrease in inter- and/or intra-molecular forces. As a result, polymer swelling occurs, which then makes the permeabilities for all feed components increase and the selectivity decrease (Schmeling, Konietzny et al. 2010).

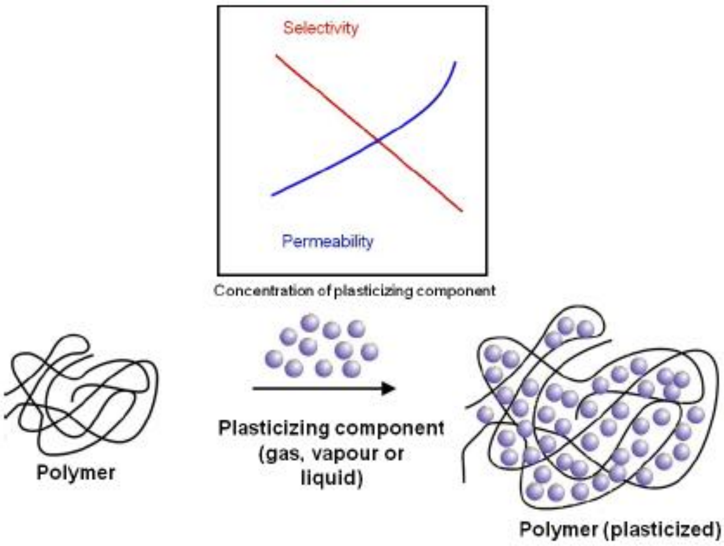


Figure 2. 11 Plasticization phenomenon and resulting effect on separation characteristics (Schmeling, Konietzny et al. 2010)

2.7 Literature reviews

Recovery of flavor compounds in fruit juice by pervaporation

The idea to recovery aroma compounds from fruit juice was a result of the need to concentrate fruit juice to prolong their-shelf life and to minimize the cost for storage and distribution. Recovery of flavors by pervaporation is not new. The process has been developed in laboratory for more than 15 years. Most of the studies were conducted using model solution because it is difficult to replicate all aroma compounds and to correlate the results with all the components in the real flavors (She and Hwang 2006).

Besides of membrane materials, in the performance of pervaporation process in the recovery flavor compounds is also influenced by operating conditions such as temperature, concentration, permeate pressure, feed flow rate and system design (Smitha, Suhanya et al. 2004). Reviews of literature on concentration of flavor compounds from fruit juices by pervaporation are summarized in Table 2.2.

Based on the literature review, membrane materials that have been used for concentration of aroma compounds in fruit juice are typically organophilic and hydrophobic membranes such as ethylene vinyl acetate (EVA), ethylene propylene dieneterpolymer (EPDM) and polyoctylmethylsiloxane (POMS). Of these, polydimethylsiloxane (PDMS) thin-film composite membrane is the most widely used due to its advantages such as having good thermal, chemical and mechanical stability, biocompatibility. Moreover it is nontoxic and can be easily and economically fabricated (Li, Verbiest et al. , Kim, Kim et al. 2009, Li, Verbiest et al. 2013).

Table 2. 2 Fruit juice studied on pervaporation aroma recovery

Fruit/Compounds	Membrane	Module	Operating range	Highlight	References
Apple/ Ethanol, Butanol, Isopentanol, Hexanol, Hexenal, tr-2-Hexenal, Butyl acetate, Isopentyl acetate, Hexyl acetate, Ethyl butanoate, Ethyl 2-methylbutanoate, Butyl butanoate	PDMS	PF	T 5 °C P3.75–4.5 mmHg F 17 L/h T 8 h	- This research wanted to found the possibility of using PV to concentrate aroma compounds in model mixture. - The result from the use of evaporation combined with PV and the use of PV only were presented very strong aroma-order, especially of esters and aldehydes. - Whereas, no apple aroma was perceptible from RO, then after combine with PV all aroma were presented but could not be calculated. - So, PV is seen to be a promising technique for recovery aroma compounds.	(Bengtsson, Trägårdh et al. 1989)

Fruit/Compounds	Membrane	Module	Operating range	Highlight	References
Pineapple and Passion fruit/ Ethyl acetate, Ethyl butanoate, Ethyl hexanoate, 1-Octen-3-ol	PDMS EPDM EVA	HF	T 25 °C P 3 mmHg F 3,000 kg/h	- The membrane between commercial and laboratory of flat and hollow fiber to recovery tropical fruit juice binary solutions were compared the capacities. - The results from experiment and simulation showed that EPDM membrane is the most effective.	(Pereira, Rufino et al. 2002)
Pineapple/ Ethyl acetate, Ethyl butanoate, Ethyl hexanoate, 1-Octen-3-ol	EPDM EVA	PF, HF	T 25 °C P 3 mmHg F 20-50 L/h t 1 h	- This research find the efficiency of flat and hollow fiber membrane which prepared in laboratory to recovery aroma model solution and compared the results with using simulation and experimental. - The results found that EPDM flat membrane presented the best performance in simulation and experimental.	(Pereira, Rufino et al. 2005)
Kiwifruit	PDMS	PF	T 25 °C P < 3.75 mmHg F 30 L/h.	- The PV was used to prevent aroma loss during production of clarified and concentrated real kiwifruit juice by an UF/OD and an UF/TSS. - The result showed after added PV directly from the fresh juice before any concentration, the majority of aroma compounds and nutrient were observed.	(Cassano, Figoli et al. 2006)

Fruit/Compounds	Membrane	Module	Operating range	Highlight	References
Strawberry/ Methyl butyrate, Ethyl butyrate, Methyl caproate, Butyl butyrate, Ethyl caproate, Linalool	PDMS	PF	T 30, 40, 50 °C P 3, 6 mmHg F 6.6 m/s	- This research studied the effect of feed temperature, concentration and permeate pressure in PV model solution - The achievement from the operating found that when increased in feed temperature or decreased in permeate pressure, the mass flux and selectivity increased. - And feed concentration increased in led to higher in organic flux but lower in selectivity.	(Isci, Sahin et al. 2006)
Orange/ ethyl acetate, ethyl butyrate, trans-2-hexeanal, octyl aldehyde, linalool, α-terpineol	PDMS	PAF	T 20 °C P 15 mmHg F 472 ml/m t 7.3 h	- This research use bath pervaporation to studied material balance to find flavor loss during process, investigate the behavior of their flavor compounds. and process simulation is used to recovery performance prediction and future process scale up. - The results showed that a considerable amount of flavor compounds could be recover at short time to reduced flavor loss rate. - Acetate and aldehyde exhibited higher enrichment factors than alcohol due to higher Henry's law and affinity with membrane. - The scale up process with larger membrane area and short operating time will be beneficial for reduced loss rate.	(She and Hwang 2006)

Fruit/Compounds	Membrane	Module	Operating range	Highlight	References
Orange/ ethyl acetate, ethyl butyrate, hexenal, linalool, limonene, α-terpineol	PDMS	PAF	T 25, 40, 50 °C P 1, 10, 20, 30, 40 mmHg Re 500, 1000, 2000, 2500 L/h t 10 h	- The objectives of this process are to investigate the effect of key parameter on pervapration process. - The results showed feed flow rate had no significant to flux and selectivity but feed temperature is the key parameter to increases flux. - Permeate pressure increased, enrichment factor of ethyl acetate, ethyl butyrate and hexenal increased, whereas linalool, limonene and α-terpineol had contra behavior.	(Aroujalian and Raisi 2007)
Bilberry/ E-2-Hexen-1-ol, n-Hexanol, E-2-Hexen-1-al, Linalool, Phenyl acetatealdehyde, Benzyl alcohol, Z-3-Hexene-1-ol, Ethanol, Water	PDMS	HF	ND	- This work developed math model simulation of PV which used as removed VOCs from waste water to predict to the behavior of PV separation aroma compounds from aqueous solution. - The results found that, higher membrane thickness resulting higher enrichment factor whereas partial fluxes decrease considerably.	(Diban, Urtiaga et al. 2008)

Fruit/Compounds	Membrane	Module	Operating range	Highlight	References
Bilberry/ trans-Hex-2-en-1-ol, Ethanol, Water	PDMS	HF	T 35-50 ℃ P < 0.75 mmHg t 7 h	- This work investigated the feasibility of PV to concentrate impact aroma compounds in mixture and studied the influence optimal performance of the system. - The results showed the very selective toward trans-Hex-2-en-1-ol leading to high enrichment factor. - And feed flow rate did not influence the flux. - Further it found that the main resistance located in the membrane.	(García, Diban et al. 2008)
Lemon α-pinene, β-pinene, Limonene	POMS	PF	T 25, 40, 60 ℃ P 1, 20, 40 mmHg Re 500, 1500, 2300, 2500 L/h t 6 h	- The research determined the effect of some operating parameter to recovery real juice. - The results found that, the decreasing permeate pressure increase both flux and enrichment factor. - While an increase in feed temperature more significantly increasing water flux than aroma compounds, as a result lower enrichment factor. - And the feed flow rate has not significant effect on PV process.	(Rafia, Aroujalian et al. 2011)

Note: PV = Pervaporation, PF = Plate and Flame, HF = Hollow Fiber, EVA = ethylene vinyl acetate, EPDM = ethylene propylene diene terpolymer, POMS = polyoctylmethylsiloxane, PDMS = polydimethylsiloxane, UF = Ultra filtration, OD = Osmotic distillation, TSS = Traditional vacuum evaporation

CHAPTER III

MATERIALS & METHODS

3.1 Chemicals

1. Orange juice model solution consists of:
   - Ethyl butyrate 99.8% was purchased from Tokyo Chemical Industry Co.,LTD
   - trans-2-Hexenal 99.6% was purchased from Merk KGaA, Germany
   - 1-Hexanol was purchased from Merk KGaA, Germany
   - D-Limonene was purchased from Merk KGaA, Germany
2. Liquid-liquid extraction solvent include of:
   - n-Pentane 99% was purchased from Merk KGaA, Germany
   - Dichloromethane 99% was purchased from Merk KGaA, Germany
3. Internal standard is 1-Pentanol 99% was purchased from Merk KGaA, Germany
4. Dry ice from Dry ice Thai
5. De-Ionized water

3.2 Materials

3.2.1 Orange juice model solution

Orange juice model solutions at various concentrations were prepared for the study of effect of pervaporation condition on separation of each component in various solution systems. The composition of each model solution is shown in Table 3.1.

Table 3.1 Compositions of flavor compounds in orange juice model solution

Flavor compounds	Concentration (ppm)		
	Original orange juice*	75-fold	150-fold
Ethyl butyrate	5.26	394.50	789.00
trans-2-Hexenal	2.94	220.50	360.00
1-Hexanol	2.45	183.75	367.50
D-limonene	69.31	5,198.25	1,0396.50

* original orange juice concentration adapted from the studies of Selli, Cabaroglu et al. , 2004 and Aroujalian and Raisi, 2007.

3.2.2 Apparatus

The equipment used for the pervaporation includes:

1. Ceramic tubular polydimethylsiloxane membrane with effective membrane area 0.005 m^2 and membrane thickness 2 μm, code PVM-035 from PERVATECH, Netherland
2. Vacuum Gauges code KVC 450 from KVC CO.,LTD
3. Vacuum pump, code E2M1.5 from EDWARDS (vapor flow rate 1.8 m^3/h)
4. Peristaltic pump of Master flex L/S code Easy-Load II model77200-60 and 77200-62 from Cole-Parmer Instrument
5. Three condensation units that are connected in series
6. 1 liter tank of duran
7. Silicone tube size 24 (Master flex, N.C.R Rubber Industry CO.,LTD)
8. TYGON Tubing size 16 (Master flex from N.C.R Rubber Industry CO.,LTD)
9. Water bath (Memmert, Germany)

10. Thermocouple code Pt100 from Engtemp
11. Temperature indicator from Digicon

Equipment used for the extraction of the permeate includes:

1. Centrifuge code U-320 from BOECO, Germany
2. Vortex Genie2, code G-560E from SCIENTIFIC INDUSTRIES, INC., USA

3.2 Methods

3.3.1 Pervaporation process

A schematic diagram of the apparatus for pervaporation by tubular membrane module employed in this study is shown in Figure 3.1.

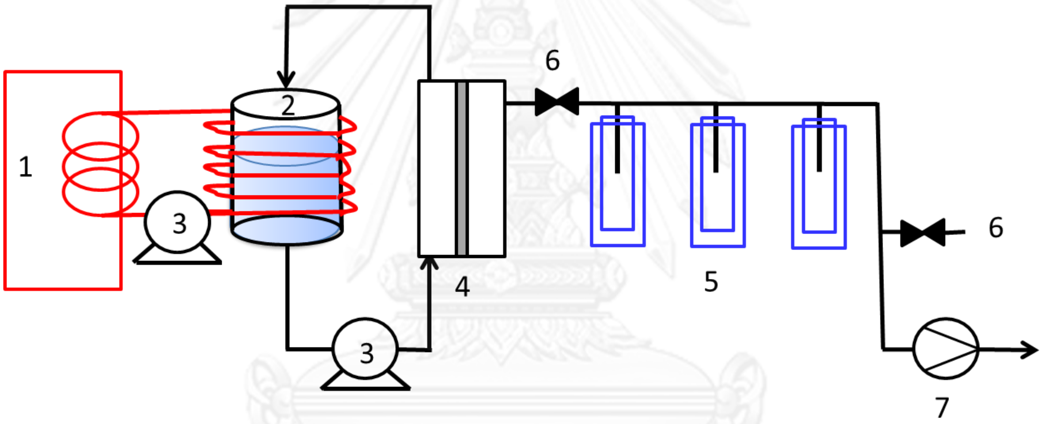


Figure 3. 1 A schematic diagram of pervaporation experimental set-up: (1) water bath; (2) feed tank; (3) feed pump; (4) PDMS tubular module; (5) cold trap; (6) valve and (7) vacuum pump

Before each experiment, air is eliminated from the system by turning on the vacuum pump for about 30 minutes. 1 liter of model solution contained in the tank was then circulated into the shell side at constant flow rate of 15 L/h. The temperatures of the system were kept constant in the range of 30-45 °C until the end of the experiment by a water bath with silicone tube wrapped around the feed tank, module and feed tube. Vacuum was provided on the tube side of the tubular membrane module, with the permeate pressure maintained in range 5-15 mmHg.

The effects of operating parameters on the pervaporation performance were studied. The parameters include operating time, feed temperature and permeate pressure. All trials were conducted at the fixed feed flow rate of 15 L/h.

Initially, the appropriate pervaporation time was investigated, at feed concentrations, varied from that of conventional orange juice, 75 and 150 folds of the original orange juice (in which the detail of composition shown in Table 3.1). For this purpose, the feed temperature and permeate pressure were fixed at 30 °C, 5 mmHg, respectively. Subsequently, the obtained optimal pervaporation time was fixed for the study to find effects of other parameters. The summary of variables in this study is shown in Table 3.2.

Table 3.2 The summary of operating condition

Variables	Fix	Vary
Operating time	Feed concentration of conventional orange juice ,75 folds and 150 folds of conventional orange juice Feed temperature 30 °C Permeate pressure 5mmHg Feed flow rate 15L/h	Operating time during 1-10h
Feed concentration/ Feed temperature/ Permeate Pressure	Operating time Flow rate 15L/h	Feed concentration of conventional orange juice ,75-fold and 150-fold of the original orange juice Feed temperature 30, 40 and 45 °C Permeate pressure 5, 10, 15 mmHg

The permeate vapor was condensed and stored in cold traps containing a dry ice (temperature -79°C) and the collected condensed permeate was weighed. After that, the permeate was extracted with solvent before analyzed the content using a gas chromatography with flame ionize detector.

3.3.2 Liquid-liquid extraction

As the permeate could not be directly analyzed by GC-FID because of its high content of water, liquid-liquid extraction was used to solve this problem.

The condensed permeate collected in a tube was extracted two times with 3 ml of n-pentane : dichloromethane (2:1) (Selli, Cabaroglu et al. 2004). After vigorously shaken for 5 minutes using a vortex mixer in order to extract the volatile fraction, the mixture was centrifuged at 4000 rpm for 5 minutes to separate the extract phase from the water phase (Tuşa, Moldovan et al. 2012). After that the sample was frozen at -20 °C (Tønder, Petersen et al. 1998). When the water phase was frozen, the extract phase was removed and the volume was adjusted to 1 ml by drying nitrogen. In to this sample, 1μl of 1-pentanol internal standard was added prior to GC-FID analysis (Olsson and Trägårdh 1999).

3.3.3 Gas chromatography analysis

The extracts were analyzed with Gas Chromatography (GC) from Agilent 6890. The GC was equipped with Flame Ionize Detector (FID) and HP-5 capillary column (30 m x 0.32 mm i.d. x 0.1 μm film thickness) (Agilent Technology, US). Helium with column head pressure of 10 psi with flow rate 2.2 ml/min was used as a carrier gas. The GC initial temperature of oven was kept with 40 °C for 3 minutes and raised up to 160 °C at the rate of 30 °C /min and keep of constant for 2 minutes, then ramp to 220 °C at the rate of 5°C/min and kept constant. The injector and detector are 220 and 250 °C, respectively. The injection volume was 1 μl and the injector operated in the split mode 10:1 (Aroujalian andRaisi2007).

CHAPTER IV

RESULTS AND DISCUSSIONS

In this research, commercial asymmetric tubular membrane made of polydimethylsiloxane polymer coated on a ceramic support layer was used to recover flavor compounds of orange juice model mixture in a batch pervaporation system. The parameters investigated include operating time, feed concentration, feed temperature and permeate pressure.

4.1 Evaluation of time to reach steady state

Pervaporation was conducted in a system as described in section 2.2.3 where the retentate was recycled to the feed reservoir. Figure 4.1 shows the time profiles of the total flux for pervaporation with different feed concentrations. It can be seen from this figure that the permeation flux at the first hour was the highest and decrease at the second hour as the membrane started to become completely wetted by the circulation of feed solution. The steady state seemed to be reached within the first 2 hours. In subsequent experiments, 6 hours was allowed to ensure that the system has reached steady state for all experimental conditions.

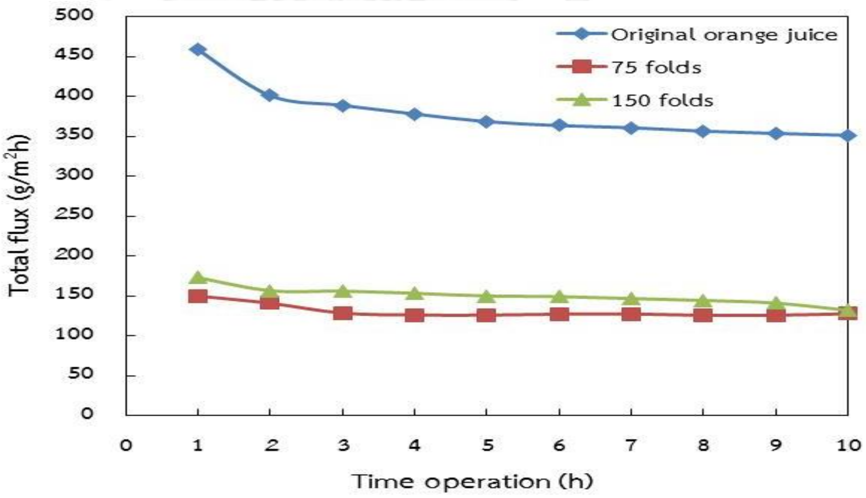


Figure 4. 1 Time profile of total flux for pervaporation at 30 °C feed temperature, 15 mmHg permeate pressure and at various feed concentrations

4.2 The effect of feed concentration and feed temperature

4.2.1 The effect of feed concentration and feed temperature on permeation flux

To evaluate the effects of feed concentration and temperature on pervaporation performance, three different feed concentrations were investigated: original orange juice concentration, 75-fold and 150-fold of the original orange juice concentration. The temperatures were varied in the range of 30 °C to 45 °C at various permeate pressure (5-15 mmHg), whereas the feed flow rate and the operating time were fixed at 15 L/h and 6 hours, respectively.

Feed Concentration effect:

Increase in feed concentration resulted in increase in the partial flux of different flavor compounds as shown in Figure 4.2 (a-d). As the feed concentration increased, the activity of flavor compounds also increased which leads to higher interaction between flavor compounds and membrane, and as a result the rate of sorption increased. In addition, the high concentration of flavor compounds inside the membrane will increase lead to membrane swelling, causing the free volume in membrane to increase, and resulted in higher diffusion rate (called plasticization phenomena), and thus increased permeation flux (Raisi, Aroujalian et al. 2009).

When considered the permeation fluxes of each aroma compounds through the membranes, from the effect of feed concentration, the permeation flux of D-limonene should greater than ethyl butyrate, trans-2-hexanal and 1-hexanol, respectively. Nevertheless, at some operating conditions, the permeation flux of 1-hexanol was larger than trans-2-hexenal as their initial feed concentration are very close and the uncertainty of the experimental results.

However, the more concentrated component did not always give the highest flux. As seen in Figure 4.3, with the feed having the same concentration as the original orange juice, the partial flux of D-limonene was the smallest even if its composition is the highest. While on the other hand, at higher feed concentrations (75 folds and 150 folds of the original orange juice concentration), the permeation flux D-limonene was found to be the highest compared with the other components. At higher feed concentrations, the permeation flux is affected by the concentration gradients, while at lower concentration, the permeability seemed to have more influence on the permeate flux. Permeability of components through the membrane depends on the solubility and diffusivity. The solubility of penetrant into the membrane surface is related to the solubility parameter, molecular size, polarity and component structure whereas the diffusivity is related to volatility of flavor of compounds and membrane structure. Considering the solubility parameter of ethyl butyrate and D-limonene shown from Table 4.1, ethyl butyrate has similar solubility parameter to the PDMS membrane and is more volatile than D-limonene. This could be a reason for higher ethyl butyrate flux at low feed concentration, compared with D-limonene, even if the composition in the feed is much lower.

Aroujalian and Raisi, 2007 conducted a study on pervaporation of orange juice model solution through a PDMS membrane. The same feed concentrations were used for both ethyl butyrate and D-limonene and the process was carried out at Re 2000 and the permeate pressure of 1 mmHg. Despite low feed concentration, their results showed that the permeation flux of D-limonene show the highest about 0.32 g/m^{2}h and the permeation flux of ethyl butyrate are about 0.02 g/m^{2}h (Aroujalian and Raisi 2007).

Table 4. 1 Some properties of flavor compounds and membrane

Flavor compounds and Membrane	Concentration of original orange juice (ppm)	Vapor pressure @20°C (mmHg)	Solubility parameter (Cal/cm^3)$^{0.5}$
Ethyl butyrate	5.26	12.5	8.5
D-limonene	69.31	1	3
Polydimethylsiloxane	-	-	8.1

As shown in Figure 4.2 (e), the water flux was close to total flux (Figure 4.2 (f)), since for the system of interest, the feed concentration is rather low, thus the interaction between water/membrane is higher than aroma compounds/membrane. In addition, water has a smaller size than aroma compounds, the water cluster can more easily permeate through the membrane than aroma compounds. Therefore at higher feed concentration, water flux is expected to be decreased as shown in Figure 4.2 (e). However, the swelling of membrane occurred at high feed concentrations can also lead to higher permeation of water through the membrane. Thus, at 150 folds of the original orange juice concentration, the membrane swelling effect was higher than that for the lower concentration (75 folds of the original orange juice). As a result the water flux for feed concentration at 150 folds of the original orange juice is higher.

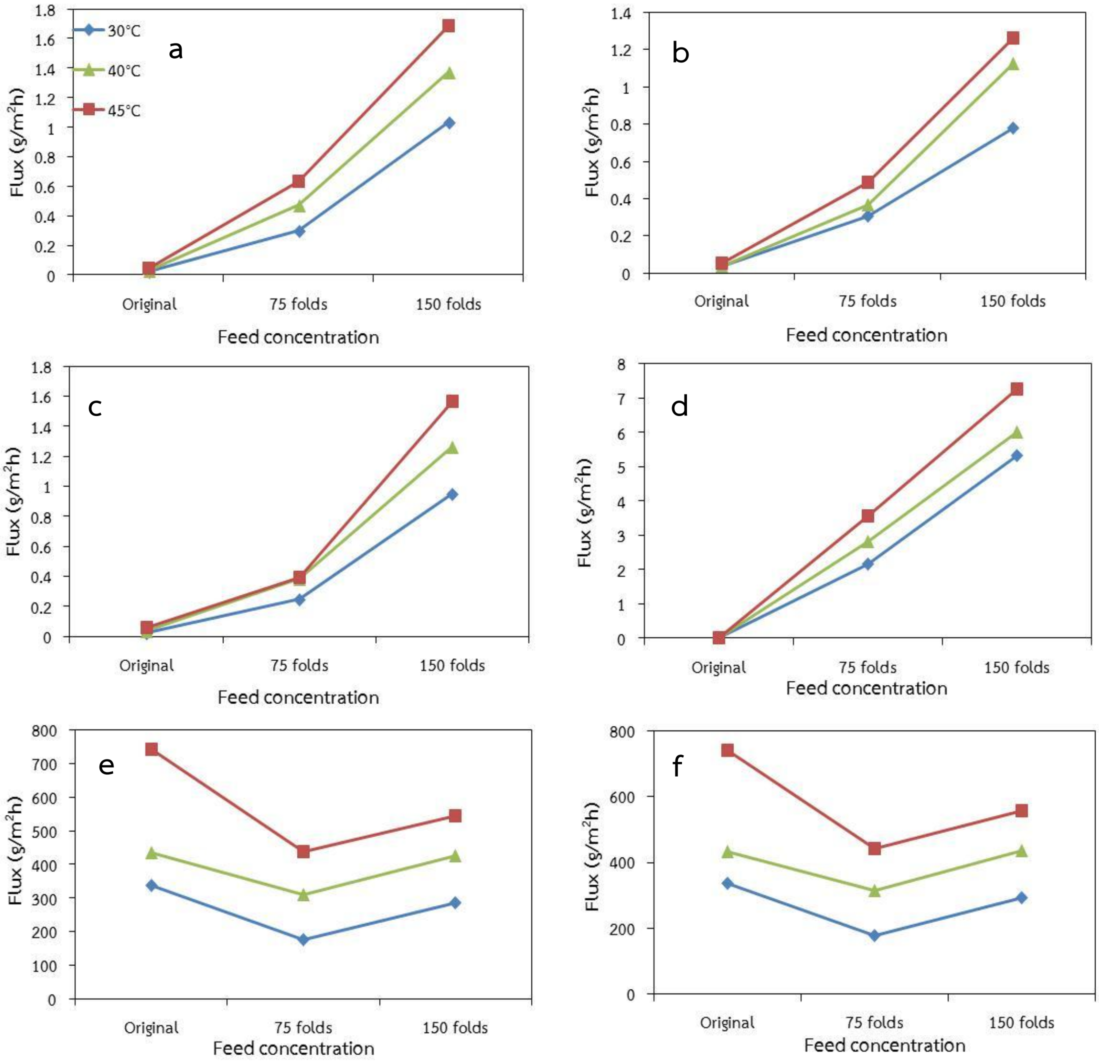


Figure 4. 2 The effect of feed concentration and feed temperature on permeation fluxes at and permeate pressure 5 mmHg of (a) ethyl butyrate, (b) trans-2-hexenal, (c) 1-hexanol, (d) D-limonene, (e) water and (f) total flux

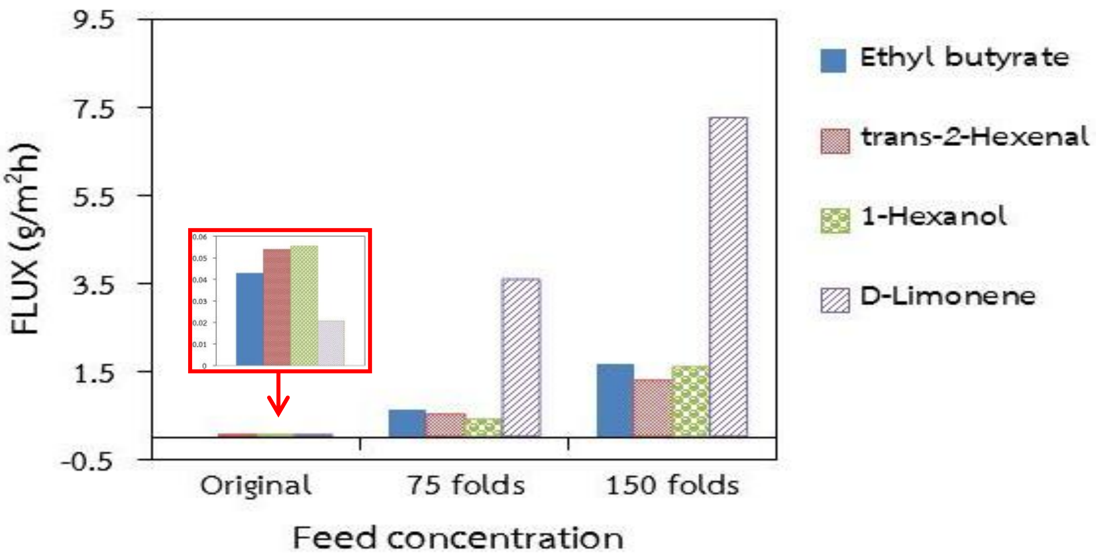


Figure 4. 3 The effect of feed concentration on permeation flux at feed temperature 45 °C, permeate pressure 5 mmHg and feed flow rate 15L/h

Feed temperature effect:

Temperature is an important parameter which directly affects diffusivity, viscosity and permeability, respectively (Garcia Villaluenga and Tabe-Mohammadi 2000).

As shown in Figure 4.2, the increase in feed temperature leads to higher permeation flux of each flavor compound due to the influence of temperature on characteristics of the membrane and the solution mentioned above.

As the range of feed temperature in this studied was larger than Tg (-125 °C) of PDMS membrane (Lötters, Olthuis et al. 1997), when increasing the feed temperature, the segmental motions of polymer chains in amorphous region of the membrane are randomly moved. The frequency and amplitude of polymer jumping chains increased, and accordingly, this increases the free volume within the membrane, causing the membrane swelling, which leads to higher solute diffusion rate of all compounds through the membrane, and thus the increase in permeation flux

(Aroujalian and Raisi 2007). Therefore, the permeation flux of each aroma compounds at 45 °C was higher than those at 40 °C and 30 °C, respectively.

Another reason is related to equilibrium vapor pressure of feed solution and the energy requirement for phase change. In pervaporation process, the permeating species requires energy for vaporization from liquid to vapor phase. Therefore the increase in feed temperature help affords the energy for phase change, then the vapor pressure of pure components at the feed side will increase whereas the vapor pressure at the permeate side was not affected. This therefore caused the increasing the driving force and resulted in the higher flux (Rafia, Aroujalian et al. 2011, Kittur, BK et al. 2013).

The increase in feed temperature generally affects more significantly the compounds with higher vapor pressure. Therefore temperature effect on ethyl butyrate should the largest, followed by trans-2-hexenal, D-limonene and 1-hexanol, respectively. The results in this study indicated that the change of permeation flux of ethyl butyrate and trans-2-hexenal are similar because of their relatively similar vapor pressures. However, the change of permeation flux for D-limonene was found to be the lowest although it is more volatile than 1-hexanol. This may be due to the fact that the molecular size D-limonene is larger than that of 1-hexanol, making it more difficult to transport through the segments of polymer chain in the membrane, thus resulting in the lowest change in permeation flux.

The effect of feed temperature on permeation flux in this research is consistent with other researches such as that seen for the recovery flavor compounds in pomegranate juice with PDMS membrane. It was found in this research that the increase in feed temperature from 30 to 45 °C led to significant increase in permeation flux of each flavor compounds (Raisi, Aroujalian et al. 2008).

The variation of permeation flux with the temperature was found to follow the Arrhenius relation in Equation (2.27). As the permeation flux depends on the activation energy of permeability and heat of vaporize for phase change, this relation is generally used to characterize the effect of temperature on permeability and driving force on the permeate (Feng and Huang 1996).

$$J = J_0 \exp\left[\frac{-E_a}{RT}\right] \tag{2.27}$$

The plot of logarithms of total flux versus the reciprocal temperature according to Arrhenius relation are shown in Figure 4.4 for pervaporation at various feed concentrations, at 5 mmHg permeate pressure. The apparent activation energy of permeation flux (E_J) can be determined from the slope of this plot, which is $-\left(\frac{E_J}{R}\right)$. Table 4.2 summarized the values of activation energy for all components obtained from experimental data for various feed concentrations.

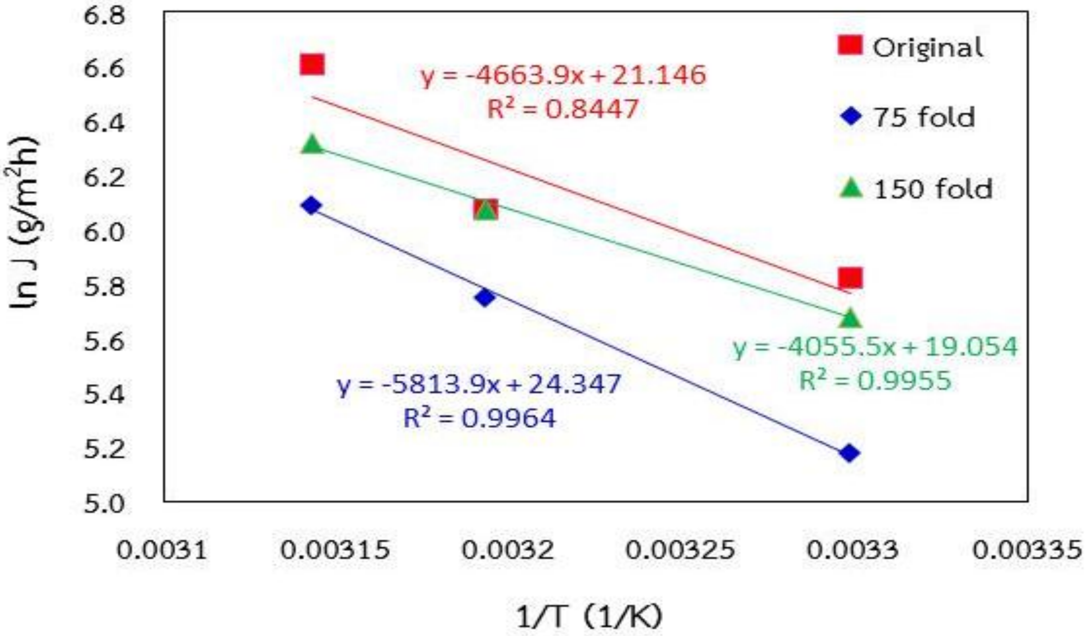


Figure 4. 4 Arrhenius type relation on total flux of various concentration at permeate pressure 5 mmHg

Table 4. 2 Activation energies which calculated from Arrhenius plot

Components	Original			75 fold			150 fold		
	P 5	P 10	P 15	P 5	P 10	P 15	P 5	P 10	P 15
	E_J (kJ/mol)			E_J (kJ/mol)			E_J (kJ/mol)		
Ethyl butyrate	22.86	36.13	30.86	38.64	35.81	31.63	25.50	40.95	37.37
trans-2-Hexenal	23.16	29.38	45.11	22.81	22.21	17.93	26.41	43.89	43.76
1-Hexanol	37.99	31.73	39.47	25.17	22.21	16.59	26.16	43.20	45.62
D-Limonene	29.21	36.91	75.42	25.43	19.24	10.18	15.32	24.85	22.80
Water	39.99	54.57	54.57	48.65	45.90	41.54	34.08	51.31	47.25
Overall	39.98	54.56	60.81	48.34	45.56	41.16	33.72	50.84	46.85

As can be observed in this table, all values of activation energy are positive, so increase in feed temperature resulted in higher permeation flux. Moreover, the apparent activation energy of water is higher than the flavor compounds, indicating that this membrane was less selective of water than flavor compounds. Owing to smaller affinity between water and membrane, more energy is required for water molecules to transport across the membrane. It can be concluded from this result that water is more sensitive to temperature change than flavor compounds. Moreover, permeate pressure also affects activation energy, such that the increase in permeate pressure led to increase in activation energy as the decrease in the driving force from the pressure difference makes it more difficult for the liquid to vaporize.

The same trend of activation energy also observed in the recovery of flavor compounds in lemon juice, the activation energy at 1 mmHg of water, α-pinene, β-pinene and D-limonene were 28.58, 15.56, 10.09 and 37.61 kJ/mole, respectively (Rafia, Aroujalian et al. 2011).

4.2.2 The effect of feed concentration and feed temperature on selectivity

Figure 4.5 show the plot the separation factor for pervaporation at different feed concentrations and at various feed temperatures. As seen from Figure 4.5 (a-c), the separation factor of flavor compounds decreased as the feed concentration increased since water flux became higher due to the effect of the swollen membrane. Therefore the selectivity of ethyl butyrate, trans-2-hexenal and

1-hexanol decreased with increasing feed concentration. From experiment, similar decrease was seen in the selectivity of trans-2-hexenal and 1-hexanol as they have nearly the same initial feed concentrations. Their decrease in selectivity was also found to be lower than that of ethyl butyrate.

However, the opposite was observed for D-limonene as seen in Figure 4.5 (d). The selectivity of D-limonene increased as feed concentration increased because of the higher flux of D-limonene at higher feed concentration. Nevertheless, the separation factor value of D-limonene is still considered very low when compared with other compounds possibly due to small permeability of D-limonene as discussed earlier. When compared with the concentration present in the feed, the selectivity of the compound therefore became small. The fact that the selectivity is lower than 1 for the original feed concentration suggested that such condition is not suitable for pervaporation of D-limonene.

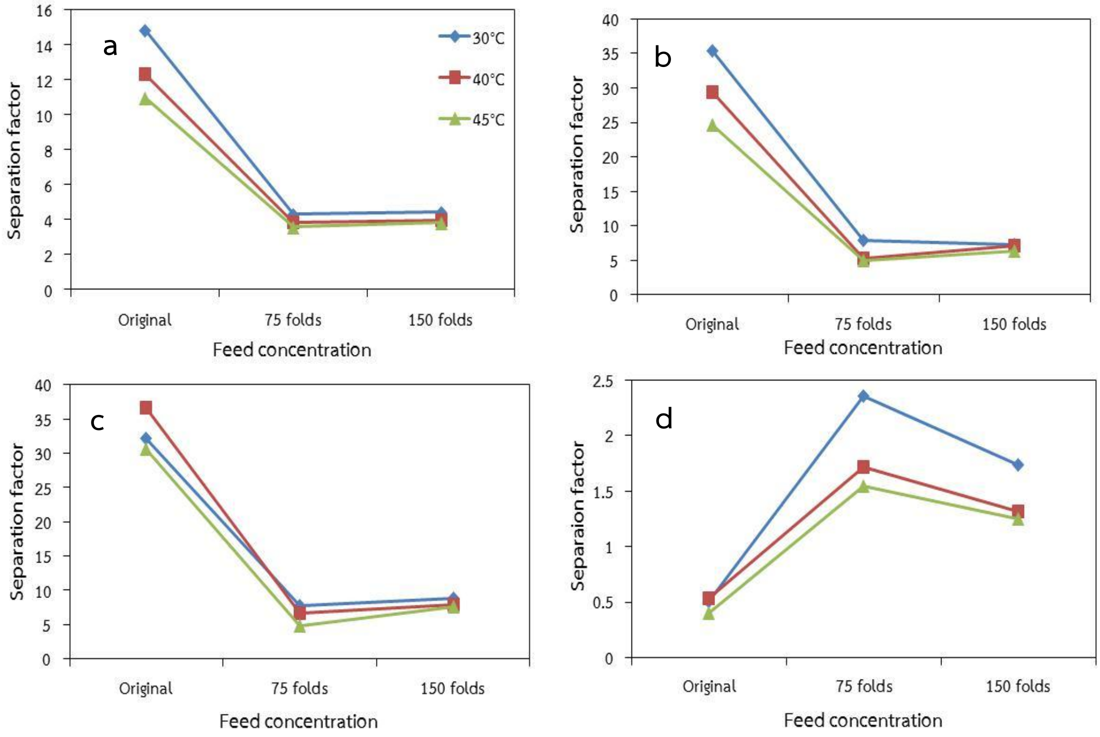


Figure 4. 5 The effect of feed concentration and feed temperature on separation factor at permeate pressure 5 mmHg of (a) ethyl butyrate, (b) trans-2-hexenal, (c) 1-hexanol and (d) D-limonene

Also seen from Figure 4.5, increase in feed temperature leads to the smaller selectivity of the flavor compounds at all feed concentrations, and the order of selectivity was found to be 1-hexanol > trans-2-hexenal > ethyl butyrate >> D-limonene. This effect is more clearly seen at the low feed concentration. An increase in feed temperature results in higher permeability of flavor compounds, while at the same time facilitates water permeation. And since water is more sensitive to temperature change than other flavor compounds due to the higher activation energy, thus the compound selectivity was lower as the temperature increased.

The same trend in the selectivity decrease due to the increase in feed temperature was observed in the recovery of lemon juice (Rafia, Aroujalian et al. 2011). In this research, the selectivity of α-pinene, β-pinene and D-limonene decreased significantly as increase feed temperature from 25 to 60 °C.

4.2.3 The effect of feed concentration and feed temperature on recovery percentages

The effect on recovery percentages of all flavor compounds by feed concentrations and feed temperatures are shown in Figure 4.6. From this figure, the recovery percentages of all flavor compounds was found to rise as the feed temperature increased due to higher permeation rate. Then the percentage recovery was generally found to be proportional to the permeation flux, the order from high to low recovery percentage was therefore 1-hexanol > trans-2-hexenal > ethyl butyrate >> D-limonene.

Since recovery percentage is the ratio of the amount of penetrants and the amount of the corresponding flavor compounds at the beginning, the recovery percentage therefore follows the same trend as that of the separation factor. That is, the recovery percentages decreased as the feed concentration increased for 1-hexanol, trans-2-hexenal and ethyl butyrate, whereas for D-limonene, the recovery percentages increased as the feed concentration increased. It is also noted that the recovery percentages for D-limonene by this pervaporative system was the smallest compared with the other compounds.

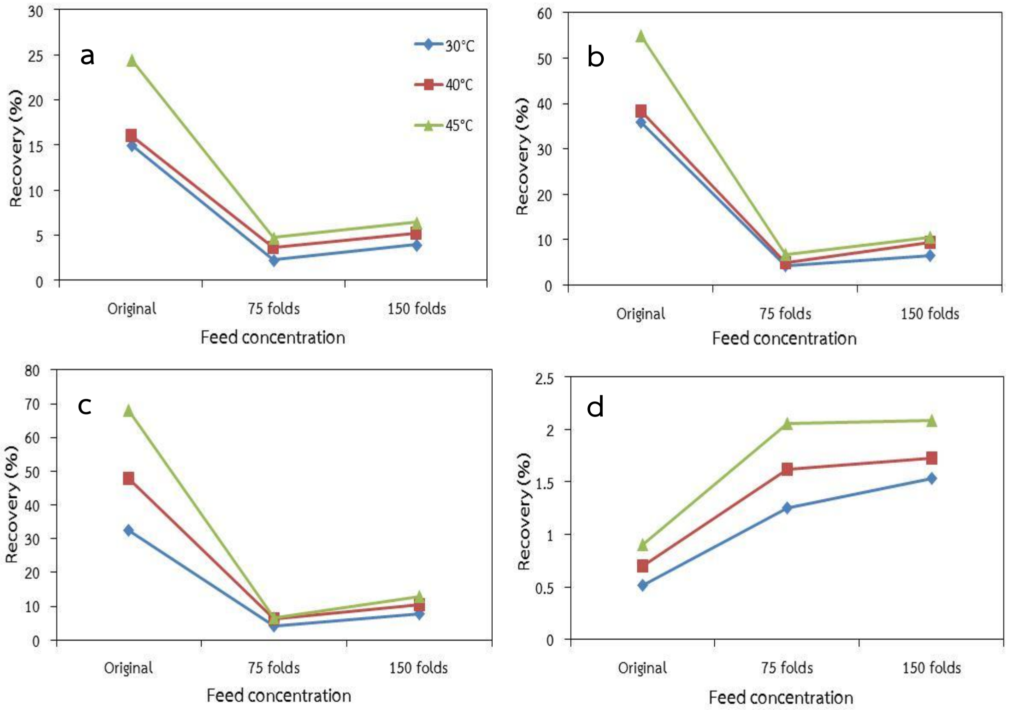


Figure 4.6 The effect of feed concentration and feed temperature on recovery percentages at permeate pressure 5 mmHg of (a) ethyl butyrate, (b) trans-2-hexenal and (c) 1-hexanol and (d) D-limonene

4.2.4 The effect of feed concentration and feed temperature on pervaporation separation index (PSI)

Generally, permeation flux of flavor compounds is inversely proportional to the compound selectivity. Therefore, the pervaporation separation index (PSI) was more often used in membrane separation processes as a criterion for the selection of appropriate conditions.

The effect of feed concentration and feed temperature on PSI is shown in Figure 4.7. From this figure, the order of the PSI values from higher to lower was: trans-2-hexenal > 1-hexanol > ethyl butyrate >> D-limonene. Furthermore, when feed temperature increased, the PSI values of ethyl butyrate, trans-2-hexenal and 1-hexanol decreased, that of D-limonene increased.

In addition, the PSI values decreased for higher feed concentration following the similar trends the selectivity. It should be noted that the negative value of PSI for

D-limonene at low feed concentration was due to the fact that to increase the PSI value of the key flavor compound like D-limonene, high feed concentration would be more appropriate, however with the expense of lower PSI values for the other compounds.

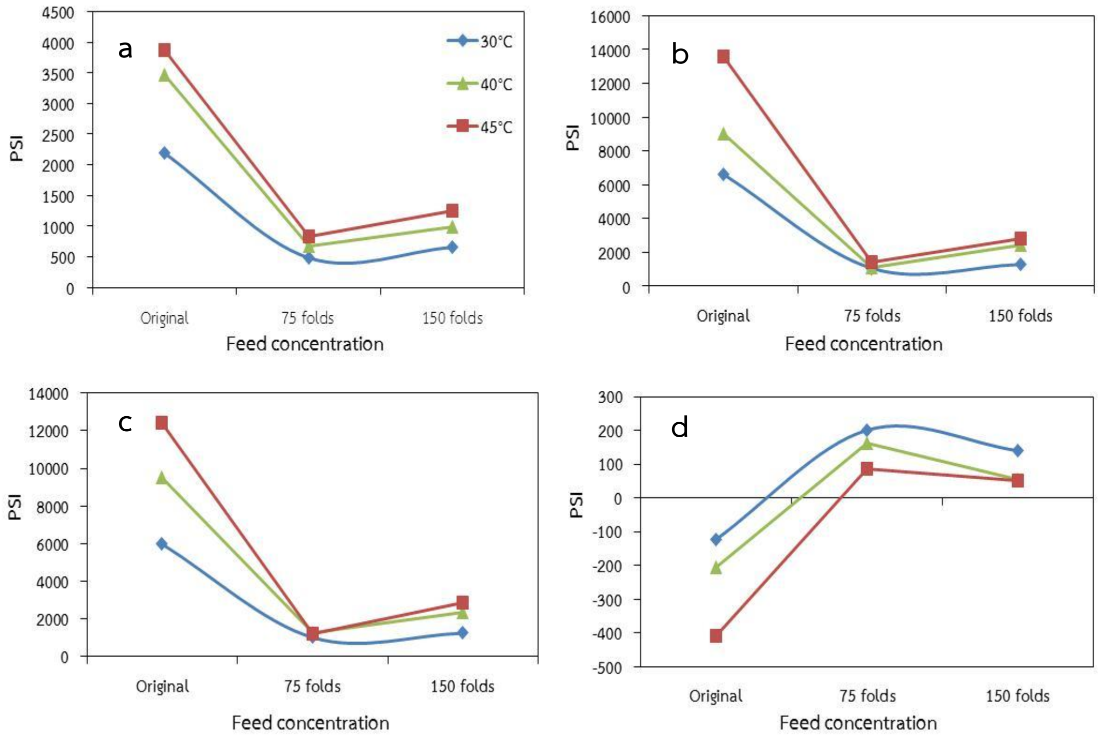


Figure 4. 7 The effect of feed concentration and feed temperature on pervaporation separation index at permeate pressure 5 mmHg of (a) ethyl butyrate, (b) trans-2-hexenal, (c) 1-hexanol and (d) D-limonene

4.3 The effect of permeate pressure

4.3.1 The effect of permeate pressure on permeation flux

The permeation flux of each flavor compounds was plotted against the permeate pressure for pervaporation at 45 °C of the orange juice model mixture at the concentration of the original orange juice as shown in Figure 4.8. From this figure, the partial flux of all flavor compounds reduced slightly as the permeate pressure increased. The similar trends were observed for the feed concentrations of 75 folds and 150 folds of the original orange juice. This is because an increase in permeate pressures leads to the reduction in the chemical potential gradient across the membrane.

In addition, the increasing of flux as the reduction of permeate pressure can be described base on pseudophase-change solution-diffusion model (Shieh and Huang 1998). This model describes how the liquid transfer depth within the membrane is affected by permeate pressure. Lower permeate pressure induces a higher pressure gradient within the membrane, and thus decreases the liquid transfer depth, while at higher permeate pressure, the liquid transfer depth is higher as liquid penetrates into the vapor transfer space. Therefore at higher permeate feed pressure, mass transfer becomes dominated by the slower liquid transfer, decreasing the total permeation rate (Aroujalian and Raisi 2007).

Pressure has a larger effect on the compounds of low volatilities, thus flavor compounds with low vapor pressures than that of water would be more greatly affected by the change of permeate pressure. As the permeate pressure increased, the decrease in permeation flux of 1-hexanol should therefore be larger than those of D-limonene, trans-2-hexenal and ethyl butyrate, respectively. However, it was found from the results in this study that the permeation flux of D-limonene was the most sensitive to the permeate pressure change, followed by 1-hexanol, whereas trans-2-hexenal and ethyl butyrate were less sensitive to the change in permeate.

The effect of permeate pressure on permeation flux in this research is consistent with the study on the recovery flavor compounds in orange juice model mixture with plate and flame PDMS membrane (Aroujalian and Raisi 2007). In this research permeate pressure was varied between 1 and 40 mmHg at fixed feed temperature 25 °C and Re 2000. It was found that an increase the permeate pressure decreased both the total flux and partial flux of each compounds. The behavior of aroma compounds such as D-limonene and linalool were also found to be more sensitive to the change of permeate pressure because due to their low vapor pressures. On the other hand, ethyl butyrate, ethyl acetate, hexanol and α-tepineol were less sensitive to permeate pressure as a result of higher vapor pressure.

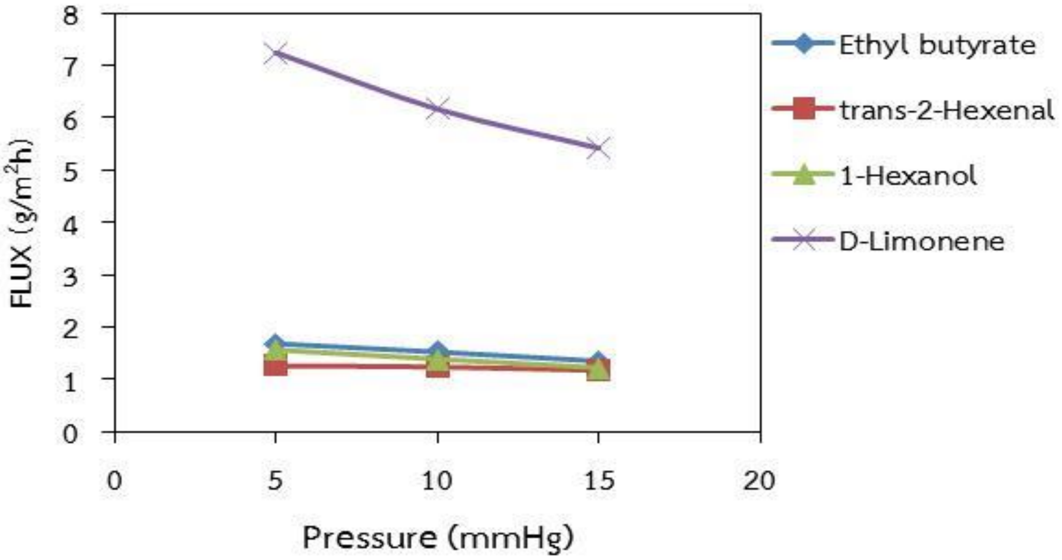


Figure 4. 8 The effect of permeate pressure on partial flux from 150 folds of original orange juice concentration at feed temperature 45 °C

4.3.2 The effect of permeate pressure on selectivity

Figure 4.9 shows that the separation factors of some flavor compounds such as ethyl butyrate, 1-hexanol and D-limonene decreased as the permeate pressure increased from 5-15 mmHg (for feed concentration of 150 folds of that of original orange juice). The effect of permeate pressure on selectivity can be described in terms of relative volatility, molecular size and hydrophobicity. From Equation (3.18) and vapor pressure of each flavor compound in Table A-1, when the permeate pressure is increased, the difference between vapor pressure of each compound and the permeate pressure decreased. Therefore, the permeation flux was decreased which led to the decline in selectivity. As seen from Figure 4.9 at original orange juice concentration the change in selectivity of 1-hexanol was greater than that of the other flavor compounds, due to its lowest vapor pressure. The same trends could also be observed for at the other two feed concentrations and other research work reported for pervaporation of lemon juice (Rafia, Aroujalian et al. 2011), pomegranate (Raisi, Aroujalian et al. 2008) and other orange research (Aroujalian and Raisi 2007).

Although the selectivity of trans-2-hexenal is also expected to decrease with increasing permeate pressure, the separation factors of the compound shown in Figure 4.9 was found to increase slightly with the same increase in permeate pressure. However this slight increase may be is within the uncertainty of the experimental results.

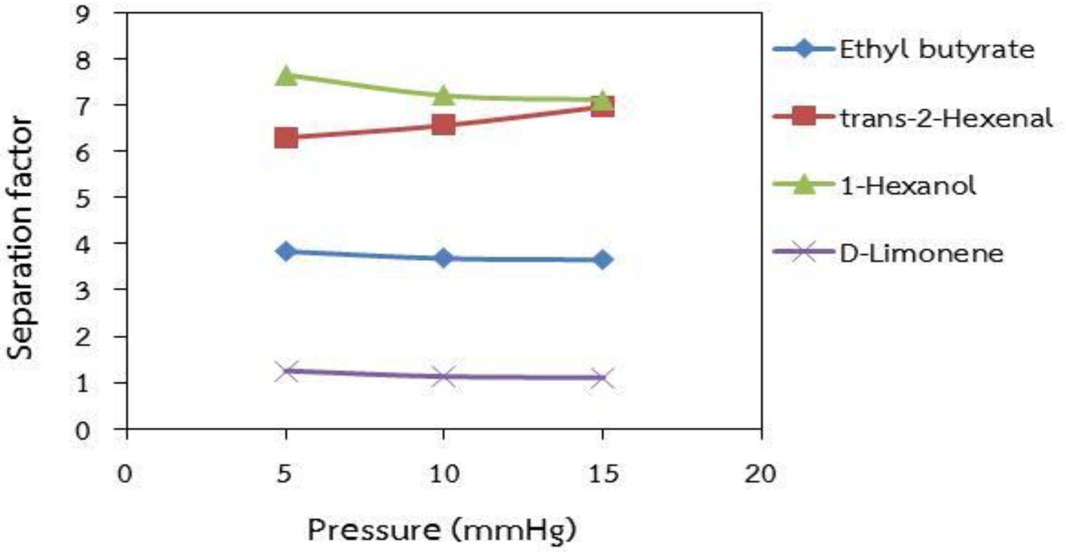


Figure 4. 9 The effect of permeate pressure on separation factor from 150 folds of original orange juice concentration at feed temperature 45 °C

4.3.3 The effect of permeate pressure on recovery percentages and pervaporation separation index

The recovery percentage of all flavor compounds for the feed concentration of 150 folds of original orange juice is shown in Figure 4.10. From this figure, as permeate pressure increased, the percent recovery of all flavor compounds decreased, as a result of the decrease in the driving force, the similar trends were also observed with the other two feed concentrations Since recover percentage generally follows the trends of the permeation flux, thus as increase the permeate pressure resulted in greater decrease of the less volatile compounds like 1-hexanol and D-limonene than ethyl butyrate and trans-2-hexenal, the more volatile compounds. When compare the effects of various parameters, permeate pressure has the least effect on recovery percentages, while feed concentration and feed temperature, respectively, have greater effects.

Finally, the effect of permeate pressure on pervaporation separation index of 150 folds orange juice concentrate was shown in Figure 4.11. The pervaporation separation index of some flavor compounds decreased as permeate pressure increased from 5 to 15 mmHg. The similar trends were observed with other feed concentrations. Therefore, lower permeate pressure of 5 mmHg was more appropriate permeate pressure for pervaporation of flavor compounds from orange juice.

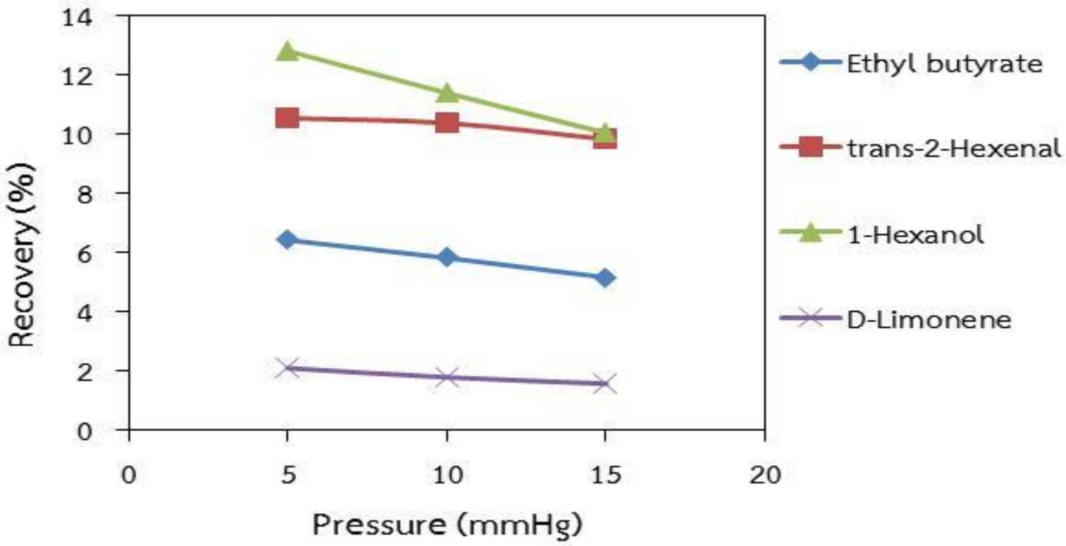


Figure 4. 10 The effect of permeate pressure on recovery percentages from150 folds of original orange juice concentration at feed temperature 45 °C

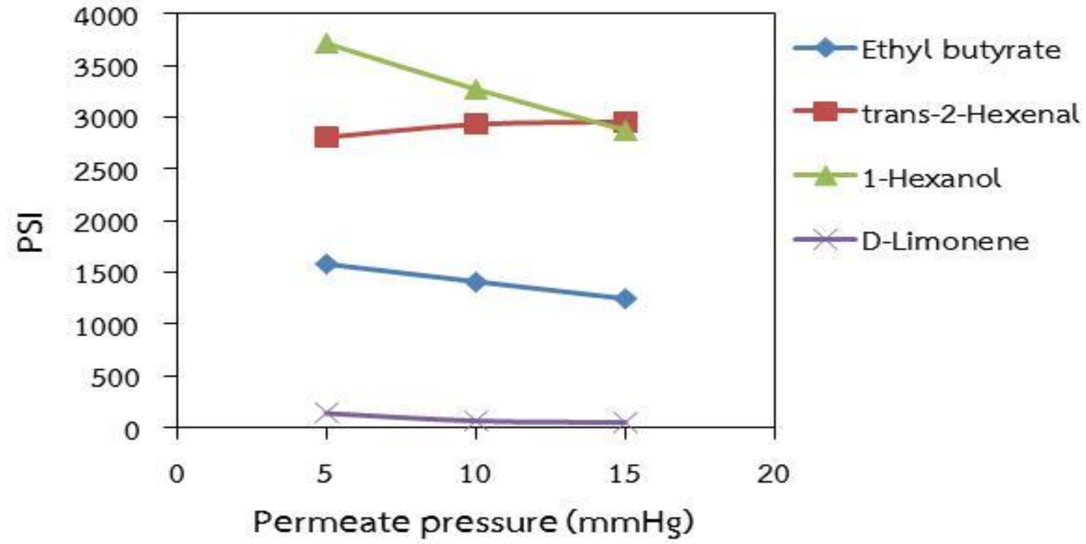


Figure 4. 11 The effect of permeate pressure on pervaporation separation index from 150 folds of original orange juice concentration at feed temperature 45 °C

CHAPTER V

CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusions

The objective of this work is to investigate the pervaporative transport behavior of orange juice model solution consisted with four key flavor compounds, namely, ethyl butyrate, trans-2-hexenal, 1-hexanol and D-limonene through the tubular polydimethylsiloxane (PDMS) membrane. The effects of variables on the separation performance were investigated after 6 h when the steady state was ensured, although it was found that steady state was established within 2 h of experimental runs. The variables studied include of feed concentration (original orange juice concentration, at 75-fold and at 150-fold of the original orange juice concentration), feed temperature (30, 40 and 45 °C) and permeate pressure (5, 10 and 15 mmHg).

As for the effect of feed concentration, it was found that the feed concentration resulted in increase in the partial flux of flavor compounds. Specifically, the permeation fluxes of each aroma compounds was found to increase as concentration increased from the original orange juice concentration to the higher concentrations of 75-fold and 150-fold. Furthermore, for higher feed concentrations (75-fold and 150-fold), the permeation flux of more concentrated aroma compounds in the orange juice is greater than that of the less concentrated compounds. Therefore, the permeation flux is in the order of D-limonene > ethyl butyrate > trans-2-hexanal > 1-hexanol, except for some operating conditions the permeation flux of 1-hexanol was larger than trans-2-hexanal as their compositions in the feed are very similar. However, at the original orange juice concentration, the permeation flux of 1-hexanol > trans-2-hexanol > ethyl butyrate > D-limonene due to the permeability seemed to have more influence on the permeate flux. Whereas the increase in feed concentration, the selectivity decreased since water flux became higher. The recovery percentages decrease as the feed concentration increase due to the fact that the recovery percentage is the ratio of the amount of penetrants and the amount of the corresponding flavor compounds at the beginning. The order of these values of flavor compounds through the membrane from high to low was: 1-hexanol > trans-2-hexenal > ethyl butyrate >> D-limonene.

Feed temperature is also another important factor affecting the performance of the process. The increase in feed temperature leads to higher permeation flux and recovery percentages of each flavor compounds, but lower selectivity. It was found that ethyl butyrate is more temperature sensitive than trans-2-hexenal, D-limonene and 1-hexanol, respectively.

Compared with feed concentration and feed temperature, permeate pressure seems to have the smallest effects on the membrane performance. Increased in permeate pressure slightly reduced the permeation flux, selectivity and recovery percentages, except for trans-2-hexenal, the selectivity increased slightly with increase in permeate pressure.

The effect of permeate pressure is larger for D-limonene than 1-hexanol, trans-2-hexenal and ethyl butyrate, respectively. Due to, permeation flux of flavor compounds is inversely proportional to the compound selectivity, the pervaporation separation index (PSI) was more often used in membrane separation processes as a criterion for the selection of appropriate conditions. Base on the PSI, it has been found that increase in feed concentration and decrease in feed temperature led to the decrease in the PSI values of ethyl butyrate, trans-2-hexenal and 1-hexanol, and the increase in PSI value of D-limonene. Whereas, increase in permeate pressure decreased the PSI values of all flavor compounds except for trans-2-hexenal. It should be noted that the PSI for D-limonene was negative at low feed concentration, and to increase the PSI value of the key flavor compound like D-limonene, high feed concentration would be more appropriate, however with the expense of lower PSI values for the other compounds. The most suitable conditions for separation of D-limonene are at 75-fold of original orange juice feed concentration, high feed temperature of 45 °C and low permeate pressure of 5 mmHg. Whereas the appropriate conditions to separate ethyl butyrate, trans-2-hexenal and 1-hexnol is operated with real orange juice concentration, feed temperature 45 °C and permeate pressure 5 mmHg.

5.2 Recommendations

5.2.1 This membrane may not be appropriate for the recovery D-limonene. To achieve the higher flux of D-limonene, the new membrane material such as poly octhylmethylsiloxane (POMS) which is more the selective to organic compounds than PDMS membrane might be more appropriate (Pereira, Ribeiro Jr et al. 2006).

5.2.2 The high range of feed concentration at 75-fold and at 150-fold of original orange juice concentration is too much for this membrane. So, higher surface membrane area might be needed for these concentrations to obtain higher recovery percentages.

5.2.3 As all flavor compounds are volatile, loss of the compounds can easily occur. Care should be taken during the preparation and extraction step and the feed tank and vacuum line must be carefully secured to avoid the flavor loss.

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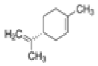
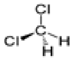
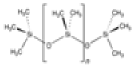
APPENDIX

APPENDIX A

Properties of substance and membrane

Tble A-1 The sumerized properties

Flavor compounds / Solvents /Internal standard/ Membrane/Water	Chemical structure	Molecular weight (g/mole)	Boiling point (ºC)	Density (g/cm^3)	Vapor pressure @20ºC (mmHg)	Solubility parameter (Cal/cm^3)$^{0.5}$	Dielectric constant
Ethyl butyrate		116.16	120	0.8807	12.5	8.5	5.1
trans-2-Hexenal		98.15	155	0.845	10	ND	ND
1-Hexanol		102.17	155-159	0.819	0.75	ND	13.3
D-limonene		136.23	176	0.841	1	3	2.3
n-Pentane		35.9	72.15	0.621	434.29	7.0	1.84
Dichloromethane		39.6	84.93	1.33	351.79	8.0	9.1
1-Pentanol		88.15	137-139	0.81	1.5	10.6	13.9
Polydimethylsiloxane		ND	ND	0.965	-	8.1	2.3-2.8
Water		18.02	100	1	17.5	23.5	80.4

Note: ND = No data

Table A-2 Retention time of aroma compounds from GC-FID analysis

Aroma compounds	Retention time (minutes)
Ethyl butyrate	7.859
trans-2-Hexenal	8.431
1-Hexanol	8.531
D-Limonene	10.364
1-Pentanol	7.577

Table A- 3 Vapor pressure of compounds

Temperature (°C)	Vapor pressure at atmosphere (mmHg)				
	Ethyl butyrate	trans-2-Hexenal	1-Hexanol	D-limonene	water
30	33.41	ND	1.22	4.38	31.74
40	49.92	ND	3.56	6.11	55.19
45	58.17	ND	4.73	6.98	71.70

APPENDIX B

Single point internal standard

The single point internal standard method required at least two analyses. The first analysis contains unknown amount of internal standard and the compounds of interest. Calculate the internal response factor (IRF) using this equation:

$$IRF = \frac{area_{IS} \times amoun_{sc}}{amount_{IS} \times area_{SC}} \tag{B-1}$$

where IS is Internal Standard

SC is Specific Compounds of Interest

Then add a known amount of internal standard to the sample containing analyzes of unknown concentrations. Calculate the amount of unknown analyze using this equation

$$amount\ of\ spesific\ compound = \frac{amount_{IS} \times area_{SC} \times IRF_{sc}}{area_{IS}} \tag{B-2}$$

TABLE B- 1 Data for calculation standard calibration curve and internal standard curve of 1-pentanol from GC-FID analysis

Peak area	Concentration (g/L)	IRF
105.8159	0.05	1
299.0169	0.3	1
906.5040	1	1
4921.2412	5	1
14522.4000	15	1
	IRF average	1
	Standard deviation	0

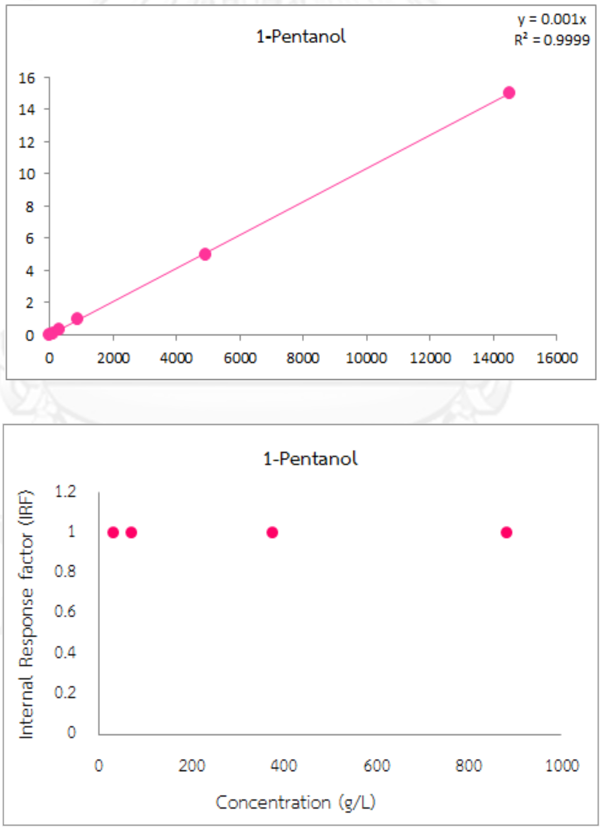


Figure B-1 (a) Standard calibration curve of 1-pentanol

(b) Internal standard curve of 1-pentanol

TABLE B-2 Data for calculation standard calibration curve and internal standard curve of ethyl butyrate from GC-FID analysis

Peak area	Concentration (g/L)	IRF
72.1271	0.05	1.4671
210.7515	0.3	1.4188
640.5673	1	1.4152
3495.8638	5	1.4077
10276.1000	15	1.4132
	IRF average	1.4272
	Standard deviation	0.0270

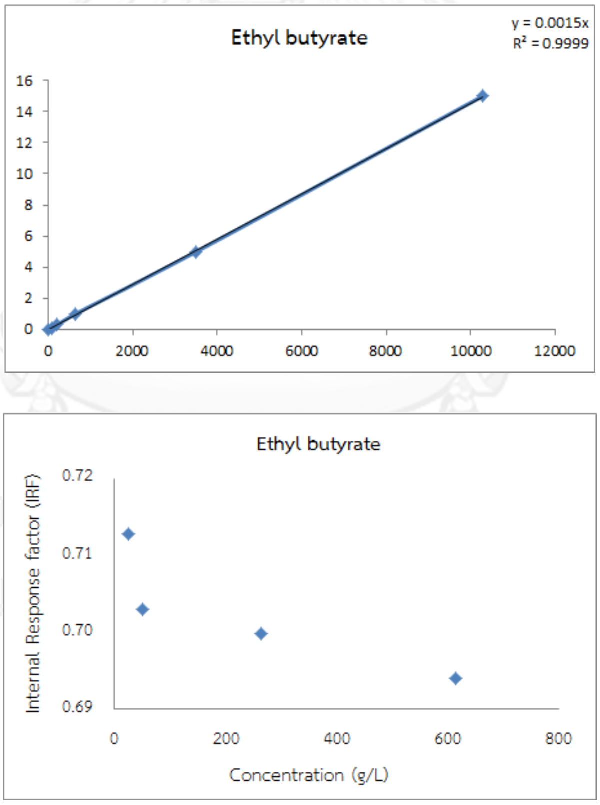


Figure B-2 (a) Standard calibration curve of ethyl butyrate and

(b) Internal standard curve of ethyl butyrate

TABLE B-3 Data for calculation standard calibration curve and internal standard curve of trans-2-hexenal from GC-FID analysis

Peak area	Concentration (g/L)	IRF
93.4830	0.05	1.1319
274.4181	0.3	1.0896
950.6786	1	0.9535
4535.5449	5	1.0850
13369.3000	15	1.0862
	IRF average	1.0650
	Standard deviation	0.0773

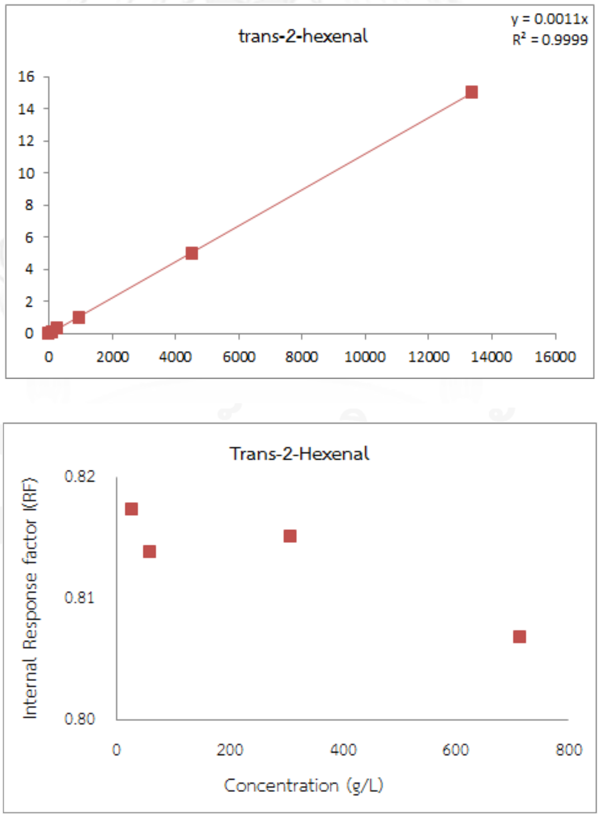


Figure B-3 (a) Standard calibration curve of trans-2-hexenal

(b) Internal standard curve of trans-2-hexenal

TABLE B-4 Data for calculation standard calibration curve and internal standard curve of 1-hexanol from GC-FID analysis

Peak area	Concentration (g/L)	IRF
107.5363	0.05	0.9840
315.5322	0.3	0.9477
950.6786	1	0.9535
5203.7627	5	0.9457
15354.0000	15	0.9458
	IRF average	0.9577
	Standard deviation	0.0178

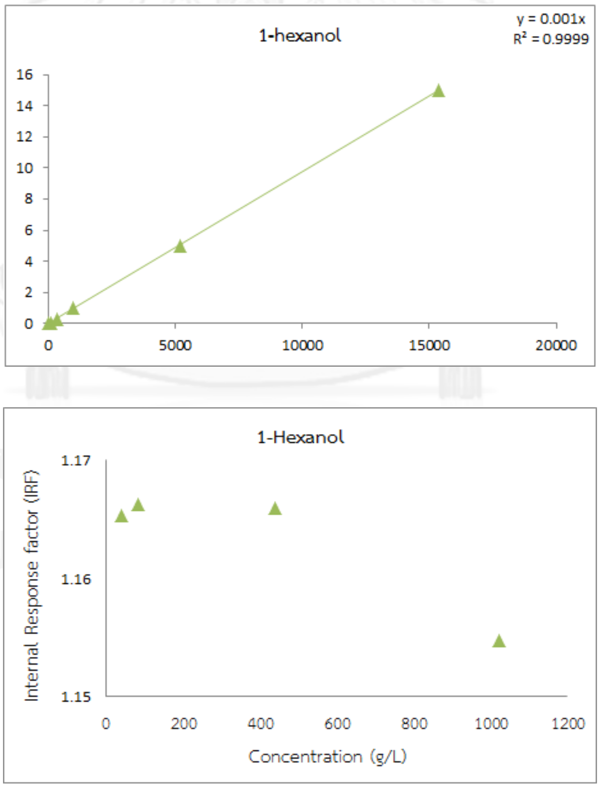


Figure B-4 (a) Standard calibration curve of 1-hexanol

(b) Internal standard curve of 1-hexanol

TABLE B-5 Data for calculation standard calibration curve and internal standard curve of D-limonene from GC-FID analysis

Peak area	Concentration (g/L)	IRF
263.8635	0.1	0.80205
770.2463	0.6	0.77642
2279.9592	2	0.79519
12444.3000	10	0.79092
37197.1000	30	0.78084
	IRF average	0.78908
	Standard error	0.01084

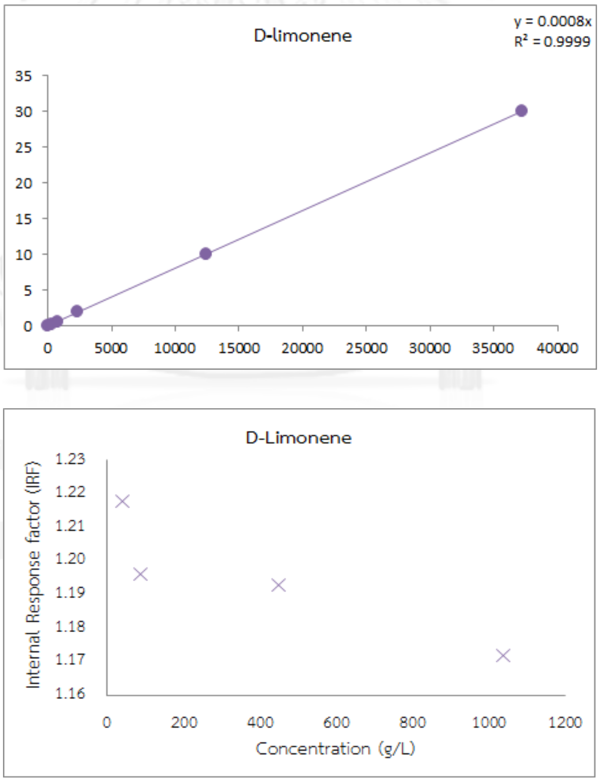


Figure B-5 (a) Standard calibration curve of D-limonene

(b) Internal standard curve of D-limonene

APPENDIX C

Effect of extraction with liquid-liquid extraction

TABLE C-1 Recovery percentage from extraction when operate with 6 hours

Aroma compounds	% recovery	Standard deviation
Ethyl butyrate	68.73	3.30
trans-2-Hexenal	63.11	2.24
1-Hexanol	64.04	1.29
D-Limonene	68.04	0.95

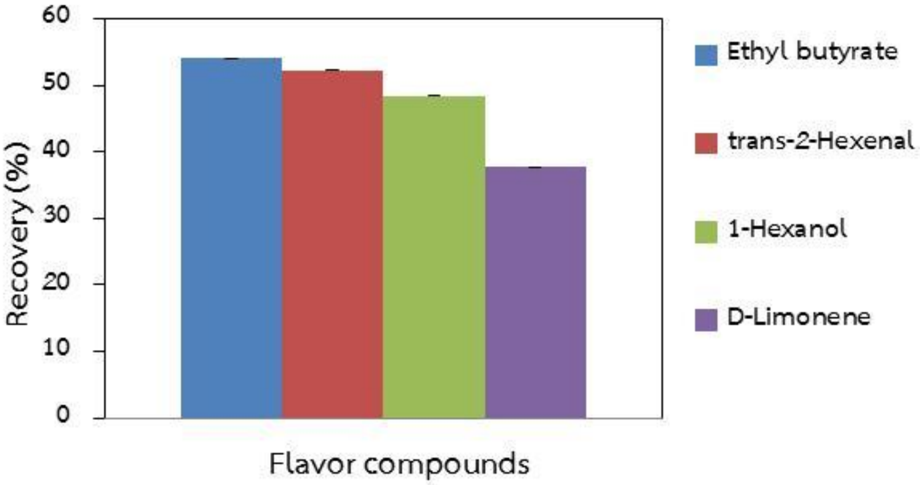


Figure C- 1 Recovery percentage from liquid-liquid extraction

APPENDIX D

Content calculation

1. Internal standard

The single point internal standard method required at least two analyses. The first analysis contains a unknown amount of internal standard and the compounds of interest. Calculate the internal response factor (IRF) using this equation:

$$IRF = \frac{area_{IS} \times amoun_{sc}}{amount_{IS} \times area_{SC}} \tag{D-1}$$

where IS is Internal Standard

SC is Spesific Compounds of Interest

Then add a known amount of internal standard to the sample containing analyzes of unknown concentrations. Calculate the amount of unknown analyze using this equation

$$amount\ of\ spesific\ compound = \frac{amount_{IS} \times area_{SC} \times IRF_{sc}}{area_{IS}} \tag{D-2}$$

2. Liquid-liquid extraction calculation

Liquid-liquid extraction can transfer some amount of aroma compounds in the permeate (water phase) to solvent, because of the different of solubility of each aroma compounds into solvent phase and loss during its step. So, we have to find the recovery percentages efficient from the extraction step of each aroma compounds and these values will add in the results from GC-FID analysis to reduce the loss during extraction.

$$\%re\cos ey\ \ from extraction = \frac{amoun_{sc} after\ extraction}{amount_{IS}\ at\ the\ beginning} \tag{D-3}$$

3. Pervaporation calculation

a. Total permeation flux (g/m^{2}h)

$$J = \frac{W}{At} \tag{D-4}$$

where W is weight of permeate (g)

A is effective membrane area (m^3)

t is permeation time (h)

b. Partial permeation flux (g/m^{2}h)

i. Ethyl butyrate flux

$$J_E = Y_E J \tag{D-5}$$

where Y_E is mass fraction of ethyl butyrate in the permeate

ii. trans-2-Hexenal flux

ฟ (D-6)

where Y_{tr} is mass fraction of tranas-2-hexenal in the permeate

iii. 1-Hexanol flux

$$J_H = Y_H J \tag{D-7}$$

where Y_H is mass fraction of 1-hexanol in the permeate

iv. D-Limonene

$$J_L = Y_L J \tag{D-8}$$

where Y_L is mass fraction of D-limonene in the permeate

v. Water flux

$$J_W = J - J_E - J_{tr} - J_H - J_L \qquad \text{(D-9)}$$

c. **Separation factor**

$$\alpha_i = \frac{C_i^P / C_j^P}{C_i^F / C_j^F} = \frac{y_i / (1 - x_i)}{x_i / (1 - x_i)} \qquad \text{(D-10)}$$

where c_i^P, c_j^P is weigh percentage of component i and j in the permeate

c_i^F, c_j^F is weigh percentage of component i and j in the feed solution

d. **Recovery percentages**

$$\%recovery = \frac{W_{ip}}{W_{if}} \qquad \text{(D-11)}$$

where W_{ip} is weight of component i in the permeate

W_{if} is weight of component i in the feed

e. **Pervaporation separation index**

$$PSI_i = J(\alpha - 1) \qquad \text{(D-12)}$$

4. Calculation example

Data for recovery flavor compounds with pervaporation 150-fold of the original orange juice concentration at 45 °C feed temperature, 5 mmHg permeate pressure, 15 L/h feed flow rate and 6 h operation time.

For example : ethyl butyrate

Weight permeate = 14.105 g

Mass fraction of ethyl butyrate in the feed = 0.00079

Concentration IS = 0.000819

IRF of ethyl butyrate = 1.427

Area ethyl butyrate from GC-FID = 1,801.1001

Area IS from GC-FID = 1116.2

Percent recovery of extraction 68.727%

$$real\,amount\,of\,ethyl\,butyrate = \frac{0.000819 \times 1801.1001 \times 1.427}{1116.28} x \frac{100}{68.727} = 0.002792$$

$$\text{Mass fraction in the permeate of ethyl butyrate} = \frac{0.0406}{14.105} = 0.00288$$

Mass fraction in the permeate of trans -2-hexenal=0.00250

$$\text{Mass fraction in the permeate of } 1 - hexanol = 0.00261$$

Mass fraction in the permeate of tD-limonene=0.0115

1. Permeation flux (g/m^{2}h)

$$J = \frac{W}{At}$$

$$J = \frac{14.105}{(0.005)6} = 470.17$$

2. Partial permeation flux (g/m^{2}h)

Ethyl butyrate: $J_E = 0.00288 x 470.167 = 1.69$

trans-2-hexenal $J_{tr} = 0.00250x470.167 = 1.26$

1-hexanol $J_{H} = 0.00261x470.167 = 1.57$

D-limonene $J_{L} = 0.0015x470.167 = 7.243$

Water

$$J_{w} = 470.167 - 1.35 - 1.18 - 1.23 - 0.71 = 465.70$$

3. Separation factor

$$\alpha_{i} = \frac{C_i^P / C_j^P}{C_i^F / C_j^F} = \frac{y_i / (1 - x_i)}{x_i / (1 - x_i)}$$

$$\alpha_{E} = \frac{y_i / (1 - x_i)}{x_i / (1 - x_i)} = \frac{0.00288 / (1 - 0.00288)}{0.00079 / (1 - 0.00079)} = 3.83$$

4. PSI

$$PSI = J_E(\alpha_E - 1)$$

$$PSI = 1.69\ \ (3.83 - 1) = 4.78$$

5. Recovery percentage

Weight of ethyl butyrate in the permeate = mass fraction x weight of permeate

$$W_{EP} = 0.00288 \times 14.105 = 0.04$$

$$\%re\operatorname{cov} ery = \frac{0.04}{0.789} = 6.41$$

APPENDIX E

The experimental data

Table E- 1 Permeate weight and total flux from original orange juice

T (°C)	P (mmHg)	area IS	Final volume (ml)	Permeate weight (g)	Total flux (g/m^2h)
30	5	848.68542	1	10.11	336.83
30	10	641.89557	1.1	6.54	218.10
30	15	867.34784	1	4.84	161.167
40	5	690.28345	1	13.02	434.13
40	10	858.15991	1	10.04	334.63
40	15	773.39227	1	9.07	302.23
45	5	1139.0172	0.9	22.24	741.47
45	10	659.99841	1.1	19.49	649.53
45	15	973.15186	0.9	15.67	522.17

Table E-2 Permeate weight and total flux from 75-fold of original orange juice

T (°C)	P (mmHg)	area IS	Final volume (ml)	Permeate weight (g)	Total flux(g/m^{2}h)
30	5	699.36255	1.1	5.32	177.42
30	10	859.53357	1	4.68	155.99
30	15	822.97229	1	4.63	154.17
40	5	804.19543	1	9.42	314.00
40	10	788.7141	1	8.88	295.98
40	15	880.70941	1	7.11	236.97
45	5	851.25952	1	13.29	443.13
45	10	1521.2308	0.7	10.79	359.64
45	15	680.16113	1.1	10.24	341.27

Table E-3 Permeate weight and total flux from 150-fold of original orange juice

T (°C)	P (mmHg)	area IS	Permeate weight (g)	Total flux(g/m^{2}h)
30	5	766.45007	5.90	294.27
30	10	864.18195	6.20	206.70
30	15	670.94141	8.83	196.73
40	5	797.43475	10.90	436.70
40	10	823.74835	12.50	416.67
40	15	752.82635	13.10	363.13
45	5	1116.27576	14.11	557.75
45	10	857.05731	15.81	526.86
45	15	745.24597	16.73	470.17

Table E-4 Mass fraction of each flavor compounds in original orange juice

T (°C)	P (mmHg)	Mass fraction in the permeate (Yi)

		Ethyl butyrate	trans-2-Hexenal	1-Hexanol	D-Limonene
30	15	7.67E-05	1.24E-04	9.32E-05	1.64E-05
30	10	7.60E-05	1.21E-04	1.05E-04	2.46E-05
30	5	7.82E-05	1.04E-04	7.88E-05	3.52E-05
40	15	6.55E-05	9.07E-05	7.97E-05	2.19E-05
40	10	6.43E-05	9.04E-05	8.86E-05	2.37E-05
40	5	6.46E-05	8.65E-05	8.98E-05	3.71E-05
45	15	4.43E-05	7.93E-05	6.067E-05	1.53E-05
45	10	5.29E-05	7.51E-05	7.08E-05	1.68E-05
45	5	5.79E-05	7.26E-05	7.48E-05	2.81E-05

Table E-5 Mass fraction of each flavor compounds in 75-fold original orange juice

T (°C)	P (mmHg)	Mass fraction in the permeate (Yi)			
		Ethyl butyrate	trans-2-Hexenal	1-Hexanol	D-Limonene
30	15	0.00164	0.00172	0.00139	0.01189
30	10	0.00169	0.00170	0.00142	0.01237
30	5	0.00171	0.00174	0.00142	0.01225
40	15	0.00152	0.00122	0.00117	0.00872
40	10	0.00151	0.00122	0.00126	0.00885
40	5	0.00152	0.00116	0.00123	0.00894
45	15	0.00135	0.00113	0.00085	0.00652
45	10	0.00141	0.00108	0.00088	0.00756
45	5	0.00143	0.00110	0.00089	0.00804

Table E-6 Mass fraction of each flavor compounds in 150-fold of original orange juice

T (°C)	P (mmHg)	Mass fraction in the permeate (Yi)			
		Ethyl butyrate	trans-2-Hexenal	1-Hexanol	D-Limonene
30°C	15	0.0034	0.0027	0.0027	0.0177

30°C	10	0.0034	0.0027	0.0031	0.0188
30°C	5	0.0035	0.0026	0.0032	0.0181
40°C	15	0.0029	0.0028	0.0027	0.0119
40°C	10	0.0029	0.0026	0.0028	0.0129
40°C	5	0.0032	0.0026	0.0029	0.0137
45°C	15	0.0029	0.0025	0.0026	0.0115
45°C	10	0.0029	0.0024	0.0026	0.0117
45°C	5	0.0030	0.0023	0.0028	0.0130

Table E-7 Permeation flux of each flavor compounds in original orange juice

T °(C)	P (mmHg)	FLUX (g/m^{2}h)			
		Ethyl butyrate	**trans-2-Hexenal**	**1-Hexanol**	**D-Limonene**
30	5	0.026	0.035	0.027	0.012
30	10	0.016	0.026	0.023	0.005
30	15	0.012	0.020	0.015	0.003
40	5	0.028	0.038	0.039	0.016
40	10	0.021	0.030	0.030	0.008
40	15	0.020	0.027	0.024	0.007
45	5	0.043	0.054	0.056	0.021
45	10	0.034	0.049	0.046	0.011
45	15	0.023	0.04	0.032	0.0080

Table E-8 Permeation flux of each flavor compounds in 75-fold of original orange juice

T °(C)	P (mmHg)	FLUX (g/m^{2}h)			
		Ethyl butyrate	**trans-2-Hexenal**	**1-Hexanol**	**D-Limonene**
30	5	0.30	0.31	0.25	2.17
30	10	0.26	0.27	0.22	1.93

30	15	0.25	0.27	0.22	1.83
40	5	0.48	0.37	0.39	2.81
40	10	0.45	0.36	0.37	2.62
40	15	0.36	0.29	0.28	2.07
45	5	0.63	0.49	0.39	3.56
45	10	0.51	0.39	0.32	2.72
45	15	0.46	0.39	0.29	2.22

Table E-9 Permeation flux of each flavor compounds in 150-fold of original orange juice

T °(C)	P (mmHg)	FLUX (g/m^2h)			
		Ethyl butyrate	trans-2-Hexenal	1-Hexanol	D-Limonene
30	5	1.04	0.78	0.95	5.33
30	10	0.71	0.56	0.63	3.88
30	15	0.67	0.53	0.53	3.48
40	5	1.37	1.13	1.27	6.00
40	10	1.19	1.08	1.16	5.36
40	15	1.06	0.10	0.99	4.33
45	5	1.69	1.26	1.57	7.24
45	10	1.53	1.24	1.39	6.17
45	15	1.35	1.18	1.23	5.42

Table E-10 The selectivity of each flavor compounds in original orange juice

T (°C)	P (mmHg)	Separation factor			
		Ethyl butyrate	trans-2-Hexenal	1-Hexanol	D-Limonene
30	5	14.86	35.41	32.18	0.50
30	10	14.49	41.23	42.94	0.36
30	15	14.58	42.10	38.06	0.24
40	5	12.29	29.41	36.64	0.54

40	10	12.22	30.75	36.18	0.34
40	15	12.45	30.85	32.55	0.32
45	5	11.00	24.70	30.54	0.41
45	10	10.06	25.56	28.89	0.24
45	15	8.43	26.98	24.76	0.22

Table E-11 The selectivity of each flavor compounds in 75-fold of original orange juice

T (°C)	P (mmHg)	Separation factor			
		Ethyl butyrate	trans-2-Hexenal	1-Hexanol	D-Limonene
30	5	4.34	7.88	7.76	2.37
30	10	4.30	7.71	7.75	2.40
30	15	4.15	7.82	7.59	2.30
40	5	3.85	5.28	6.68	1.73
40	10	3.83	5.55	6.84	1.71
40	15	3.85	5.54	6.39	1.68
45	5	3.62	4.99	4.84	1.55
45	10	3.58	4.91	4.78	1.46
45	15	3.43	5.13	4.62	1.26

TABLE E- 12 The selectivity of each flavor compounds in 150-fold of original orange juice

T (°C)	P (mmHg)	Separation factor			
		Ethyl butyrate	trans-2-Hexenal	1-Hexanol	D-Limonene
30	5	4.47	7.36	8.81	1.76
30	10	4.37	7.56	8.33	1.82
30	15	4.33	7.51	7.34	1.71
40	5	3.40	7.18	7.92	1.32

40	10	3.65	7.189	7.59	1.24
40	15	3.72	7.66	7.423	1.15
45	5	3.84	6.30	7.66	1.25
45	10	3.68	6.57	7.21	1.13
45	15	3.66	6.97	7.12	1.11

Table E-13 Percent recovery of each flavor compounds in original orange juice

T (°C)	P (mmHg)	Recovery percentages			
		Ethyl butyrate	trans-2-Hexenal	1-Hexanol	D-Limonene
30	5	15.01	35.77	32.51	0.51
30	10	9.46	26.97	28.10	0.23
30	15	7.05	20.35	18.40	0.11
40	5	16.00	38.30	47.72	0.70
40	10	12.26	30.87	36.32	0.34
40	15	11.28	27.97	29.51	0.28
45	5	24.49	54.93	67.94	0.90
45	10	19.61	49.80	56.29	0.47
45	15	13.20	42.26	38.79	0.35

TABLE E-14 Percent recovery of each flavor compounds in 75-fold of original orange juice

T (°C)	P (mmHg)	Recovery percentages			
		Ethyl butyrate	trans-2-Hexenal	1-Hexanol	D-Limonene
30	5	2.31	4.19	4.12	1.26
30	10	2.01	3.60	3.62	1.11
30	15	1.92	3.61	3.51	1.06
40	5	3.62	4.97	6.28	1.62
40	10	3.39	4.93	6.07	1.51
40	15	2.73	3.93	4.53	1.19

45	5	4.81	6.63	6.43	2.06
45	10	3.86	5.30	5.15	1.57
45	15	3.51	5.25	4.72	1.28

Table E-15 Percent recovery of each flavor compounds in 150-fold of original orange juice

T (°C)	P (mmHg)	Recovery percentages			
		Ethyl butyrate	**trans-2-Hexenal**	**1-Hexanol**	**D-Limonene**
30	5	3.94	6.48	7.75	1.54
30	10	2.70	4.68	5.15	1.12
30	15	2.56	4.42	4.32	1.00
40	5	5.23	9.39	10.34	1.73
40	10	4.55	8.96	9.47	1.55
40	15	4.04	8.32	8.07	1.25
45	5	6.41	10.52	12.79	2.09
45	10	5.81	10.36	11.37	1.78
45	15	5.15	9.81	10.03	1.57

Table E-16 PSI of each flavor compounds in original orange juice

T (°C)	P (mmHg)	PSI			
		Ethyl butyrate	**trans-2-Hexenal**	**1-Hexanol**	**D-Limonene**
30	5	4668.48	11589.10	10501.50	-165.77
30	10	2935.17	8773.32	9147.72	-140.72
30	15	2188.36	6624.37	5972.58	-123.12
40	5	4899.38	12334.44	15473.52	-201.90
40	10	3753.04	9956.26	11771.81	-220.09
40	15	3461.09	9020.99	9534.15	-206.79
45	5	7414.09	17570.55	21905.16	-440.92
45	10	5887.49	15950.24	18114.54	-492.05

45	15	3878.29	13566.76	12407.88	-407.07

Table E-17 PSI of each flavor compounds in 75- fold of original orange juice

T (°C)	P (mmHg)	PSI			
		Ethyl butyrate	trans-2-Hexenal	1-Hexanol	D-Limonene
30	5	592.72	1221.41	1198.86	243.80
30	10	514.80	1047.25	1052.70	217.88
30	15	485.61	1051.71	1015.83	200.97
40	5	893.63	1343.73	1782.17	227.86
40	10	835.94	1347.54	1728.88	209.92
40	15	674.81	1075.61	1276.34	161.88
45	5	1160.04	1767.99	1700.30	243.95
45	10	926.57	1408.03	1359.06	164.84
45	15	828.98	1409.36	1233.56	87.12

Table E-18 PSI of each flavor compounds in 150-fold of original orange juice

T (°C)	P (mmHg)	PSI			
		Ethyl butyrate	trans-2-Hexenal	1-Hexanol	D-Limonene
30	5	1021.34	1871.55	2296.87	222.23
30	10	696.55	1355.16	1515.60	169.94
30	15	655.51	1279.90	1248.11	140.01
40	5	1309.12	2698.86	3021.12	141.49
40	10	1104.00	2577.51	2746.93	100.38
40	15	985.85	2416.83	2334.51	54.21
45	5	1583.55	2956.98	3716.09	140.76
45	10	1413.95	2932.88	3273.06	67.07
45	15	1249.72	2807.82	2879.32	51.95

VITA

Miss Anongnart Khawsang was born in Phatthalung, Thailand on June 19, 1988. She finished her secondary course from Phatthalung School in 2007. She continued her undergraduate study in Chemical Engineering at the Faculty of Engineering, Thammasat University and graduated in 2011. She has then enrolled in the Master’s degree program in Chemical Engineering at Chulalongkorn University and has joined the Biochemical Engineering Research Laboratory since 2012. She completed her Master’s degree study in July, 2014.