CONCENTRATION OF FEIJOA AND BOYSENBERRY FRUIT AROMA CONDENSATES USING PERVAPORATION

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ERRATA

Page 64 The r^2 for the ethanol calibration curve was 0.64.

Page 74 Table 4.4 , the ATV of ethanol should be changed from "NF" to " 0.28-9%". ATV of ethanol is 0.28-9 g/100g; it is different from other aroma compounds such as geraniol (ATV: 0.001-0.01 mg/kg), linalool (ATV: 0.001-0.01 mg/kg).

Page 74 Table 4.4, the AV of ethanol should be changed from "NF" to "2.2 ".

Page 107 Table 4.22, the concentration of ethanol at the flow rate of 1.4×10^{-5} m^3s^{-1} should be changed from "10044" to " 10044*".

Page 108 Table 4.23, the enrichment factor for ethanol at the flow rate of 1.4×10^{-5} m^3s^{-1} should be changed from "8.6 ± 0.5" to"8.6 ± 0.5*".

Abstract

This present work aimed to investigate pervaporation for aroma recovery and concentration from fruit aroma condensate collected during evaporation of fruit juices. A 5% ethanol solution, feijoa and boysenberry aroma condensates were concentrated in a pervaporation apparatus fitted with polydimethyl siloxane (PDMS: GFT1060, GFT1070) and poly-ether-block-amide (PEBA, GKSS) membranes, under the following operating conditions: feed temperature of 30°C, feed flow rate of 8.3×10^{-6} m^3 s^{-1}, 1.1×10^{-5} m^3 s^{-1} or 1.4×10^{-5} m^3 s^{-1}, and permeate pressures of 100 Pa or 1000 Pa. Feijoa and boysenberry aroma condensates were also concentrated by vacuum distillation. Aroma compounds and their concentrations in the feed, retentate and permeate were identified and determined by gas chromatography (GC) and a mass spectrometer coupled to a GC.

The three membranes investigated for pervaporation gave different total fluxes, partial fluxes, mass transfer coefficients, enrichment factors and aroma compositions for feijoa and boysenberry condensate. PEBA membranes proved to have best performance for concentration of feijoa and boysenberry aroma due to high enrichment factors and mass transfer coefficients for the important aroma compounds of both feijoa and boysenberry.

Increasing the feed flow rate from 1.1×10^{-5} m^3 s^{-1} to 1.4×10^{-5} m^3 s^{-1} did not affect the total flux, but increased significantly the partial fluxes and enrichment factors of preferentially permeating compounds such as methyl benzoate, ethyl benzoate and linalool. Decreasing permeate pressure significantly increased the total flux, the partial fluxes and enrichment factors for higher boiling aliphatic alcohols. The mass transfer resistances of methyl benzoate, ethyl benzoate and linalool was dominated by the boundary layer effects. The mass transfer resistances of high boiling aliphatic alcohols, hexanol, Z-3-hexenol and E-2-hexenol were strongly influenced by permeate pressure.

Compared with vacuum distillaltion, pervaporation showed better performance for producing concentrated feijoa and boysenberry aromas which were highly enriched in the important flavour compounds for each fruit.

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List of nomenclature

Roman letters

A_m	membrane area	m^2
ATV	aroma threshold value	kg m^{-3}
AV	aroma threshold	-
C_i	mass concentration of component i,	kg kg^{-1}(wt/wt)
CF	concentration factor	-
D	diffusion coefficient	m^2 s^{-1}
J	flux	kg m^2 s^{-1}
k	mass transfer coefficient	kg m^2s^{-1}
M	mass	kg
m	mass flow rate	kg s^{-1}
n	number of samples for each mean	-
P	partial pressure	Pa
Q_m	total mass flow	kg s^{-1}
R	universal gas constant	J mol^{-1} K^{-1}
Re	Reynolds number	-
SD	standard deviation	-
SE	standard error	-
t	time	s
T	absolute temperature,	K
V	molar volume of component i	m^3 mol^{-1}
x	length coordinate	m
Δx	membrane thickness	m
Y	yield	%

Greek symbols

α	separation factor, selectivity	
β	enrichment factor	
φ_i	partition coefficient of component *i*.	kg kg^{-1}

subscripts

bl	boundary layer
f	feed
fm	membrane at its feed side
i	preferentially permeating component *i*
j	non-preferentially permeating component *j*
m	membrane
over	overall
p	permeate
pm	membrane at its permeate side

Chapter One

Introduction

In fruit juices and beverages, the aromas consist of various organic compounds present in low concentration. Organic aroma compounds are comprised of compounds from the following classes: alcohols, aldehydes, esters, lactones, carboxylic acids, hydrocarbons, phenols, ethers and terpenes (Karlsson & Trägårdh, 1997).

When an evaporator is used to concentrate fruit juice, the fruit aroma compounds are driven off with the evaporated water vapours. This reduces the final juice concentrate product quality. The lost aroma can be recovered from the vapour and added back to the concentrated juice or used in the flavour and fragrance industry. To prevent excessive product dilution, aroma added back has to be concentrated by a factor of 100 or more (Chardon et al., 1990).

Usually the evaporator condensate containing the fruit aromas is concentrated by distillation or partial condensation systems (Chardon et al., 1990). However, distillation is an energy-intensive and capital expensive process. This is especially so for condensates that contain relatively small concentrations of organic compounds in large volumes of water. Another problem is that the high temperatures involved in distillation may change the sensitive aroma compounds (Remtake et al., 1990; 1993a; 1993b). Aroma recovery by distillation produces low yields and low enrichment factors (Chardon et al., 1990). Membrane technologies such as pervaporation have been reported to be able to concentrate organic aroma compounds (Fleming, 1992).

Membrane technology uses a semi-permeable membrane as a selective barrier to separate one or more components from a solution (Fleming, 1992). It has recently emerged as an important separation and purification technique because it offers advantages such as high selectivity, low energy consumption, ambient temperature operation, moderate cost and

modular design (Blume & Baker, 1990). Depending on the driving force available, membrane characteristic and transport mechanism, there are different membrane processes available. Non-porous membrane techniques include reverse osmosis, pervaporation, gas separation, osmotic distillation, membrane distillation and direct osmotic concentration. Membrane techniques using porous membranes include ultrafiltration, microfiltration, nanofiltration, dialysis and electrodialysis (Wong, 1997). The mechanism of mass transfer in non-porous membrane techniques involves the dissolution of the transferring molecule into the membrane matrix and the diffusion across the layer into the permeate stream. The mechanism of mass transfer in the porous-membranes involves flow through open pores driven by a hydraulic pressure gradient. The fouling and maximum concentration levels can limit the practical application of membrane technology (Fleming, 1992).

Pervaporation is a membrane separation technique, in which a liquid feed mixture is separated by means of partial vaporization through a non-porous permselective membrane, and a permeate is recovered from the vapour phase. The mass transfer driving force is based on the chemical potential gradient between the feed side of membrane and the permeate side of membrane. This is achieved by decreasing the permeate pressure. The mechanism of separation of individual compounds was based on the fact that different compounds have different mass flow through the membrane. Compared to other membrane techniques such as reverse osmosis, pervaporation does not have large limitations due to fouling and operating pressure (Fleming, 1992). Pervaporation has been used for a wide range of applications. Applications will depend on the membrane type. Applications include the dehydration of organic compounds, recovery of organic compounds from water, and separation of organic mixtures. Since 1983, over one hundred plants have been established around the world to use pervaporation with hydrophilic membranes for dehydration of solvents (Ferreira, 1998). Pervaporation with hydrophobic membranes has been used in wastewater treatment and for dealcoholization commercially (Fleming, 1992). Pervaporation with hydrophobic membranes used to recover the volatile compounds during beverage processing or biotechnological processing has been proven to be one of its most promising applications (Karlsson & Trägårdh, 1996).

Feijoa (*Feijoa sellowiana)* fruit is a native to South America. The plant grows as a small evergreen tree tolerating a wide range of climatic and soils conditions. Feijoa is commercially grown in New Zealand, Israel and South Russia. Feijoa has become attractive due to its distinctive fruity character (Shaw et al., 1990)

Boysenberry (*Rubus sp. hybrid*) fruit is grown commercially on the West Coast of the United States and in New Zealand. The bulk of New Zealand's boysenberries are exported as frozen individual berries or in a juice concentrate form for use in the manufacture of fruit juice, yogurt, jam and puree (Porter, 1988)

The fresh fruit and concentrated juice of feijoa and boysenberry were important export products from New Zealand. The aroma condensates of feijoa and boysenberry are collected during the production of concentrated fruit juice.

The objectives of this project were to investigate the aroma compositions of feijoa and boysenberry aroma condensate; to study the feasibility of recovery and concentration of aroma compounds from aroma condensate using pervaporation; and to compare the pervaporation technique with vacuum distillation.

Chapter Two

Literature Review

2.1 Fruit aromas and volatile constituents of feijoa and boysenberry

2.1.1 Fruit aromas

A fruit aroma is produced from a number of volatile aroma compounds which combine to provide the characteristic aroma for that fruit. Every fruit aroma is a mixture of different aroma components such as organic acids, alcohols, aldehydes, ketones, lactones, esters, and terpenes (Sulc, 1984). Compounds of different molecular size and different volatility will impart different characteristics (Karlsson et al., 1995). Some aroma components may have an intense aroma, some may have a weak aroma or some may even be odourless. The individual components are present in fruit at different concentrations and in different combinations, varying between 1-20 ppm or even less (Sulc, 1984). In order to take into account the intensities of different aroma compounds, an aroma threshold value (ATV_i) is defined as the lowest concentration in a water solution at which the aroma compound is perceptible by a trained panelist (Karlsson et al., 1995). To indicate the importance of the aroma compound in the fruit product, aroma value AV_i is defined according to

$$AV_i = \frac{C_i}{ATV_i} \tag{2.1}$$

C_i is the concentration of the aroma compound i in a fruit product. A high AV_i means the aroma compound has a large influence on the fruit product aroma. However, some aroma compounds which are not perceptible by themselves, enhance the intensity of another aroma compound present (Karlsson et al., 1995).

If fruit aromas are lost during processing, the quality of the fruit product is reduced (Karlsson & Trägårdh, 1994). It is very hard to preserve and recover small amounts of aroma, during the processing of fruit juice and during juice concentration (Sulc, 1984).

Several hundred different aroma components have been identified for fruit products. For example, 130 compounds have been identified in strawberry aroma and more than 300 compounds have been found in apple aroma (Maarse, 1981). In many fruit, the important compounds impacting fruit character have been discovered and identified.

2.1.2 Fruit aroma biogenesis, post-harvest change and processing change

Fruit aroma compounds are primarily formed from aroma precursors, which are normally intermediate metabolic products or derivatives of lipids, amino acids and carbohydrates. Pre-climacteric fruit produce a small amount of ethylene that induces biochemical, physical and chemical changes in colour, texture and flavour. During this stage, volatile compounds are produced or converted from aroma precursors (Berger, 1991).

The conversion of precursor substrates into volatile flavours can be from endogenous substrates or they may be exogenously supplied substrates. Storage variation, such as controlled atmosphere storage (CA) and precursor atmosphere storage (PA) have been shown to change aroma composition of the fruit (Berger, 1991). For example, increased carbon dioxide concentration was favourable for the production of aroma in stored strawberries. PA-storage of apples, pears, cherries, strawberries has shown to enhance the ester content (Berger, 1991).

Processing can cause great change in the aroma composition of fruit product including chemical changes and physical loss. Chemical changes can occur due to heat-induced oxidation or Maillard reactions. This can result in the lose of some of the original aroma

compounds or formation of new aroma compounds from the original aroma or other compounds present (Karlsson & Trägårdh, 1997).

Physical loss of aroma mainly occurs during the evaporation stage of fruit juice production. The relative amount of aroma lost from the evaporated juice is related to the evaporation degree (ED). ED is the evaporated volume in relation to the initial volume (Karlsson & Trägårdh, 1997). Sulc (1984) divided aroma compounds into three fractions according to their volatile potential. The first fraction was referred to as highly volatile and was almost completely lost at very low ED, e.g. acetone and ethyl pentanoate. The second fraction was referred to as medium volatile and was lost at ED of 30-60%, e.g. hexanol. The third fraction was referred to as the low volatility fraction and only was lost at very high ED, e.g. ethanol, isobutanol, acetic acid and geraniol.

According to the behavior of each fruit aroma during evaporation, Sulc (1984) classified all fruit aromas into four groups. The first group was referred to as highly volatile fruit aromas, which were lost at 15% ED e.g. apple. The second group was referred to as medium volatile fruit aromas, which were completely lost at 50% ED, e.g. plum and grape. The third group was referred to as low volatile fruit aromas, which 75-82% were lost at 50% ED, e.g. apricot and peach. The fourth group was referred to as very low volatile fruit aromas, which 60-70% were lost at 50% ED, e.g. strawberry and raspberry.

2.1.3 Volatile constituents of feijoa fruit

The volatile flavour constituents of feijoa has been the subject of several GC-MS studies (Hardy & Michael, 1970; Shaw et al., 1983; Shaw et al., 1989; Shaw et al., 1990).

Hardy & Michael (1970) identified 16 constituents from a steam distillate of whole feijoa fruit, in which ethyl benzoate and methyl benzoate constituted 90% of the aroma compounds in feijoa fruit. Feijoa was the only fruit found to contain benzoate esters as the major aroma compound (Hardy & Michael, 1970). Shaw et al. (1983) examined the

composition of volatile constituents in the headspace surrounding intact fruit at different stages of ripeness. They suggested that ethyl benzoate may be an important compound in determining optimum ripeness of feijoa and concluded that ethyl butanoate, methyl benzoate and ethyl benzoate are important volatile aromas in aroma of intact feijoa fruit. Shaw et al. (1989, 1990) examined the volatile constituents from skin and flesh. In feijoa skin oil Z-3-hexenol, linalool and methyl benzoate made up 53% of the oil (Shaw et al., 1989). In fruit flesh, methyl benzoate contributed to 82% of the volatile aroma (Shaw et al., 1990). Table 2.1 lists the volatile aroma constituents in feijoa fruit flesh.

2.1.4 Volatile constituents of boysenberry fruit

Porter (1988) used GC-MS to identify and determine the major volatiles from boysenberry fruit by headspace trapping and vacuum distillation. Fourteen volatile constituents were identified, including seven alcohols, two esters, one aldehyde and two terpenes (Table 2.2).

Allen et al. (1996) isolated the volatile constituents from ripe boysenberry fruit by vacuum steam distillation, then used GC, GC-MS and an olfactory GC-sniffing technique to analyse volatile constituents. Thirty-two volatile compounds were identified. The major volatile compounds were ethanol, linalool and α-terpinerol with relative concentrations of 54.1%, 23.5% and 5.1%, respectively. Linalool, nerol and geraniol were judged to have sweet floral and rose-like aroma attributes and were considered important contributors to boysenberry aroma.

Table 2.1 Volatile aroma compounds in feijoa fruit flesh

Aroma compound	Retention time (CW20M)[a]	Retention time (OV-101)[b]	Relative concentration (%)
Ethyl butanoate	7.9	11.7	0.3
Hexanal	9.1	11.6	0.5
Z-3-Hexenal	10.9	12.8	2.2
E-2-Hexenal	13.9	13.2	1.7
E-β-Ocimene	15.4	20.1	1.3
Z-3-hexenyl acetate	18.3	18.3	0.7
Hexanol	20.0	13.9	0.2
Z-3-Hexen-ol	21.8	13.9	0.2
Octan-3-ol	24.5	19.0	2.2
Z-3-hexenyl butanoate	26.6	24.4	0.2
Methyl benzoate	36.6	21.5	81.9
Isopropyl benzoate	38.4	29.1	0.5
Ethyl benzoate	39.0	24.0	0.5
Methyl anisate	63.3	30.0	0.2
Z-Hex-3-enyl benzoate	64.3	37.1	0.2

Source: Shaw et al. (1990)

a: Gas chromatography retention time on CW20M column.

b: Gas chromatograph retention time on OV-101 column.

Table 2.2 Major volatile composition of boysenberry fruit by headspace trapping and vacuum distillation

Aroma compound	Headspace (% peak area, n = 3)	Distillation (% peak area, n = 3)
Ethyl acetate	5.3	2.1
Ethanol	14.3	22.7
Pinene	2.5	0.9
Butan-2-ol	6.1	1.4
Propanol	Nd	4.1
Ethyl butanoate	Nd	1.5
Butan-1-ol	0.2	1.7
3-methyl-butanol	1.0	0.04
E-2-hexenal	1.2	0.09
Heptan-2-ol	3.5	10.6
E-2-hexenol	0.2	10.2
Terpinerol	0.2	25.3
Linalool	37.4	2.9
Geraniol	1.3	1.3

Source: Porter (1988).

Nd: Not detected.

2.1.5 Review of techniques for analysis of aroma compounds

Flavour chemists have developed new methods and techniques, and/or used existing instruments for isolation, separation and identification of the volatile compounds in food and beverages (Maarse, 1981). Aroma compounds from fresh fruit and fruit juice have been analysed using gas chromatography, mass spectrometry, infrared spectroscopy or nuclear magnetic resonance techniques (Harmon, 1997).

2.1.5.1 Isolation and concentration

Headspace analysis can be used for studying volatile compounds which are directly responsible for the odour of foods and beverages (Maarse, 1981). It is a rapid and simple method, but the primary problem is that often, too little sample is available for instrument analysis. Headspace concentration is necessary for analysis of trace food volatiles and can be achieved by using cryogenic trapping, adsorption or on-column vapour trap methods (Reineccius, 1984).

Distillation is the oldest method for flavour isolation. It takes advantage of the volatility of flavor compounds and non-volatility of the major food constituents to achieve separation. This method includes steam distillation and high vacuum striping, but still requires a method to concentrate the dilute aqueous flavour distillate (Maarse, 1981).

Solvent extraction may be used to either extract a food directly or to recover a volatile compound from the dilute aqueous flavour distillate. Solvent selection is primarily determined by the components that are to be extracted from the aqueous system. Usually non-polar, low-boiling solvents can be used such as pentane and hexane. Supercritical carbon dioxide (CO_2) fluid is also an ideal solvent (Reineccius, 1984).

Solid phase extraction (SPE) is based on adsorption of volatile compounds onto a solid matrix. As a liquid sample is passed through the SPE column, compounds are extracted from the sample onto the adsorbent material in the column. Interferences can then be

selectively removed from the column through the correct choice of wash solvents. Finally, the desired analytes may be selectively recovered from the column by an elution solvent, resulting in a highly purified extract. SPE offers many benefits and advantages over traditional sample preparation techniques, including high recoveries of the analytes, concentration of the analytes and highly purified extracts (Harmon, 1997).

Solid-phase microextraction (SPME) is a relatively new technique for the rapid, solventless extraction or preconcentration of volatile and semi-volatile organic compounds (Harmon, 1997). It integrates sampling, extraction, concentration and sample introduction into a single step. Its principal is based on an organic compound's partition between a bulk aqueous or vapour phase and the thin polymeric films coated onto fused silica fibers in the SPME apparatus (Harmon, 1997). SPME is an equilibrium technique. The factors affecting equilibrium include the component's polarity, volatility, organic/water partition coefficient, the volume of the sample, the volume of the headspace, the rate of agitation, the pH of the solution and the temperature (Harmon, 1997). Accurate quantitative analysis requires incorporation of an internal standard into the matrix, constant specific sampling time and careful control of the extraction (Ibanez et al., 1998).

2.1.5.2 Separation

Gas chromatography is the single most wildly used and most important technique in flavour chemistry. Gas chromatography has tremendous separating power, often in excess of 200,000 theoretical plates per column. This attribute is essential for the separation of complex flavor concentrates (Reineccius, 1984). Single dimension gas chromatography is capable of revealing several pieces of key information regarding the volatile composition of a flavour sample, but it's limitation is it does not provide definitive qualitative information regarding the analysed sample and it is unable to separate complex flavours (Wright, 1997). As a result of this limitation, various techniques have been employed to increase both the quality and quantity of information on flavor composition using multidimensional gas chromatography, supercritical fluid chromatography (Wright, 1997).

2.1.5.3 Identification

Information on the properties of an aroma compound including mass spectra, infrared spectra, and nuclear magnetic resonance spectra, Kovats index on apolar high-resolution gas chromatography columns, and its characteristic odor can help to make an identification (Maarse, 1981). Techniques that combine gas chromatography and mass spectra with a mass spectrometer computer library are most widely applied in flavour research. In coupling mass spectrometry to gas chromatograph (GC-MS), the GC technique separates the components of the mixture and delivers pure substances to the mass spectrometer. The mass spectra obtained contain a large amount of information and are generally sufficient to characterise unknown compounds. The mass spectrum of compounds can be related to the structure of the molecule. In many cases positive identification can be made by comparison with a library of spectra (Kameoka, 1986).

2.2 Aroma recovery during beverage processing

During the first stage of juice evaporation, only 6% of the water may vaporise, but all desirable aromas and volatiles are almost completely evaporated along with the vapour. The vapours containing enriched aromas are condensed in a condensor (Lazarides et al., 1991). In order to rectify and concentrate aromas from condensate containing fruit aromas, many techniques have been used commercially, e.g. distillation, partial condensation, gas injection. A number of new techniques for aroma concentration have been developed, e.g. pervaporation, absorption, and supercritical fluid extraction and reverse osmosis (Karlsson & Trägårdh, 1997).

2.2.1 Aroma recovery by evaporation and distillation

Distillation is a mass transfer operation used for removal and recovery of volatile compounds from liquid foods (Saravacos, 1994). The striping of volatile compounds from liquid mainly depends on mass transfer within the liquid phase and at the liquid/vapour interface (Saravacos, 1994). The driving force for mass transfer is a partial pressure

gradient. The fundamental principle of separation by distillation is based on the fact that different components in the liquid have different vapour-liquid equilibrium due to differences in volatility (Karlsson & Trägårdh, 1997). Most aroma compounds have high volatility relative to water, so they would be enriched in the vapour (Saravacos, 1994).

Distillation can be operated at atmospheric pressure or at reduced pressures. If the aroma recovery occurs at atmospheric pressure, the temperature is high, normally 100-105°C, and there is a larger risk of thermal damage to heat sensitive aroma. However if the aroma recovery occurs at reduced pressure, the separation can be achieved at 40-100°C (Karlsson & Trägårdh, 1997). In 1944, distillation was first used for aroma recovery and separation of apple aroma. Since then, there have been modifications and improvements in commercial aroma recovery plants (Karlsson & Trägårdh, 1997)

Ramteke et al. (1990, 1993a, 1993b) investigated the change in aroma composition from different fruit juices during aroma concentration by evaporation and distillation. The composition change was different in different fruit juices due to the highly complex nature of aroma compounds.

2.2.2 Aroma recovery and concentration by partial condensation

Partial condensation is based on the principle that different vapour compounds exhibit different vapour- liquid equilibrium at different temperatures and pressures. When the vapours containing aroma compounds are transferred into a partial condensor, some compounds will condense more than others. The less volatile compounds will be enriched in the liquid, and more volatile aroma compounds will be concentrated in the vapour (Karlsson & Trägårdh, 1997).

2.2.3 Aroma recovery and concentration by gas injection techniques

Aroma recovery by gas injection involves the formation of the vapour-liquid equilibrium and the selective enrichment of volatile components in the vapour phase. When an inert gas, such as nitrogen or air is injected into the liquid condensate containing the aroma, the gas will strip aroma from the liquid. The resulting aroma rich gas is cooled in order to condense the aroma (Karlsson & Trägårdh, 1997). The technique combining gas stripping and distillation has been commercially used in the recovery of coffee aroma compounds (Karlsson & Trägårdh, 1997).

2.2.4 Aroma recovery by adsorption

Adsorption is based on the phenomenon that a solid has the ability to bind components, from a liquid or a gas, to it's surface. Depending on it's properties, the solid surface will selectively bind some materials more than others. Adsorption can be used to recover aroma compounds from process streams. The regeneration of the adsorbent can be completed by displacing adsorbed compounds and washing with a liquid or a gas. The regeneration also can be done by lowing or removing the ability of the solid to adsorb the adsorbate, which can be achieved by increasing the temperature or by lowing the pressure (Karlsson & Trägårdh, 1997).

Krings et al. (1993) compared 31 different adsorptive materials including zeolite, cyclodextrin and modified activated carbon for removal of aroma compounds from a fermentation process. Zeolite was found to be the most suitable adsorbent.

Bittew and Rosset (1988) used octadecyl-bonded silica and a styrene-divinylbezene co-polymer for the recovery of blackcurrant aroma compounds from aroma condensate.

2.2.5 Aroma recovery by supercritical fluid extraction

During supercritical fluid extraction, a component is removed or separated from a system by contact with another material having a higher affinity for that particular component. Supercritical fluids are characterized by high densities, low viscosities and diffusivities intermediate to that found in gases and liquids. They are considered very good solvents. The supercritical fluid can mix easily with the raw material and selectively extract the aroma compounds. The aroma is separated from the supercritical fluid by decreasing the pressure and/or increasing the temperature (Karlsson & Trägårdh , 1997).

Temelli et al. (1988) used this technique for extraction of citrus oil from citrus fruit peel. They demonstrated that supercritical fluid extraction could maximize product recovery and improve product quality while minimizing energy requirements.

2.2.6 Aroma recovery by reverse osmosis

Reverse osmosis is a membrane-based separation technique, which uses a dense semi-permeable membrane, highly permeable to water and highly impermeable to microorganisms, colloids, dissolved salts and organics (Pozderovic & Moslavac, 1999). The loss of volatile aroma compounds is significantly smaller in fruit juice concentration by reverse osmosis compared to concentration by thermal evaporation. Pozderovic & Moslavac (1999) investigated the application of reverse osmosis for apple aroma concentration from an evaporator condensate. A higher retention of aromas, recovered in the retentate, was achieved at higher processing pressures and lower processing temperatures, this was due to decreased aroma permeation through the membrane.

2.2.7 Aroma recovery by pervaporation

Pervaporation is a membrane separation technology in which components in a liquid feed mixture are transferred through a non-porous permselective membrane by means of partial vaporization and are collected as a vapour in the permeate side (Bengtsson et al., 1992).

The driving force for the mass transfer of permeate from the feed side of membrane to the permeate side is created by a chemical potential gradient established by a difference in partial pressure between the feed side and permeate side (Lipnizki et al., 1999a). This is achieved by reducing the permeate pressure by means of a condenser and vacuum pump system or by sweeping with an inert gas (Lipnizki et al, 1999a).

The separation principal is based on the fact that different compounds permeate through the membrane at different rates, some compounds which are at low concentration in the feed side can be highly enriched in the permeate side (Fleming, 1992).

The components of the feed solution permeate the membrane at rates determined by their feed solution vapour pressure, that is, their relative volatilities and by their intrinsic permeabilities through the membrane (Wijmans et al., 1993). The permeability of the compounds depends on their solubility within the membrane and on the diffusivity of compounds present (Bengtsson et al, 1992). Compared to conventional equilibrium- based separation processes, pervaporation is a nonequilibrium-based process (Fleming, 1992).

A pervaporation system generally consists of a pervaporation module, recirculating feed pump, a condenser and vacuum pump. The pervaporation membrane determines the separation performance and application. Pervaporation with hydrophobic polymer membranes can be applied to separate and recover organics from dilute organic-water mixtures. In this application, when the aroma condensate containing fruit volatile aromas was recirculated past a hydrophobic pervaporation membrane, aromas are transported from the liquid feed to the vapour permeate, the fruit volatile aroma compounds will be enriched in the permeate side (Karlsson &Trägårdh, 1997). Several researchers have reported pervaporation as potential technique for aroma recovery during beverage processing (Bengtsson et al., 1989; Blume & Baker, 1990; Zhang & Matsuura, 1991; Bengtsson et al., 1992; Rajagopalan & Cheryan, 1995).

2.3 Mass transfer process in pervaporation

2.3.1 Review of mass transfer models

The solution-diffusion model is one model widely used to represent the mass transfer process in membrane separation processes. The solution-diffusion model assumes that the overall mass transport through the membrane from the feed side to the permeate side is completed by sorption of permeating component into the membrane and diffusion through the membrane followed by desorption from the membrane (Ferreira, 1998; Lipnizki et al., 1999a). The solution-diffusion model is based on Fick's law (Karlsson et al., 1995) and thermodynamic equilibrium assumed between the liquid phase and the membrane on the feed side, and between the vapour phase and the membrane on the permeate side. (Karlsson et al., 1995)

The solution-diffusion model applied to pervaporation assumes the controlling step is the diffusion across the membrane. This diffusion rate is dependent on resistance to diffusion across the membrane (Böddeker, 1990a). The driving force for diffusion across the membrane is a partial pressure gradient between the liquid feed and the permeate vapour. Pervaporation membrane permeability is a function of solubility and diffusivity of the permeate in the polymer phase of the membrane under this driving force (Böddeker, 1990a). Solubility refers to permeate solubility in the membrane on the feed side of the membrane, and is approximated by liquid-phase equilibrium sorption (Böddeker, 1990a).

Several researchers have reported that the mass transfer process in pervaporation was not always dominated by the membrane resistance. The resistance on the feed side and on the permeate side may play an important role. Karlsson & Trägårdh (1993a) reported that the feed flow rate significantly affected the pervaporation performance. Wijmans et al. (1996) also reported that pervaporation was dominated by boundary layer effects, when removing aroma compounds benzene, toluene, ethylbenzene and xylenes from water. Nguyen (1987) found that the resistance on the vapour side was not negligible compared to the membrane

resistance. Fouda et al. (1993) found that modeling pervaporation processes with the solution-diffusion model lead to an over-estimation of pervaporation performance.

The resistance-in-series model was developed to consider the overall mass transfer resistance from liquid feed to the vapour permeate (Gref et al., 1992). In the resistance-in-series model, the mass transfer from liquid feed to the vapour permeate can be described as follows:

Total resistance = (resistance on the feed side) + (membrane resistance) +(resistance on the permeate side).

The resistance on the feed side is due to resistance to mass transfer across the boundary layer adjacent to the membrane. The membrane resistances are associated with solute sorption into the membrane, diffusion across the membrane and desorption from membrane. The resistance on the permeate side is due to resistances associated with transport of the vapour across the porous support, transport of the vapour to the condenser, and condensation of the permeate (Beaumelle et al., 1992).

In the resistance-in-series model, the overall mass transfer of a component *i* from the bulk of feed to the bulk of the permeate is described by the following equation (Gref et al., 1992):

$$J_i = k_{ov,i}(C_{f,i} - C_{p,i}) \qquad (2.2)$$

Where $C_{f,i}$ = the concentration of aroma compound *i* in the feed solution (kg kg^{-1}).

$C_{p,i}$ = the concentration of aroma compound *i* in the permeate side (kg kg^{-1}).

$k_{ov,i}$ = the overall mass transfer coefficient for aroma compound *i* (kg m^{-2} s^{-1}).

J_i = the flux of aroma compound *i* (kg m^{-2} s^{-1}).

The overall mass transfer coefficient ($k_{ov,i}$) for a component *i* is the sum of individual resistances to mass transfer. The individual resistances are defined by a mass transfer coefficient for the feed boundary layer $k_{bl,i}$, a mass transfer coefficient for the membrane $k_{m,i}$ and a mass transfer coefficient for the permeate side $k_{p,i}$

$$\frac{1}{k_{ov,i}} = \frac{1}{k_{bl,i}} + \frac{1}{k_{m,i}} + \frac{1}{k_{p,i}} \qquad (2.3)$$

The resistance-in-series model separates the membrane and boundary layer resistances, making it possible to compare different membrane materials based on membrane permeability (Ji, 1994a). The resistance-in-series model has been demonstrated to be used effectively to describe or predict the permeation rate and the permeate composition under different operating conditions during pervaporation (Gref et al., 1992; Fouda et al., 1993; Hickey & Gooding, 1994; Ji et al., 1994a; Ji et al., 1994b; Bode & Hoempler, 1996).

2.3.2 Mass transfer on the feed side of the membrane

A boundary layer is that region within a fluid, adjacent to the surface of a membrane (Field, 1993). In membrane processes, the flux of permeate through the membrane causes a convective flow of both preferentially and non-preferentially permeating compounds towards the membrane. Due to the selectivity of the membrane, non-preferentially permeating compounds accumulate on the feed–side of membrane and their concentration on the face of the membrane increases above the bulk value (Field, 1993). Mass transfer within the boundary layer therefore can occur due to the concentration gradient from the more concentrated boundary solution to the less concentrated bulk (Huang & Rhim, 1991). This phenomenon is known as concentration polarization. In pervaporation, the compounds are permeating through membrane with different permeation rates. The concentration of non-preferentially permeating compounds increases in the boundary layer near the membrane surface. In the boundary layer, the convective mass transport of non-preferentially permeating compounds away from the membrane is limited and the diffusive mass transport is rate determining. Preferentially permeating compounds will be transported through the boundary layer with a diffusive mechanism toward the membrane and the concentration of these preferentially permeating compounds will decrease towards the membrane surface. (Karlsson & Trägårdh, 1993b)

The mass transfer coefficient for the feed side boundary layer $k_{bl,i}$ can be calculated using an semi-empirical Sherwood correlation. According to the Sherwood correlation, the resistance to mass transfer on the feed side is affected by several factors, such as crossflow velocity/ stirring speed, flow regime, geometric profile of the membrane module, viscosity of the fluid and diffusivity of the components (Karlsson & Trägårdh, 1993b).

Raghunath & Hwang (1992) investigated the boundary layer effects in a tubular membrane module by varying the fluid velocity or Reynolds number for a constant membrane thickness. In this experiment, benzene, chlorobenzenze and toluene solutions were fed to a pervaporation unit using polydimethyl siloxane (PDMS) membranes. Raghunath & Hwang (1992) concluded that the boundary layer resistance on the feed side was the most significant contributor to the overall transport resistance during the pervaporation separation of volatile dilute organic solutes from aqueous solutions. It was also found that the construction of the membrane module (flow geometry) influenced the efficiency of the pervaporation.

Bengtsson et al. (1993) studied the boundary layer effect on the rate of removed of butyl butyrate from a very dilute aqueous solution. The flux of butyl butyrate through the membrane increased with increasing Reynolds number, by increasing feed velocities from 1 $\times 10^{-3}$ ms^{-1} to 3.9 $\times 10^{-2}$ ms^{-1}.

Dotremont et al. (1994) studied the boundary layer effects on the pervaporation separation of chlorinated hydrocarbons (Cl-HC). The results indicated that the flux of Cl-HC was a function of the feed flow rate. The maximum flux was achieved when the feed flow rate was 5×10^{-5} m^{3}s^{-1} (Re = 380). Below this critical flow rate the Cl-HC with high membrane permeability showed a considerable flux decline. For organic compounds with low permeability, e.g. propanol, the decrease in flux was negligible. Dotremont et al., (1994) also found that the presence of salt, such as NaCl, caused flux decline. The viscosity of the feed solution affected both the trichlorinated hydrocarbons and water flux, and pH did not influence the flux.

Karlsson et al. (1993a) studied the resistance in the boundary layer during pervaporation using a multicomponent aroma model solution, consisting of 2-methyl-propanal, 2-methyl-butanal, 1-pentene-3-ol, trans-2-hexenal and linalool. Pervaporation with PDMS membranes was carried out at different crossflow velocities and hydraulic diameters. They found that the total flux was relatively constant with increasing crossflow velocity, but the partial fluxes of aroma compounds were strongly affected by the Reynolds number.

2.3.3 Mass transfer through the membrane

The mass transfer through the membrane is based on the assumption that thermodynamic equilibriums are established at the membrane surface during sorption and desorption from the membrane. Fick's law described the mass diffusion through the membrane (Liu et al., 1996). The flux of individual components i through the membrane is described by the following equation:

$$J_i = -D_i \frac{dC_{m,i}}{dx} \tag{2.4}$$

where, $C_{m,i}$ = the concentration of permeate i in the polymer membrane (kg kg^{-1}).

x = the position in the membrane from the feed side of the membrane (m).

D_i = the diffusion coefficient of the component i in the polymer membrane (m^2s^{-1}).

The diffusion coefficient of a component in a polymer membrane is concentration dependent and affected by the presence of other components in the membrane.

$$D_i = D_{o,i} \exp(\tau C_{m,i}) \tag{2. 5}$$

where, $D_{o,i}$ = the diffusion coefficient at infinite dilution (m^2s^{-1}).

τ = the coefficient for the interaction between the permeate and the membrane.

Diffusion is also strongly temperature dependent. The dependence of temperature on process can be described with an Arrhenius equation.

$$D_{o,i} = D_{oo,i} \exp(-E_a / RT) \tag{2.6}$$

where, $D_{oo,i}$ = the diffusion coefficient at infinite temperature ($m^2 s^{-1}$).

R = universal gas constant (J mol^{-1} K^{-1}).

E_a = activation energy (J mol^{-1}).

T = operating temperature (K).

From equation (2.4), the flux of a single component can be described by the following equation:

$$J_i = \frac{D_{o,i}}{\Delta x}(C_{fm,i} - C_{pm,i}) \tag{2.7}$$

where, $C_{fm,i}$ = the concentration of compound i inside the membrane at its feed side (kg kg^{-1}).

$C_{pm,,i}$= the concentration of compound i inside the membrane at its permeate side (kg kg^{-1}).

Δx = the thickness of the membrane (m).

The flux of a component across the membrane will consequently be dependent upon its diffusivity in the membrane; its concentrations inside the membrane at both feed side and permeate side, and the thickness of the membrane. $C_{fm,i}$ and $C_{pm,,i}$ are determined based on the assumption of the formation of a thermodynamic equilibrium (Lui et al., 1996).

$C_{fm,i}$ is proportional to the component i activity in the phase adjacent to the membrane:

$$C_{fm,i} = \varphi_{f,i} \frac{P_{f,i}}{P_i^o(T_1)} \tag{2.8}$$

where, $\varphi_{f,i}$ = the partition coefficient for component i at feed side surface (kg kg^{-1}).

$P_{f,i}$ = the partial pressure of compound i at feed side (Pa).

$P_i^o(T_1)$ = the saturation vapour pressure of pure compound i at feed temperature (Pa).

T_1 = the feed temperature (K).

On the permeate side, thermodynamic equilibrium yields the following equation:

$$C_{pm,i} = \varphi_{p,i} \frac{P_{p,i}}{P_i^o(T_2)} \exp\left[-\frac{V_i}{RT_2}(P_{f,i} - P_{p,i})\right] \tag{2.9}$$

where, $\varphi_{p,i}$ = the partition coefficients for component i at permeate side surface (kg kg^{-1}).

$P_{p,,i}$ = the partial pressure of compound i at permeate side (Pa).

$P_i^o(T_2)$ = the saturation vapour pressure of pure compound i at permeate temperature (Pa).

T_2 = permeate temperature (K).

V_i = molar volume of component i (m^3 mol^{-1}).

However, for multi-component mixtures, mass transfer through the membrane is usually more complex than for single components. The permeating components interact not only with the membrane but also with each other. This phenomenon is called flow coupling. It has been observed that the sorption of permeate components into the membrane and the orientation of the dissolved permeate molecules changes the configuration of the microvoids between the polymer chains of the membrane. These changes facilitate or inhibit the transfer of individual components (Kedem, 1989; Drioli & Basile 1993; Heintz & Stephan, 1994a). Karlsson & Trägårdh (1994) investigated the effects of flow coupling on pervaporation performance by varying ethanol and aroma concentration in the feed. The results indicated that when the concentration of organic compounds was low, it caused little

or no swelling of the membrane, thus, the transport properties of the individual organic compounds were unaffected. The fluxes of ethanol, water and aromas had a simple linear relationship with their feed concentrations. Karlsson & Trägårdh (1994) also found that in some cases the flux of the aroma component was affected by the ethanol concentration when ethanol was present at relatively high concentration.

2.3.3 Mass transfer on the permeate side of the membrane

The mass transfer resistance produced by crossing the membrane porous support layer and transport to the condenser has usually been neglected when a good vacuum is maintained on the permeate side of the membrane. Although the vapour phase mass transfer coefficient is greater than the mass transfer coefficient in the active membrane, the vapour diffusion distance is much longer than the active membrane layer thickness. Mass transfer resistance on the permeate side of the membrane can therefore be relatively important (Lui et al., 1996). The diffusion coefficient in the porous support was estimated with a combination of molecular diffusion and viscous diffusion. Mass transfer resistance on the permeate side of the membrane was affected by the total permeate pressure, distance between the module and the condenser and the temperature of the condenser (Marin et al., 1996).

Nguyen (1987) also found that the vapour side resistance could not be neglected compared to the membrane resistance. Hickey et al. (1992) and Beaumelle et al. (1992) have found that the permeate pressure affected pervaporation performance due to resistances on the permeate side. Bode et al. (1993) investigated the resistance of transport across an interface between the membrane polymer and vapour phase. The result was that interface resistance should be of concern only for thin membranes and for permeates with low solubility in the membrane polymer. Marin et al. (1996) considered that modification of the downstream equipment can improve the permeate recovery. This research showed that multi-stage condensation could be very efficient for extracting volatile organic compounds diluted in aqueous mixtures (Marin et al., 1996).

2.4 Factors affecting performance of pervaporation membranes

Pervaporation performance can be characterized by the performance parameters of flux and selectivity. Both parameters reflect industry necessities. The flux determines the membrane area, the installation size and cost and the selectivity determines the quality of the product (Baudot & Marin, 1997). The flux J is the flow rate of permeates per unit membrane area. The selectivity of pervaporation is defined with two parameters, separation factor and enrichment factor. Separation factor $\alpha_{i/j}$, describes the ability to separate substance i and substance j, defined as the concentration ratio in the permeate ($C_{p,i}$ /$C_{p,j}$) divided by the concentration ratio in the feed ($C_{f,i}$ /$C_{f,j}$).

$$\alpha_{i/j} = \frac{C_{p,i} / C_{p,j}}{C_{f,i} / C_{f,j}} \tag{2.10}$$

where, $C_{p,i}$ = The concentration of compound i in the permeate (kg kg^{-1}).

$C_{p,j}$= The concentration of compound j in the permeate (kg kg^{-1}).

$C_{f,i}$ = The concentration of compound i in the feed (kg kg^{-1}).

$C_{f,j}$ = The concentration of compound j in the feed (kg kg^{-1}).

Enrichment factor β_i indicates the degree of enrichment of compound i. It is the relationship between the concentration of the component i in the permeate ($C_{p,i}$) and the concentration of component i in the feed ($C_{f,i}$).

$$\beta_i = \frac{C_{p,i}}{C_{f,i}} \tag{2.11}$$

The membrane primarily governs the pervaporation performance. The nature of the aroma compounds and other compounds present in the liquid feed also influence the pervaporation performance. Performance is also affected by operating conditions including feed temperature, feed concentration, feed composition, feed flow rate, permeate temperature, permeate pressure and condenser condition (Huang & Rhim, 1991).

2.4.1 Pervaporation membranes

For pervaporation, the membrane must have a high flux and a large separation factor. Membrane permeability is governed by chemical nature and physical structure of the membrane polymer (Baudot & Marin, 1997). The membrane separation factor for a solute is the result of solubility selectivity and diffusivity selectivity (Zhang & Drioli, 1995). In general, diffusivity is dependent on the molecule size. The diffusion of a small molecule across the dense membrane is favored. The solubility of a molecule is dependent on the chemical affinity between the solute and the membrane (Zhang & Drioli, 1995).

Pervaporation membranes are divided into two types, hydrophilic and hydrophobic. Hydrophilic membranes are made up of hydrophilic polymers as the membrane material, while hydrophobic membranes are made up of hydrophobic polymers as the membrane material. Usually hydrophilic membranes are glassy polymers, which have a glass transition temperature above 20°C and preferentially permeate water. Hydrophobic membranes are rubbery polymers, which have a glass transition temperature below 20°C and preferentially permeate organic substances (Börjesson et al., 1996).

2.4.1.1 Hydrophobic pervaporation membranes

Hydrophobic pervaporation membranes consist of composite membranes and non-composite membranes. Non- composite membranes are only composed of a selective layer of unbaked homogeneous polymer film, for example poly-ether-block-amide (PEBA) membranes (GKSS Germany). Composite membranes consist of a selective thin active layer deposited on thicker support layer. The support layer can be composed of polyacrilonitrile on a polyester or of non-woven polyester covered by microporous polyetheramide (Baudot & Marin, 1997). The active layer of these membranes are either a homogeneous polymer film such as polydimethylsiloxane (PDMS) or poly-ether-block-amide (PEBA), or an adsorbent-filled polymer film such as the silicalite-filled PDMS membrane (Karlsson & Trägårdh, 1993b).

PDMS membranes have high overall fluxes and good selectivity (Hennepe, 1994). Lee & Oh (1993) added a hydrophobic zeolite silicalite to PDMS, the process resulted in a membrane with higher fluxes and higher selectivity than ordinary PDMS membranes. Poly-1-trimethyl silyl-1-propyne (PTMSP) membranes showed higher ethanol selectivity and higher flux than PDMS membranes. PEBA membranes showed lower selectivity for alcohols, but higher selectivity for aromatic compounds than PDMS membranes (Karlsson & Trägårdh, 1993b). Polyurethane membranes (PUR) showed lower selectivity and flux for organic compounds than PDMS and PEBA membranes (Karlsson & Trägårdh, 1993b). Polyoctylmethyl siloxane membranes (POMS) were more selective for aroma compounds than the PDMS membranes (Sampranpiboon et al., 2000).

Börjesson et al. (1996) investigated the performances of six different pervaporation membranes. In this research, PDMS (GFT1060), PDMS (GFT1070), PDMS (PT1100), POMS (PEI), POMS (PVDF) and PEBA (GKSS) membranes, were used to recover apple aroma compounds from a model solution. The results showed that the mass transfer coefficients and enrichment factors corresponding to different membranes were different for each group of aroma compounds. PDMS (PT1100), POMS (PEI) and POMS (PVDF) membranes yielded higher enrichment factors and higher mass transfer coefficients than PDMS (GFT1060), PDMS (GFT1070) and PEBA membranes.

The development of high-flux-high-selectivity membranes for pervaporation focuses on minimizing the thickness of the dense active layer without defect and maximizing the porosity of the support layer without losing its mechanical stability (Rautenbach & Helmus, 1994).

Membranes can be set in a flat sheet module, spiral wound module, or capillary and hollow fiber form (Fleming, 1992).

2.4.2 The nature of the aroma compounds

The more hydrophobic an organic compound is, the more it will be extracted with a hydrophobic pervaporation membrane. However, the selectivity of pervaporation hydrophobic membranes is very dependent on the chemical class of the organic compound (Baudot & Marin, 1997).

Lactones are high molecular weight compounds, and their saturated vapour pressures are extremely low at ambient temperature. Using pervaporation with hydrophobic membranes, lactones are concentrated 10 to 100 fold more than by vacuum distillation. However, their transmembrane fluxes were generally very low, 10 times smaller than esters, alcohols or aldehydes (Baudot & Marin, 1997).

Esters are very hydrophobic compounds of low molecular weight. Their saturated vapour pressure are high. The selectivity offered by pervaporation with hydrophobic membranes was close to the vapour- liquid equilibrium. However, the esters that contain the benzene group have the higher selectivity, due to their very high hydrophobicity (Baudot & Marin, 1997).

Alcohols and aldehydes are hydrophilic organic compounds. During pervaporation with hydrophobic membranes, the selectivity of these compounds is usually higher than the vapour- liquid equilibrium selectivity. Hydrophobic pervaporation membranes are very selective to molecules containing a benzene nucleus (benzyl alcohol, o-creasol, linalool, thymol, 2,5-xylenol, benzadehyde). But the organic partial fluxes are very low due to the very low saturated vapour pressures (Baudot & Marin, 1997).

For ketones with small carbon chains, the selectivity of hydrophobic pervaporation membranes was lower than the vapour-liquid equilibrium performance. The transmembrane fluxes of these ketones were 10 times smaller than that obtained with esters, alcohols or aldehydes. However, pervaporation proved to be very efficient for the recovery of large hydrophobic ketones with more than six carbon atoms (Baudot & Marin, 1997).

Baudot & Marin (1997) concluded that pervaporation with hydrophobic membranes is more selective than the vapour-liquid equilibrium for molecules that have low relative volatility, high molecule weight and high hydrophobicity. For low relative volatility compounds, the low transmembrane driving force is likely to be counterbalanced by a strong sorption effect which promotes the organic compound transport through the membrane (Baudot & Marin, 1997)

2.4.3 Feed composition

Feed concentration directly affects the sorption phenomena at the liquid- membrane interface and affects diffusion of the component in the membrane. As flow coupling occurs during pervaporation, feed composition influences the pervaporation performance (Huang & Rhim, 1991).

Böddeker et al. (1990) studied the behavior of butanol isomers and benzyl alcohol through PEBA membranes and found that the organic compound's permeation rates increased with increasing concentrations of organic compounds in the feed. Rajagopalan & Cheryan (1995) used PDMS membranes to separate grape aroma compounds. When the methyl anthranilate concentration was below 50ppm, they found that the flux of methyl anthranilate was linearly dependent on its concentration on the feed side of the membrane only.

Beaumelle et al. (1992) found ethanol concentration to have an effect on the mass transfer of aroma compounds. Aroma fluxes were higher when 10% ethanol was added to the feed mixture. Ji et al. (1994a) studied the optimization of multicomponent pervaporation for removal of volatile organic compounds from water. They found that the membrane area required to remove volatile compounds from their multicomponent feed mixtures was less than that from a binary feed solution. This was due to the facilitated flow coupling transfer

occurring between aroma compounds and membrane polymer. Molina et al. (1997) also found similar flow coupling effects with ethanolic solutions of linalool.

Groβ & Heintz (1999) investigated the sorption isotherms of seven individual compounds and mixtures of them with PEBA membranes. They found there was no flow coupling between a mixture of phenol and aniline, whereas the sorption of pyridine in the membrane was increased by the presence of phenol at a concentration > 1000 ppm. The compound which had the higher solubility in membrane enhanced the solubility of the compound which had lower solubility in the membrane (Groβ & Heintz, 1999).

2.4.4 Feed temperature

The solubility and diffusion of the feed mixture components in polymeric membranes is dependent on operating temperature (Beaumelle et al., 1992). When feed temperature changes, the partial pressure changes at the feed side of membrane, which also affects pervaporation performance. Diffusion and permeation rate increases with increasing temperature and temperature affects can be described with the Arrhenius equation (Beaumelle et al., 1992; Karlsson et al., 1995).

Karlsson et al. (1995) studied the performance of pervaporation for recovery of aroma compounds from Muscat wine through a PDMS (GFT 1060) membrane at four different feed temperatures, 6, 15, 25 and 35°C. It was observed that the partial fluxes of eight aroma compounds across the membrane were increased with increasing operating temperature. Individual aroma compounds were affected differently by the temperature change, and this resulted in a change in the permeate concentration. It was concluded that it is important to know the temperature dependence of the different aroma compounds (Karlsson et al., 1995).

Rajagopalan et al. (1994) found temperature to have a positive effect on selectivity, when dairy aroma (diacetyl) recovery by pervaporation with polydimethylsiloxane-polycarbonate

copolymer (PDMS-PC) membranes was carried out. The selectivity for diacetyl increases from 33 fold at 24°C to almost 41 fold at 43.5°C. Rajagopalan & Cheryan (1995) investigated the effect of temperature on the pervaporation of a concord grape juice model solution containing methyl anthranilate. Three different membranes were used including PDMS-PC, PEBA, and GFT-1070. Flux and selectivity increased with increasing temperature from 33°C to 52°C for the three different membranes. Baudot & Marin (1996) also reported that the selectivity of the PDMS 1070 membrane for aroma recovery was slightly higher at a feed temperature of 50°C than at the feed temperature of 30°C.

In contrast, Beaumelle et al. (1992) studied the pervaporation of aroma compounds in water-ethanol mixtures through PDMS membranes using propanol, ethyl acetate and ethyl butyrate model solution. They found a small decrease in selectivity with increasing temperature.

2.4.5 Feed flow velocity

In pervaporation, concentration polarization results in a decrease in flux and selectivity. For dilute feed solutions, where the concentration of organics is 5-500 ppm, as found in aroma condensates obtained from fruit juice evaporation, concentration polarization controls the mass transfer rate (Beaumelle et al., 1992). In order to minimize the effect of the concentration polarization phenomenon and to improve the mass transfer rate, optimization of the feed circulation velocity is very important (Bengtsson et al., 1993).

The effect of feed flow rate was different for different aroma compounds, depending on the aroma compound's permeability across the membrane and the aroma concentration in the feed. Changing of the feed flow rate resulted in changes to the permeate composition (Karlsson et al. 1993a).

Olsson & Trägårdh (1999) found that increasing the feed flow velocity did not significantly increase the recovery of the alcohols, whereas it greatly increased ester recovery. Hence, feed flow velocity will affect permeate composition (Olsson & Trägårdh, 1999).

2.4.6 Permeate pressure

Permeate pressure strongly influences pervaporation performance by affecting the driving force for mass transfer (Huang & Rhim, 1991). If the permeate pressure is zero, the maximum driving force for mass transfer across the membrane can be achieved. In contrast, if the permeate pressure is equal to, or higher than the pressure of the components in the feed, the mass transfer through the membrane follows liquid-vapour equilibrium separation. Increases in permeate pressure resulted in linearly decreasing fluxes (Wijmans et al., 1996). Beaumelle et al. (1992) found permeate pressure did not significantly influence selectivity. The effect of permeate pressure was dependent on aroma properties and feed temperature (Ten & Field, 2000).

Permeate pressure was found to influence selectivity and was dependent on the boiling point of aroma compounds (Böddeker & Bengtsson, 1990; Böddeker et al., 1990). Böddeker et al. (1990) found the permeation rate of the high boiling n-butanol (117.7°C) increases significantly as the permeate pressure was reduced, while that of the low boiling tert-butanol (82.5°C) was only slightly affected. Böddeker & Bengtsson (1990) studied pervaporation of low volatility aromatics from water. It was observed that water permeability depended little on permeate pressure, whereas for phenol (boiling point 182°C) its enrichment factor increases strongly as the pressure is lowered from 1000 Pa to 100 Pa. Baudot & Marin (1997) concluded that permeate pressure does not affect the selectivity of pervaporation except in the case of the extraction of high boiling point compounds. It is because desorption resistance is the permeation rate limiting factor for large molecules with low volatility (Baudot & Marin, 1997).

Rajagopalan & Cheryan (1995) found flux and selectivity decreased linearly with increasing permeate pressure from 132 Pa to 264 Pa. However, Ji et al. (1994a) found permeate pressure could have positive or negative effects on the separation factor depending on the ratio of overall organic permeability to water permeability.

Baudot and Marin (1996) studied the influence of various operating parameters on recovery of the two dairy aroma compounds; methylthiobutanoate (boiling point 142°C) and diacetyl (boiling point 88°C) through the PDMS1070 and PEBA 40 membranes. The permeate pressures were set in the 250 Pa-2500 Pa range. It was observed that total flux and aroma partial flux decreased with increasing in permeate pressure.

Ten & Field (2000) developed a comprehensive mathematical model to examine the effect of permeate pressure on performance.

2.4.7 Condensation conditions

Modification of downstream equipment can improve pervaporation performance by lowing the resistance of mass transfer in the permeate side. Lowing condensation temperature or using multi-stage condensation systems were found to enhance the selectivity of aroma compounds in pervaporation (Baudot & Marin, 1996; Marin et al., 1996).

2.5 Applications of pervaporation

Compared with other traditional separation techniques, advantages offered by pervaporation are less energy, operation at ambient temperature or minimal temperature change, no additives, continuous operation, no reactions with the stream to be separated and, easy to install and to scale up (Blume & Baker, 1990). Since 1917, when pervaporation was first discovered, there was no great progress in fundamental research and application study for this separation technique until the end of the 1970s. Since the late 1970s, considerable research into pervaporation was been undertaken (Zhang & Drioli,

1995). In 1982, the first commercial full-scale pervaporation plant was installed in Brazil by Deutsche Carbone AG of Germany, for production of anhydrous ethanol (Huang & Rhim, 1991). Pervaporation has been used worldwide since then. Fleming (1992) classified pervaporation applications into three major categories:

1. Using hydrophilic membranes to remove water from liquid organic solutions.
2. Using hydrophobic membrane to remove organics from aqueous solutions.
3. Organic-organic separations.

Pervaporation applications for the removal of water from liquid organic streams using hydrophilic membranes has been promoted commercially worldwide for solvent dehydration (Fleming, 1992).

The application of pervaporation for the removal of organic compounds from water using hydrophobic membranes is limited and only commercially available around 1989 (Fleming, 1992). However, studies on the modification of existing membranes, on the development of new membranes for improved performance, and on the applications for this area have continued (Zhang & Drioli, 1995). The dealcoholization of beers, wines and other liquids and treatment of wastewater using PDMS (GFT) membranes are examples of commercial processes using pervaporation (Fleming, 1992). Meanwhile, pervaporation application for recovery of aroma compounds in biotechnology and beverage processing has been found to be a promising technique (Karlsson & Trägårdh, 1996).

The application for organic-organic separation is least developed, because of the limitation of membranes suited for this purpose (Fleming 1992). However, it seems to have good opportunity for reducing energy and process costs if suitable pervaporation membranes can be developed (Ferreira, 1998). Moganti et al. (1994) investigated the feasibility of separating benzene and cyclohexane combining pervaporation and distillation. Twenty percentage cost savings were achieved compared to distillation only. Doghieri et al. (1994) showed feasibility of the separation methanol from methyl tert-butyl ether solution through pervaporation with modified poly-membranes (phenylene oxide). Roizard et al. (1998)

found pervaporation with a membrane of dense films containing lewis base groups achieved the separation of alcohol and ether.

Pervaporation based hybrid processes in which pervaporation is combined with distillation and with chemical reactors has been realised on an industrial scale and has been proved to have economic potential for waster water treatment, and biotechnology application (Meckl & Lichtenthaler 1996; Lipnizki et al., 1999b).

2.5.1 Solvent dehydration

Solvent dehydration is the major application of pervaporation. Usually solvent dehydration is achieved by distillation. In the distillation process, an azeotropic forms. Azeotropic distillation is a very energy consuming process. Pervaporation is not restricted by operating pressure and is able to break the azeotrope point. Pervaporation is now considered to be a useful and economical process for dehydration of organic solvents (Maeda & Kail, 1991).

The dehydration of ethanol is the most important pervaporation application. The largest capacity plant is installed in France, which processes 150,000 l/hr of 99.95%(v/v) ethanol through 2,4000 m^2 of membrane. Ethanol dehydration with pervaporation can be carried out directly after fermentation or following primary distillation. Pervaporation is suitable for concentrating ethanol feeds of 85% or higher (Ferreira, 1998). Hybrid pervaporation and distillation for the production of anhydrous ethanol is considered the best option, due to savings on capital, operating costs and energy (Stephen et al., 1995).

A number of hydrophilic and ion-exchange polymeric membrane materials have been found to exhibit favorable selectivity and fluxes for water. The polyvinylalcohol (PVA) asymmetric composite membrane is the only commercial membrane. Most commercial processes have the following operating conditions, feed temperature of 50°C to 100°C, permeate pressures of 500-2000 Pa absolute pressure, condensation temperatures from 30°C to -20°C. The membrane selectivity can be between 50 - 2,000 fold for fluxes below

1.1×10^{-3} kg $m^{-2}s^{-1}$ depending on feed concentration and operating condition (Fleming, 1992).

Several different membrane modules have been designed for dehydrating ethanol. A single membrane module or multiple membrane modules have been designed for production of ethanol 99.95% from feed ethanol of 80-90%. An integrated multistage distillation/ pervaporation system was designed for ethanol production of 99.5% ethanol from a feed of 6% ethanol (Fleming, 1992).

2.5.2 Wastewater treatment

Pervaporation can be used in wastewater treatment to produce a high purity water and recover valuable organic substrates (Blume & Baker, 1990). Pervaporation can recover organic compounds and water to a high standard without additional processing and additives, compared with traditional wastewater treatment techniques (Lipnizki et al, 1999a). Pervaporation also offers potential energy savings, and environmental and economical benefits to industry.

Blume & Baker (1990) filed a US patent in which 0.1wt% of dissolved organic solvent wastewater was treated by pervaporation. Urtiaga et al.(1999) presented a mathematical model for pervaporation separation of chloroform from an aqueous solution in hollow fiber membranes. Abou-Nemeh et al. (1999) also presented the feasibility of separation and recovery of trichloroethylene (TCE) from surfactant-containing aqueous solution by a composite hollow fiber membrane-based pervaporation process.

Lipnizki & Field (1999) investigated the influence of different process modules and design parameters on the pervaporation performance for recovery of phenol and pyridine from wastewater and gave the guidelines for the process design for hydrophobic pervaporation.

2.5.3 Pervaporation in biotechnology processes

In microbiological fermentations, the volatile by-products include ethanol, butanol, acetone, 2,3-butanediol, glycerol, isopropanol or acetic acid. All of these fermentation products are product-inhibiting which means the bio-conversion rate decreases with increasing product concentration. Pervaporation can improve both overall process efficiencies and product quality in biotechnology in the following areas: the direct recovery of by-products from the fermentation broth; the removal of process-inhibiting volatile by-products; the concentration and purification of thermally unstable, sensitive volatile by-products; the dehydration of organic solvents (Strathmann & McDonogh, 1993). In comparison with the other methods such as extraction, perstraction and distillation, pervaporation does not harm the fermenting microorganism, does not remove reactor ingredients from the reaction mixture, and concentrates the product (Strathmann & McDonogh, 1993).

Böddeker et al. (1990) studied pervaporation for the recovery of isobutanol from acetone-butanol fermentation and compared pervaporation with other separation techniques such as evaporation, reverse osmosis rejection and adsorption by zeolites. In this research, the performance of PDMS, PUR and PEBA membranes to separate isomeric butanols and the effect of the thermodynamic condition of the aqueous feed solution and the permeate side were investigated. They found that the PEBA membranes provided the highest selectivity while the PDMS membranes gave the highest flux.

Voilley et al. (1990) compared two pervaporation membranes for recovery of 1-octen-3-ol from fermentation broth. They found the flux was similar for the two membranes, while selectivity of the silicon rubber membrane appeared to be five times greater than the selectivity of the microporous membrane.

Hickey et al. (1992) investigated the effects of membrane and process parameters on the performance of a pervaporation module combined with an acetone-butanol-ethanol fermentation process. They found POMS membranes showed higher selectivity towards n-

butanol than the PDMS membranes. The result was that flux increased with increasing temperature, and with decreasing permeate pressure.

Feng & Huang (1992) compared the performance of PDMS and silicone polycarbonate membranes for separation of isopropanol from water. PDMS membranes showed better performance than the silicone polycarbonate membrane.

Ogbomo et al. (1993) studied the possibility of monitoring the substrate or product continuously in immobilized enzyme bioprocesses. In this research, the ethanol in beer and baker's yeast culture was determined in-line, based on its extraction by means of pervaporation through a porous hydrophobic membrane. The results showed good reproducibility and good monitoring for bioprocesses.

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is the most important flavour compound used in food flavouring, which can be obtained by bio-conversion of natural vanillin precursors, e.g., eugenol. Böddeker et al. (1997) investigated the recovery and/or purification of vanillin from an aqueous solution using pervaporation with PEBA membranes. Pervaporation obtained the higher purity vanillin (99%) compared to the conventional method (95%)

The aroma produced by yeast during wine-must fermentation comprises up to 800 aroma compounds. Schafer et al. (1999) proved that pervaporation can be highly suitable for the continuous recovery of very complex and declicate aromatic compounds which contributed the wine-must aroma profile.

Lamer et al. (1996) studied the pervaporation recovery of benzaldehyde produced by microorganisms. The result was that minimum permeate pressure and maximum feed flow rate resulted in high flux of benzaldehyde.

Qureshi et al. (1999) used a silicalite/silicone membrane to recover the butanol from a fermentation broth. The silicone membrane incorporated with silicalite had higher flux and selectivity for the butanol during pervaporation than non-silicalite membranes. Feed concentration, temperature and membrane thickness affected the flux and selectivity for butanol.

2.5.4 Pervaporation aroma recovery in beverage processing

Pervaporation has proved to be an effective method for the concentration of organic aroma compounds in beverage processing. Model aroma compound solutions have been used to study the feasibility of pervaporation for aroma recovery in beverage processing.

Bengtsson et al. (1989) studied the recovery of apple aroma compound with pervaporation using a model solution containing 12 of the most important apple aroma compounds. Aroma compounds were extracted by pervaporation from three different feeds, a model apple juice, a condensate from evaporative concentration of the model apple juice and a permeate from reverse osmosis concentration of the model apple juice. These feeds were concentrated by pervaporation at 5°C, through a PDMS membrane, with a permeate pressure of 500-600 Pa. The permeate obtained from the model apple juice was found to have a similar enrichment factor to the permeate obtained from the evaporator condensate. The reverse osmosis permeate was found to contain little or no aroma compounds. The pervaporation permeate obtained from the evaporated condensate had been enriched in aroma compounds 5 to 13 fold for the alcohols, 50 fold for the aldehydes and 83 to 125 fold for the esters. The conclusion was the recovery of aroma compounds from evaporator condensates could be advantageous.

Bengtsson et al. (1992) concentrated apple juice aroma condensate by pervaporation and compared this to the conventional distillation method. In this study, the pervaporation experiment was conducted on the same apparatus used by Bengtsson et al. (1989), but different total concentration ratios of 1:100, 1:200, or 1:1000 were achieved at operating

temperatures of 5°C and 20°C. Twelve selected compounds in the apple aroma condensate were identified and their enrichment factors were determined. The aroma enrichment factors were 2 - 22 fold for alcohols, 100 fold for esters and 16 - 67 fold for aldehydes. They also found that the aroma recovery was higher when the concentration ratio was 1:100 or 1:200, and the greatest losses occurred while achieving the concentration ratio of 1:1000.

Zhang & Matsuura (1991) also studied the recovery and concentration of apple aroma from an apple essence by pervaporation using PDMS membranes, at 22°C and permeate pressure of 300 Pa. They found that low boiling point flavour compounds can be enriched to above 20 fold. Higher boiling point compounds had lower enrichment factors.

Blume & Baker (1990) reported on the concentration and/or recovery of orange aroma from orange juice aroma condensate by pervaporation. A sample of orange juice aroma condensate was feed to a spiral-wound PDMS membrane module with approximately 0.17 m^2 membrane, at a temperature of 30°C, permeate pressure of 260 Pa, and feed flow rate of 8.3×10^{-5} m^3s^{-1}. The permeate flux was 8.2×10^{-4} kg $m^{-2}s^{-1}$. The combined alcohol content was enriched four fold, and several of aroma compounds were enriched 20 fold.

A model flavour solution of concord grape juice containing methyl anthranilate was used to evaluate the effects of feed concentration, permeate pressure and temperature on the flux and separation factor (Rajagopalan & Cheryan, 1995). Commercial grape essence 150 fold was concentrated using pervaporation with GFT 1070 membranes at room temperature or at 5°C with permeate pressure less than 130 Pa. The permeate was enriched in several compounds. The enrichment factor of methyl anthranilate was similar to that obtained using a model solution. Ethyl acetate that accounts for about 90% of all esters in concord grape juice was also enriched by a factor of 35 - 40. All pervaporation permeate samples were tasted by experts to be of good quality and equivalent to a 1000 fold essence.

Moutounet et al. (1992) investigated the feasibility of the production of spirits from wine by pervaporation and compared the product obtained with distillated spirits. The

pervaporation system included PDMS membranes and was operated at a temperature of 35°C and a permeate pressure of 250 Pa. Firstly, the feed wine produced the primary spirit containing 19% ethanol. Then this primary spirit was pervaporated to produce the final spirits containing 41% ethanol which was lower in ethanol concentration than the spirits produced by continuous distillation and pot distillation, 63% and 73% respectively. The product of pervaporation was found to be free of copper.

Karlsson et al. (1995) used PDMS membranes to recover aroma compounds from a muscat wine. They found that varying the temperature lead to changes in the total aroma concentration and relative concentration of aroma in the permeate.

Karlsson & Trägårdh (1993a), Karlsson & Trägårdh (1994), Rajagopalan & Cheryan (1995), Souchon et al (1996) and Olsson & Trägårdh (1999) used the fruit aroma model solutions to investigate the performance of pervaporation for aroma recovery. The performance of pervaporation was found to be affected by operating temperature, feed concentration, permeate pressure, ethanol concentration and feed flow rate. The enrichment factor of aroma by pervaporation was higher than that by vapour-liquid equilibrium separation.

2.6 Conclusion

Contributing to feijoa flavour, ethyl butanote, methyl benzoate and ethyl benzoate were the important aroma compounds for feijoa. Linalool, nerol and geraniol, contribute to the sweet, floral and rose-like aroma important for boysenberry aroma. Linalool and methyl benzoate have potential to be extracted more by pervaporation than by liquid-vapour equilibrium separation based on their molecular structure, hydrophobicity and boiling point.

The resistance-in-series model is an effective model for describing the pervaporation mass transfer process, taking into account the overall mass transfer resistance from feed side to permeate side. The resistance to mass transfer on the feed side is increased with low feed

concentration, low feed flow rate, and high membrane selectivity. The resistance to mass transfer in the membrane is dependent on the solubility and diffusivity of the permeate on the membrane, the membrane thickness, the feed composition and the operating temperature. The resistance to mass transfer on the permeate side may play an important role in the mass transfer process, especially when the permeate pressure is high.

The pervaporation performance for extraction of organic compounds is mainly dependent on the affinity relationship between the membrane polymer and the organic compound. PDMS hydrophobic membranes had high flux and reasonable selectivity toward organic compounds. PEBA membranes were less selective toward ethanol and more selective toward aromatic organic compounds than PDMS membranes. Compared with PDMS, PTMP was an ethanol selective membrane with higher flux, while POMS membranes yield higher flux and higher selectivity for the aroma compounds. The performance of pervaporation was also influenced by the operating conditions such as the feed temperature, feed composition, feed flow rate, permeate pressure and condensation conditions.

Commercial apple, grape, orange aroma condensates have been concentrated by pervaporation. Apple aroma compounds have been concentrated 10-100 fold by pervaporation from apple aroma condensate. Orange aroma compounds have been concentrated to 10-50 fold using pervaporation from orange aroma condensate. Grape essence has been concentrated to 35-40 fold by pervaporation. Several model fruit aroma solutions have been used to investigate the pervaporation performance for aroma recovery and concentration. The pervaporation technique has excellent potential for aroma recovery and concentration in the beverage processing industry.

Chapter Three

Experimental

3.1 Terms and Definition

Aroma condensate: The aroma condensate is a condensed aroma collected from a juice concentration plant during evaporation. In this study, the aroma condensates were used as the feed for pervaporation or vacuum distillation.

Feed: The feed is defined as the solution used for pervaporation or concentration by vacuum distillation.

Retentate: After the feed was concentrated by pervaporation or vacuum distillation, the feed has lost some volatile components. The retentate was defined as the feed which was retained after concentrating.

Permeate: The permeate is defined as the concentrated aroma product collected from the pervaporation system. The permeate is that which has passed through the pervaporation membrane.

Aroma concentrate: The product collected during the concentration of the aroma condensate by pervaporation or vacuum distillation. In pervaporation it is equivalent to the pervaporation permeate.

Feed flow rate (Q_f)*:* Is the feed flow rate recirculated across the membrane, units ($m^3 s^{-1}$).

Total permeate flow rate (m_p)*:* Mass flow rate of permeate collected during pervaporation, units ($kg\ s^{-1}$).

$$m_p = \frac{M_p}{t} \tag{3.1}$$

where, M_p = mass of the permeate (kg).

t = experiment duration (s).

Total permeate flux *(J)*: Mass flow rate of permeate collected during pervaporation, per unit area of membrane, units (kg m^{-2} s^{-1}).

$$J = \frac{m_p}{A_m} \tag{3.2}$$

where, J = total permeate flux (kg m^{-2} s^{-1}).

A_m = membrane area (m^2).

Partial flux *(J_i):* The partial flux of each individual compound was calculated by the following eqaution

$$J_i = J \times C_{i,p} \tag{3.3}$$

where, $C_{i,p}$ = the concentration of aroma compound i in pervaporation permeate (g g^{-1}).

Enrichment factor *(β)*: A measure of the enrichment of each aroma compound during pervaporation. The enrichment factor of an aroma compound is the ratio of its concentration in the permeate to its concentration in the feed. In this study, feed was recirculated past the membrane and feed / retentate concentration changed during pervaporation. Therefore, the mean of feed and final retentate concentrations were used to represent the average feed concentration.

$$C_{i,a} = \frac{C_{i,f} + C_{i,r}}{2} \tag{3.4}$$

$$\beta = \frac{C_{i,p}}{C_{i,a}} \tag{3.5}$$

where, $C_{i,p}$ = the concentration of aroma compound i in the permeate (μg g^{-1}).

$C_{i,f}$ = the concentration of aroma compound i in the feed (μg g^{-1}).

$C_{i,r}$ = the concentration of aroma compound i in the final retentate (μg g^{-1}).

$C_{i,a}$ = the mean concentration of i in the feed and retentate (μg g^{-1}).

Concentration factor *(CF):* The ratio of aroma compound concentration in the aroma concentrate to its concentration in the original aroma condensate.

$$CF = \frac{C_{i,c}}{C_{i,f}} \tag{3.6}$$

where, $C_{i,c}$ = the concentration of aroma compound i in the aroma concentrate (μg g^{-1}).

Yield *(Y):* The ratio of the mass of aroma concentrate to mass of aroma condensate.

$$Y = \frac{M_{i,p}}{M_{i,f}} \tag{3.7}$$

where, $M_{i,p}$ = Mass of the pervaporation permeate or aroma concentrate (kg).

$M_{i,f}$ = Mass of the aroma condensate (feed) (kg).

3.2 Materials

3.2.1 Aroma condensate

The feijoa aroma condensate was supplied by Park Estate Ltd (Hawkes Bay, N.Z.). It was recovered during evaporative concentration of feijoa juice. The concentration of the feijoa aroma condensate was 2% (v/v), this corresponded to a 1:50 fold aroma concentration based on the initial volume of juice.

The boysenberry aroma condensate was supplied by Berryfruit Export N.Z. Ltd (Nelson, N.Z.). It was recovered during evaporative concentration of boysenberry juice. The concentration of boysenberry aroma condensate was 1% (v/v), this corresponded to a 1:100 fold aroma concentration based on the initial volume of juice.

The aroma condensates were stored at $-18^{\circ}C$ prior to use.

3.1.2 Liquid nitrogen and dry ice

The liquid nitrogen and dry ice (CO_2) were supplied by BOC Gases Ltd (N.Z.)

3.1.3 Membranes

Table 3.1 shows the details of the three types of membranes used in this research

Table 3.1 Membrane characteristics

Membrane type	Active layer	Supplier	Thickness[a] (μm)	Thickness[b] (μm)
GFT1060	Poly(dimethyl siloxane)	GFT/Deutsche Carbone AG, Germany	170	10
GFT1070	poly(dimethyl siloxane)+silicalite	GFT/Deutsche Carbone AG, Germany	200	30
PEBA	poly-ether-block-amide	GKSS, Germany	200	58

Data sourced from Ferreira (1998).

a: Total thickness of membrane.

b: Thickness of the active layer of membrane.

3.2.4 Pervaporation apparatus

Cold trap

Three glass traps (Quickfit, England) were used to collect the permeate with the liquid nitrogen.

Feed pump

The feed pump was a telflon diaphragm pump (Masterflex, No: 755375, U.S.A.). The speed of the pump was controlled with a variable speed controller (Masterflex, U.S.A.).

Feed tank

The stainless steel jacketed feed tank (Massey University, N.Z.) was approximately five litres in capacity.

High accuracy vacuum pressure gauge

A high accuracy vacuum pressure gauge was used to monitored the permeate pressure. The pressure gauge system consisted of a high accuracy 170 series sensor pressure head (MKS

BARATRON, England), a 170M-6C Range multiplier (MKS BARATRON, England), a 170M-35 Building Block head adapter (MKS BARATRON, England) and an oil vacuum pump (Edwards, England).

Membrane cell

Figure 3.1 is a schematic diagram of the pervaporation membrane cell. Figure 3.2 is a photograph of the pervaporation membrane cell. The diameter of membrane cell was 40 mm, corresponding to an effective membrane area of 1.26×10^{-3} m^2. The membrane cell consisted of three parts: a top flange, a middle membrane holder and a base. The membrane sat on the membrane holder, which was a sintered stainless steel plate. The three sections were sealed with teflon gaskets when clamped together. The feed enters via the inlet port, passes over the membrane, and then exits via four outlet ports, as shown in Figure 3.1.

Permeate pressure gauge

The pressure on the permeate side of the membrane was also monitored with a second vacuum pressure gauge (Pirani 10, England)

Stainless steel dewar flask

Liquid nitrogen was contained in two litre stainless steel dewar flasks (Thermout-D2000, Japan)

Temperature monitoring

A T-type thermocouple was connected to a data logger (Series 1000, Squirrel, Grant, England)

Vacuum pump

The vacuum pump was a high pressure vacuum pump (Speediva ED75, England).

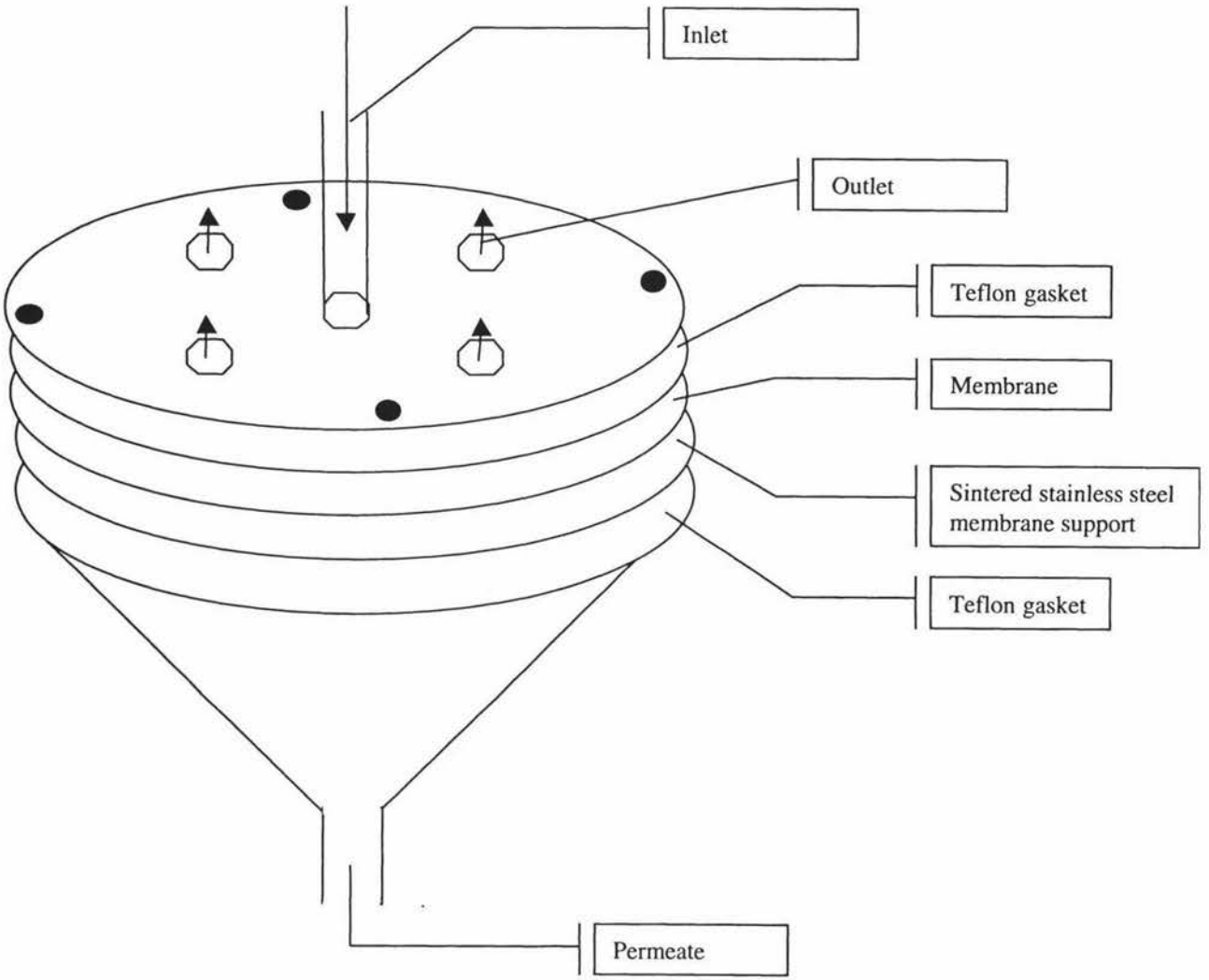

Figure 3.1 Schematic diagram of pervaporation cell

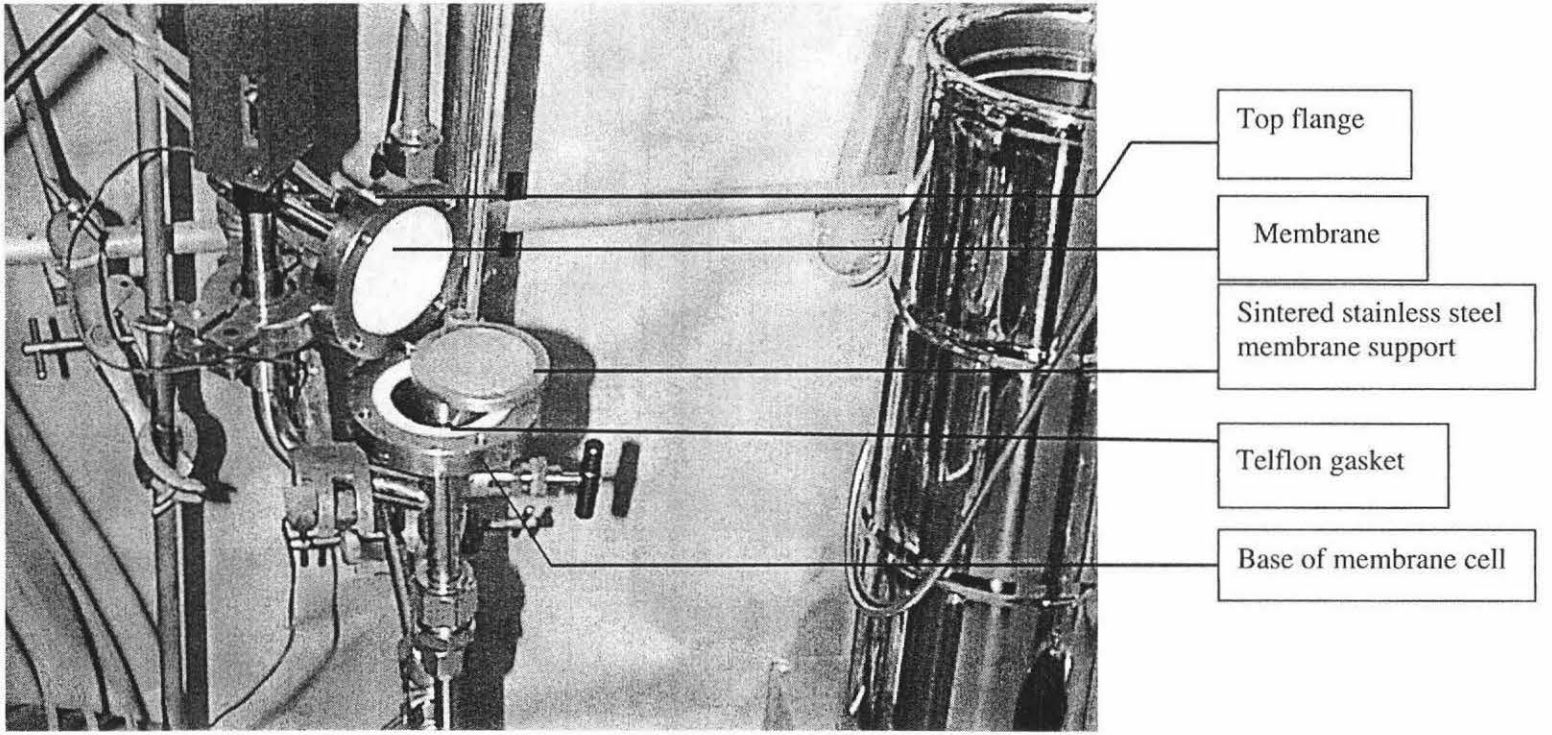

Figure 3.2 Pervaporation membrane cell

Water bath

The temperature range of the water bath (Grant, England) was 5 - 99°C.

Figure 3.3 is a schematic diagram of the pervaporation apparatus used in this research The feed solution was placed into the jacketed feed tank. The temperature of the solution in the feed tank was maintained at the desired temperature by circulating water from the controlled temperature water bath. The temperature within the membrane cell was monitored with a thermocouple placed in the middle of the membrane cell. The thermocouple was connected to the data logger. From the feed tank, the feed solution was pumped into the membrane cell using a feed pump with a variable speed controller. A vacuum was maintained on the permeate side with the vacuum pump.

The permeate side of pervaporation apparatus consisted of two glass cold traps connected in parallel to the permeate line on the permeate side (Figure 3.3 and 3.4). These were connected to another single trap, which was placed prior to the vacuum pump to prevent any solvent from entering the vacuum pump. Three dewar flasks containing liquid nitrogen were placed under the three traps respectively. The Pirani pressure gauge was placed immediately after the permeate chamber to measure the permeate pressure. The high accuracy pressure gauge system was also linked to the permeate side to measure the permeate pressure accurately.

Two needle valves were placed between the membrane cell and the two glass cold traps. Several teflon stopcock valves were present between the cold traps and vacuum pump to adjust the permeate pressure.

3.2.5 Vacuum distillation apparatus

Figure 3.5 shows the apparatus used for concentrating the aroma condensate using the vacuum distillation technique.

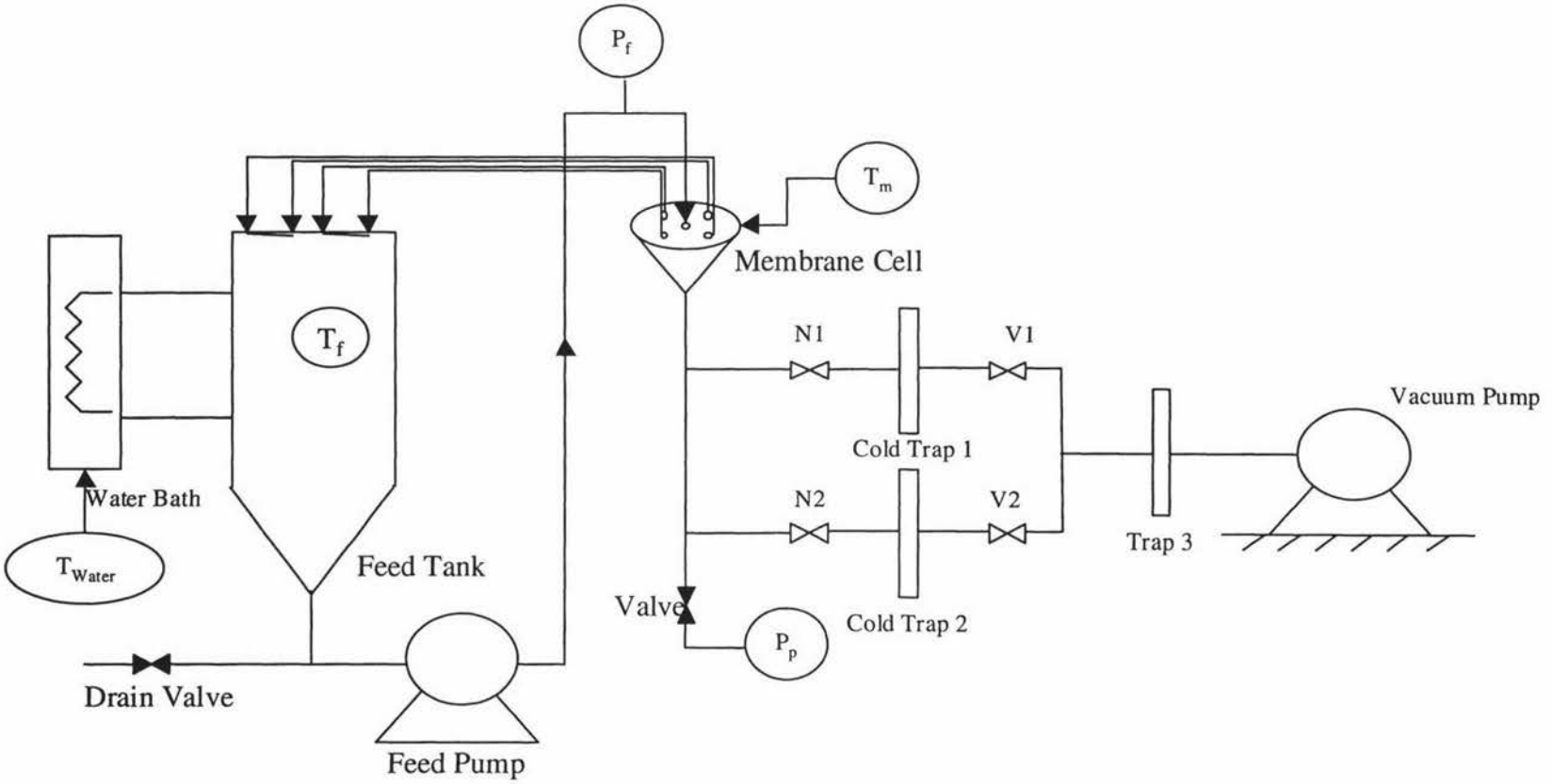

Figure 3.3 Schematic diagram of pervaporation apparatus
P_f: Feed flow pressure; P_p: Permeate pressure.
T_{water}: Temperature of water in water bath; T_f: Feed temperature; T_m: Temperature of membrane.
N1: Needle valve for Trap 1; N2: Needle valve for Trap 2
V1: Telfon valve between Trap 1 and Trap 3; V2: Telfon valve between Trap 2 and Trap 3.

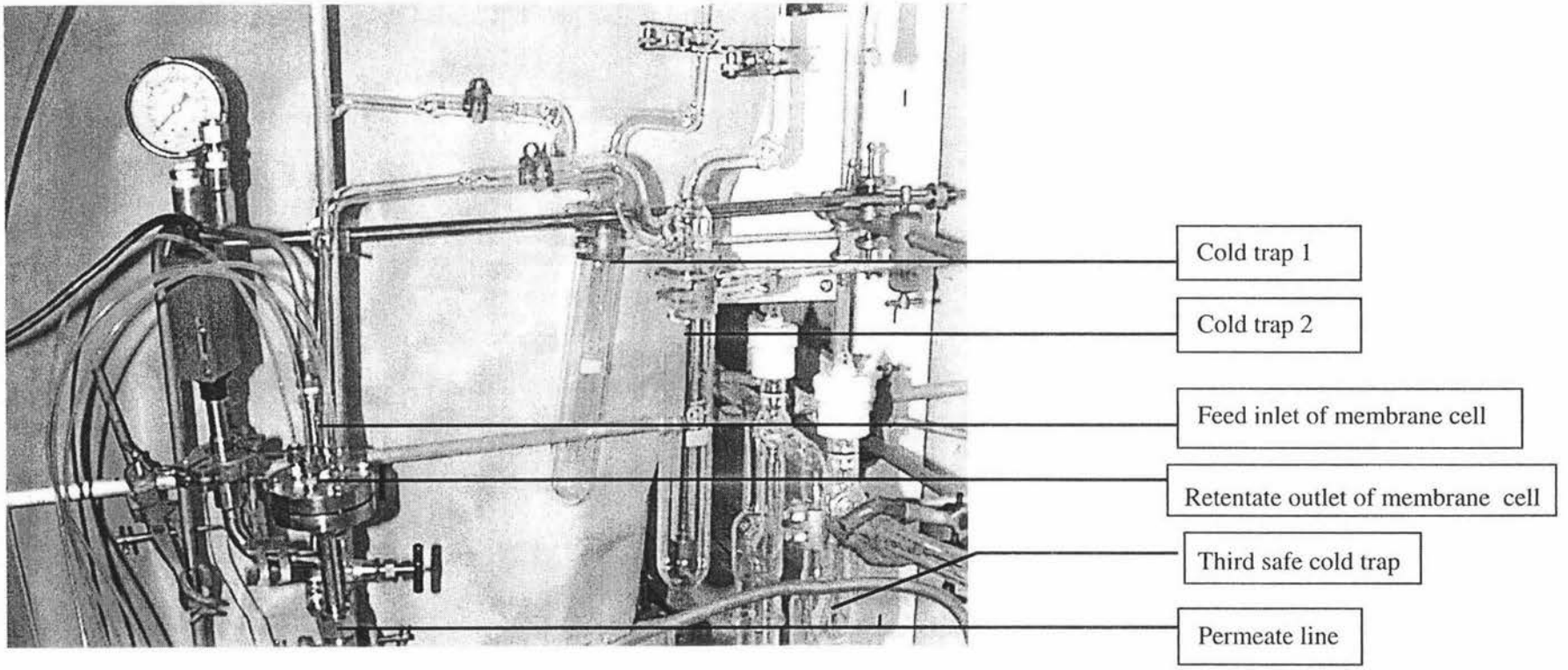

Figure 3.4 Permeate side of pervaporation apparatus

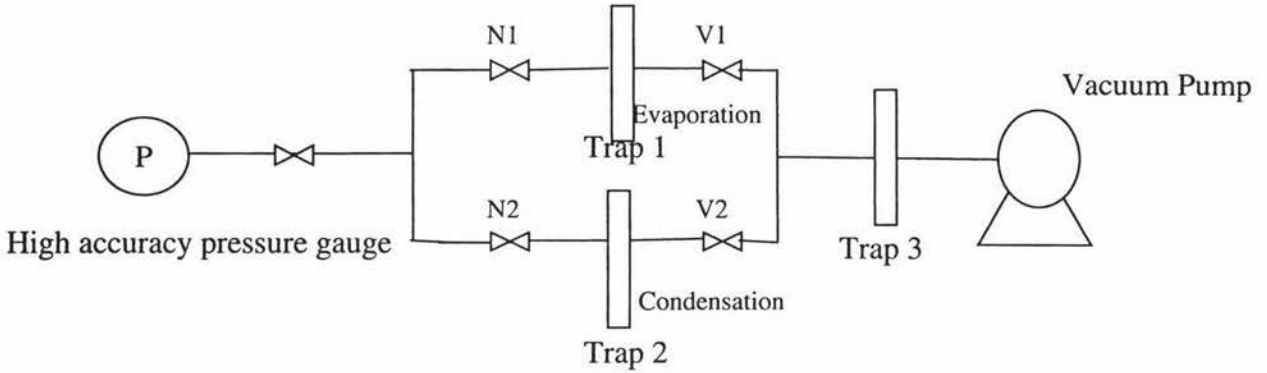

Figure 3.5 Vacuum distillation apparatus
N1: Needle valve for Trap 1: V1: Telfon stopcock valve between Trap 1 and Trap 3
N2: Needle valve for Trap 2; V2: Telfon stopcock valve between Trap 2 and Trap 3

In the vacuum distillation apparatus, two traps were placed in parallel plus one safety trap before the vacuum pump. Trap 1 was for holding fresh feijoa or boysenberry aroma sample, as the evaporating trap. Trap 2 was used to collect and condense any distilled aroma and was cooled with liquid nitrogen. Trap 3 also cooled with liquid nitrogen prevented any solute from reaching the vacuum pump. The high accuracy pressure gauge was linked to a junction between Trap 1 and Trap 2.

3.2.6 Materials for analytical techniques

External standard solutions

Eighteen aroma compounds used to make up the mixed external standards were all of analytical grade. Ethanol (99.9%), hexanol, Z-3-hexenol, E-2-hexenol, 2-methyl propanol, 3-methyl butanol, 2-heptanol, hexanol, ethyl acetate and ethyl butanoate were supplied by BDH Chemicals (England). Methyl benzoate, ethyl benzoate, linalool, α- terpinerol, nerol, geraniol, hexanal and E-2-hexenal were supplied by Sigma Chemicals (U.S.A.).

Internal standard solution

Ethyl octanoate was analytical grade and supplied by Sigma Chemicals (U.S.A.). Standard solution was made with 4.08 mg ethyl octanoate dissolved in 1 ml hexane (Sigma Chemicals, U.S.A.).

Solid Phase Extraction (SPE) column

Isolute SPE column C18 was supplied by International Sorbent Technology Company (U.S.A.).

Extraction solutions

Diethyl ether (99.5%) was analytical grade and supplied by AJAX Chemicals (Australia) Methanol (99.5%) and hexane (99.5%) were analytical grade and supplied by Sigma Chemicals (U.S.A.).

Gas chromatograph

The gas chromatograph used was an HP 6890 (Hewlett Packard, U.S.A.) which was equipped with a flame ionisation detector, connected to a DB-WAX 122-7033 column (30m × 0.25mm, film 0.5μm, J&W Scientific Inc., U.S.A.).

Gases

Helium (instrument grade) was used as a carrier gas, hydrogen (instrument grade) was used for FID detection. Helium and hydrogen were supplied by BOC Gases Ltd (N.Z.).

Mass spectrometer coupled with gas chromatograph

Varian VG-70SE mass spectrometer directly coupled to a Hewlett Packard HP 5890 gas chromatograph.

3.3 Vacuum distillation procedure

A schematic diagram of the vacuum distillation system used was shown in Figure 3.5. Before turning on the vacuum pump, Traps 1 and 2 were separated by closing needle valves N1 and N2, and teflon valves V1 and V2. An aroma condensate sample was placed into Trap 1 and frozen slowly with liquid nitrogen. After the sample in Trap 1 was totally frozen, the two needle valves and two teflon valves were opened. The whole system was evacuated by the vacuum pump until the pressure in the system was 0.0 ± 0.5 Pa absolute pressure. Trap 1 was then disconnected from Trap 2 and the vacuum pump by closing the needle valves and the two teflon valves. The aroma condensate sample in Trap 1 was then warmed up to room temperature. The aroma condensate was then frozen again with liquid nitrogen and the degassing procedure above was repeated until the pressure gauge showed 0.0 ± 0.5 Pa absolute pressure.

After degassing the system, Trap 1 was kept at 30 ± 1°C using a dewar flask containing water at 30 ± 1°C. Trap 2 was kept cold with liquid nitrogen. The two needle valves

(N1,N2) between Trap 1 and Trap 2 were opened to begin the evaporation of feijoa or boysenberry aroma by vacuum distillation. The valves prior to the vacuum pump (V1,V2) were kept closed. Once the sample collected in the Trap 2 was approximately 1 - 2g depending on the experiment, Trap 2 was disconnected from Trap 1 and the vacuum pump. Trap 2 was warmed upto room temperature and the distilled sample was recovered and weighed.

3.4 Pervaporation operating procedure

A schematic diagram of the pervaporation set up was shown in Figure 3.3. A new membrane was conditioned for 24 hours with 5% (w/w) aqueous ethanol solution. The ethanol solution, at 30°C, was pumped into the pervaporation cell at feed flow of 8.1×10^{-6} $m^3 s^{-1}$. During conditioning, permeate pressure was 100 ± 5 Pa absolute pressure, dry ice was used to condense the permeate.

For each experimental trial, before the feed recirculation pump was started, the vacuum pump was turned on to establish the permeate side pressure. The feed solution was equilibrated to the desired temperature in the feed tank. The feed solution was then pumped through the membrane cell for three hours to equilibrate the membrane. During these three hours, the permeate collected in the cold traps was thawed and poured back into the feed tank to limit the lose of aroma from the feed. At the start of the fourth hour, permeate collection began and the flux determined from this point.

Feed temperature (T_f) in the feed tank was controlled by circulating water from the controlled temperature water bath. For all experimental trials the temperature of the feed solution and membrane were maintained at 30°C ± 1°C.

The flow rate (Q_f) from the feed pump was calibrated against feed pressure, which was measured at the entrance to the membrane cell with a pressure gauge. At 30°C when feed pressure was 1×10^4 Pa absolute pressure, the feed flow rate was 8.1×10^{-6} $m^3 s^{-1}$; when the

feed pressure was 1.5×10^4 Pa absolute pressure, the feed flow rate was$1.1 \times 10^{-5} m^3 s^{-1}$; when the feed pressure was 2×10^4 Pa absolute pressure, the feed flow rate was $1.4 \times 10^{-5} m^3 s^{-1}$.

The permeate pressure (P_p) was controlled by adjusting the two needle valves (N1, N2) between the traps and membrane cell and the teflon valves (V1, V2) between the traps and vacuum pump. The permeate pressure was monitored by the high accuracy pressure gauge system. The permeate pressure were controlled at 100 ± 5 Pa absolute pressure or 1000 ± 50 Pa absolute pressure depending on the experiment.

The permeate was collected in glass cold traps which were cooled to -196°C by liquid nitrogen. After each experiment, the permeate sample was thawed at room temperature, transferred to a glass test tube with a teflon lined cap and stored in the freezer at -18°C. Samples of the feed and retentate were also stored at -18°C

After each experiment, the apparatus was rinsed with distilled water for 1 hour, then with 5% (w/v) ethanol for 1 hour. After turning off the feed pump, the membrane was dried for 1 hour by maintaining a vacuum on the permeate side.

3.5 Pervaporation experimental procedure

3.5.1 Influence of membrane type on pervaporation performance

The pervaporation performance of three different membrane types was determined with 5% (w/w) ethanol solution, feijoa and boysenberry aroma. The three membranes used were GFT1060, GFT1070 and PEBA. For each experiment, 0.4 kg of feijoa or boysenberry aroma condensate was used as the feed solutions. For all experiments, the feed temperature was 30 ± 1°C, feed flow rate was $1.4 \times 10^{-5} m^3 s^{-1}$ and the permeate pressure was maintained

at 100 ± 5 Pa absolute pressure. Experiments for each membrane were completed in duplicate.

3.5.2 Effect of permeate pressure on pervaporation performance

The effect of permeate pressure on pervaporation performance was determined using 5% (w/w) ethanol solution, feijoa and boysenberry aroma condensate. For these experiments, the GFT 1060 membranes were only used. The feed volume at the start was 0.4 kg of feijoa or boysenberry aroma condensate. The feed temperature was maintained at 30 ± 1°C, feed flow rate was 8.3×10^{-6} m^3 s^{-1}. The permeate pressure was varied between 100 ± 5 Pa and 1000 ± 50 Pa absolute pressure. Experiments were completed in duplicate.

3.5.3 Effect of feed flow rate on pervaporation performance

The effect of feed flow rate on pervaporation performance was determined using feijoa aroma condensate only. For this experiment, the GFT1060 membranes were used. The feed volume at the start was 0.4 kg of feijoa aroma condensate. The feed temperature was maintained at 30 ± 1°C, the permeate pressure was 100 ± 5 Pa absolute pressure. The feed flow rate was varied between 1.1×10^{-5} m^3 s^{-1} and 1.4×10^{-5} m^3 s^{-1}. Experiments were completed in duplicate.

3.5.4 Vacuum distillation for aroma recovery

Aroma recovery from feijoa and boysenberry aroma condensates was also completed by vacuum distillation and compared to pervaporation performance. For these experiments, the feed volume at the start was 20 g of feijoa or boysenberry aroma condensate. The feed temperature was maintained at 30 ± 1°C. Experiments were completed in duplicate.

3.6 Procedure for the analysis of the aroma solutions

Firstly, the volatile components of the aroma condensates (feed sample) of feijoa and boysenberry were identified. The solid phase extraction (SPE) method was used to prepare samples for gas chromatography (GC) or mass spectrometer coupled with GC (GC-MS). This extraction method concentrated the analytes to a higher degree from a diluted aqueous sample and also gave high recoveries of the analytes. The direct solvent extraction technique with internal standard was used to determine the individual aroma concentration of all feed, retentate and permeate samples because it was a faster method and less sample was required for extraction.

3.6.1 Solid phase extractions (SPE)

The following four-step procedure was followed:

1. SPE column solvation: Ten millilitres of methanol (99.5%) was passed through the column to wet the adsorbent and ensure interaction of the adsorbent and the analytes.
2. SPE column equilibration: The column was treated with 6 ml distilled water to maximise retention of the analyte by the adsorbent.
3. Sample loading: One millilitre of sample was loaded onto the column at an optimum flow rate of 20 drops per minute.
4. Analyte elution: 1.5ml diethyl ether (99.5%) eluted the analytes with an optimum flow rate of 10 drops per minute.

3.6.2 Direct solvent extraction

One millilitre of sample was placed into a clean 10 ml test tube. Ten microlitres of internal standard solution was added. Diethyl ether (2 ml) was added to extract the organic compounds. The test tube was capped with a teflon lined cap and the solutions were mixed. Using a 500 µl syringe and needle the aqueous fraction at the bottom of the test tube was carefully removed and placed into a clean test tube. A second aliquot of diethyl ether (2 ml) was added into the aqueous fractions to extract the remaining organic compounds. A third

extraction of the aqueous phase using another 1 ml of diethyl ether was carried out. The diethyl ether fraction containing the organic compounds in three tubes was combined to one. This combined diethyl ether solution containing the extracted organic compounds was injected into the GC.

3.6.3 Gas chromatographic analysis

The aroma compounds were analysed with the Hewlett Packard 6890 gas chromatograph. The carrier gas was helium at a flow rate of 77.4 ml/min. The separation was conducted using the following temperature program: 35°C holding for 6 min; from 35°C to 102°C at 3°C/min; from 102°C-196°C at 5°C/min; 196°C for 5min. The temperature of the injection port and detector were 150°C and 200°C, respectively. The flow rate of hydrogen and air were set at 40ml/min and 450ml/min respectively. Injection was in splitless mode at a pressure of 14.89 psi. The sample volume injected was 1 µl.

3.6.4 Gas chromatograph – mass spectrometer (GC-MS)

GC-MS was carried out on a Varian VG-70SE spectrometer directly coupled with Hewlett Packard 5890 gas chromatograph, operated in the electron impact mode at 70ev. GC conditions were similar to the conditions in section 3.6.3. Volatile aroma compounds were identified by comparison of 70eV electron ionization mass spectra with mass spectra in the GC-MS computer library.

3.6.5 Identification of aroma compounds

Two methods were used to identify aroma components in the feijoa and boysenberry condensate. The first method was by comparison of the GC retention times with a mixed external standard solution of known composition. Table 3.1 and Table 3.2 show the volatile compounds used in the external standard for feijoa and boysenberry, respectively. The selections of external standards for feijoa and boysenberry were chosen for the following

reasons. Firstly, the volatile compounds chosen have been reported to be important contributors to the fruit aroma, such as methyl benzoate, ethyl benzoate for feijoa, and linalool, terpinerol, nerol, geraniol for boysenberry (Shaw et al., 1990; Allen et al., 1996). Secondly, some of these compounds were found to be quantitatively the major volatiles such as ethanol, Z-3-hexenol for feijoa (Shaw et al., 1990) and ethanol, 3-methyl butanol

Table 3.2 External standards for feijoa volatile compounds

Alcohol	Aldehyde	Ester
Ethanol	Hexanal	Ethyl acetate
Hexanol	E-2-hexenal	Ethyl butanoate
Z-3-hexenol		Methyl benzoate
E-2-hexenol		Ethyl benzoate
Linalool		

Source: Shaw et.al.(1983; 1990).

Table 3.3 External standards for boysenberry volatile compounds

Aliphatic alcohol	Terpene alcohol	Aldehyde	Ester
Ethanol	Linalool	E-2-hexenal	Ethyl acetate
Propanol	Terpinerol		Ethyl butyrate
2-methyl propanol	Nerol		
3-methyl butanol	Geraniol		
2-heptanol			
Hexanol			
E-2-hexenol			

Source: Allen et al. (1996)

for boysenberry (Allen et al., 1990). Finally, hexanal and E-2-hexenal were selected to represent the aldehydes.

The second method of identification was by using a mass spectrometer (MS) coupled to a GC.

3.6.6 Quantitative analysis by gas chromatogram

The concentrations of aroma compounds were determined by integration and quantification of peak area using the Hewlett Packard ChemStation program. Quantification of peak area was used to determine the concentration of an organic compound in a sample by comparison with an external standard or an internal standard concentration.

Using external standards, the aroma concentration of the individual compounds in the sample, isolated by SPE, was calculated from the ratio of the peak areas of the individual aroma compound to the average peak areas of the external standard solution compounds identified under the same conditions.

$$\text{Concentration} = \left[\frac{\text{peak area of sample}}{\text{peak area of external standard}} \right] \times \text{concentration in the external standard}$$

Using the internal standard for calculation, the concentration of aroma compounds in the samples isolated by direct solvent extraction were analysed with a standard of ethyl octanoate in hexane (4.08 mg /ml).

Five different levels of internal standard were added to external standard solutions of feijoa or boysenberry to construct for each compound a calibration curve. A calibration curve was constructed by calculating an amount ratio (R_a) and a response ratio (R_r) for each level of a particular peak in the calibration table. The amount ratio (R_a) is the amount of the compound divided by the amount of the internal standard at this level. The response ratio

(R_r) is the area of the compound divided by the area of the internal standard at this level. A plot of R_a vs R_r generated a straight line. The gradient of the line was defined as RF_x.

$$RF_x = \frac{R_a}{R_r} \tag{3.8}$$

The equation of the line is $R_a = RF_x \times R_r$ (3.9)

An equation for the linear relationship of the five calibration points was calculated using linear regression (Microsoft Excel, U.S.A.).

The calibration curves of all aroma compounds except ethanol were linear ($r^2 \geq 0.99$).

The concentration of each aroma compound in the sample was calculated by using the following equation:

$$C = R_r \times RF_x \times I \times D \tag{3.10}$$

where, C = the concentration of individual aroma compound in the sample, ($\mu g\ g^{-1}$).

R_r = the ratio of the area of the individual aroma compound to the area of the internal standard.

I = the concentration of the internal standard, ($\mu g\ g^{-1}$).

D = the dilution factor.

For each sample, individual aroma concentrations determined were based on duplicate direct solvent extractions and on duplicate injections of each extracted sample. The values of the aroma concentration varied by ± 5% except ethyl acetate and ethanol which varied by ±10%.

3.7 Statistical analysis of data

The mean, standard deviation (SD) and standard errors (SE) for the aroma concentration in the feed, retentate, permeate for each experimental trial were determined from two samples obtained from duplicate experiments. Each sample was analysed based on duplicate direction solvent extraction and duplicate injection of each extracted sample.

The mean, standard deviation (SD) and standard errors (SE) about the total flux, partial fluxes, mass transfer coefficients, and enrichment factors for each experimental trial were determined from the duplicate experiments.

The significance of differences in the individual aroma concentrations, total fluxes, partial fluxes, mass transfer coefficients, and enrichment factors between the three different membranes was analysed by MINITAB (MINITAB, U.S.A.).

The significance of differences in the total fluxes, partial fluxes and enrichment factors between the two different permeate pressures and two different feed flow rates were analysed by t-test for 97.5% confidence.

Chapter Four

Results and Discussion

4.1 Identification of aroma composition in aroma condensate

4.1.1 Feijoa

The aroma components in feijoa aroma condensate were isolated by solid phase extraction (SPE) for identification of the key aroma compounds present using GC-MS and GC. To quantify the aroma compounds in feijoa aroma condensate, the aroma compounds were extracted by direct solvent extraction with diethyl ether. The gas chromatogram for feijoa aroma condensate is shown in Figure 4.1. Fourteen components were identified by GC-MS. Nine compounds were confirmed by GC retention times using a mixed standard solution, as shown in Table 4.1. For the nine compounds identified by GC, their concentrations and relative concentrations were determined using an internal standard, ethyl octanoate (Table 4.1). The aroma threshold values, aroma values and properties of each aroma compound are presented in Table 4.2.

The fourteen aroma compounds identified in the feijoa condensate consisted of alcohols, aliphatic esters, aromatic esters and aldehydes. Ethanol was quantitatively the main volatile compound in the condensate with a relative concentration of 80.9%. The next major alcohol present was Z-3-hexenol, which contributed 4.9% of the total aroma compounds. Ethyl acetate was the main aliphatic ester with a relative concentration of 3.8%, while methyl benzoate was the main aromatic ester with a relative concentration of 4.9%. E-2-hexanal was the only aldehyde identified.

Shaw et al. (1983) reported the volatile flavour composition of intact feijoa fruit after using a headspace trapping technique. It was noted that most of the fruit aroma in the headspace

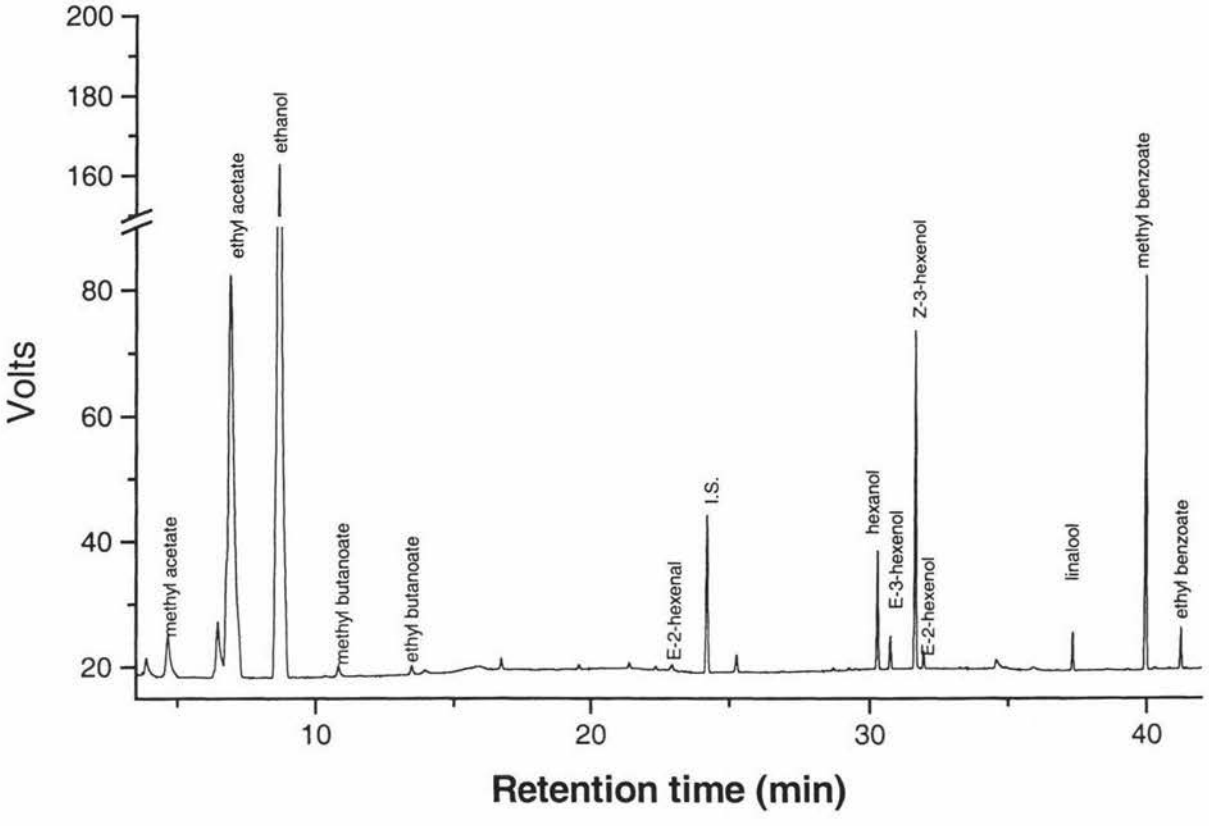

Figure 4.1 Gas chromatogram of the feijoa aroma condensate (feed sample). I.S.=Internal Standard

Table 4.1 The volatile compounds in feijoa aroma condensate

Component	Identification method	Retention time (min)[a]	Concentration (ug/g)		Relative concentration (%)	
			Batch[b] 1	Batch 2	Batch 1	Batch 2
Methyl acetate	MS	4.67	ND	ND	ND	ND
Ethyl acetate	MS,RT	6.46	52.0 ± 0.5	58.0 ± 0.5	4.7	3.8
Methanol	MS	6.99	ND	ND	ND	ND
Ethanol	MS,RT	8.80	872 ± 21	1246 ± 21	80.0	81.9
Methyl butanoate	MS	10.79	ND	ND	ND	ND
Ethyl butanoate	MS,RT	13.44	3.3 ± 0.0	4.5 ± 0.0	0.3	0.3
E-2-hexenal	RT	22.93	3.6 ± 0.0	5.5 ± 0.0	0.3	0.3
Hexanol	MS,RT	30.35	20.0 ± 0.2	25.2 ± 0.2	1.8	1.7
E-3-hexen-1-ol	MS	30.76	ND	ND	ND	ND
Z-3-hexen-1-ol	MS,RT	31.73	58.5 ± 0.2	75.2 ± 0.2	5.3	4.9
E-2-hexen-1-ol	MS	32.36	ND	ND	ND	ND
Linalool	MS,RT	37.33	5.4 ± 0.1	6.7 ± 0.1	0.49	0.4
Methyl benzoate	MS,RT	40.00	64.2 ± 0.2	87.1± 0.2	5.9	5.7
Ethyl benzoate	MS,RT	41.23	5.0 ± 0.0	8.0 ± 0.0	0.5	0.5

MS: Mass spectrometer coupled with GC.

RT: Comparison of the GC retention time with a mixed external standard solution.

ND: Not determined by GC, compound was not included in mixed standard.

a: Retention time was obtained on a DB-WAX column.

b: Two different batches of feijoa aroma condensate were used during this research.

Table 4.2 Aroma threshold value, aroma value and properties of aroma compounds identified and studied in fejioa aroma condensate

Compound	ATV[a]	AV[b]	MW[c] (g/mol)	BP[d] (°C)	WS[e] (mg/l)	Log P[f]	VP[g] (Pa)
Ester							
Ethyl acetate	1.0	52	74.1	34.5	6.04×10^{4}	0.89	7.1×10^{4}
Ethyl butanoate	0.00001	330000	102.2	92.3	2.13×10^{3}	2.03	6.8×10^{3}
Methyl benzoate	NF	NF	138.2	199	2.10×10^{3}	2.12	50.0
Ethyl benzoate	NF	NF	150.2	211	7.20×10^{2}	2.64	35.0
Aldehyde							
E-2-hexenal	0.1	36	98.2	146.5	5.26×10^{3}	1.58	8.7×10^{2}
Alcohol							
Ethanol	0.28-9%	<1	46.1	78.3	1.00×10^{6}	-0.31	7.8×10^{3}
Hexanol	0.1.	200	102.2	157.1	5.90×10^{3}	2.03	1.2×10^{2}
Z-3-hexenol	NF	NF	100.6	156.5	1.60×10^{4}	1.61	73.0
Linalool	0.005	1100	154.3	195	1.59×10^{3}	2.97	21.0

a: Aroma threshold value; sourced from Larsen et al (1992).
b: Aroma value obtained from the ratio of concentration of aroma/ aroma threshold value.
c: Molecular weight (g/mol).
d: Boiling point (°C).
e: Water solubility at 25°C (mg/l).
f: Hydrophobicity constant.
g: Vapour pressure at 25°C (Pa).
c,d,e,f,g, sourced from Howard & Meylan (1997)

NF: Published information not found.

of feijoa intact fruit was composed of volatile esters and ketone compounds. Esters constituted approximately 93% of the total aroma concentrate whereas acyclic monoterpenes and aliphatic ketones represented 5% and 2%, respectively. Methyl benzoate, ethyl butanoate and ethyl benzoate are important aroma compounds in intact fruit with relative concentrations of 39.3%, 29.6% and 10.6% respectively.

Shaw et al. (1990) also reported the volatile composition in feijoa fruit flesh isolated by low-temperature vacuum steam distillation and subsequent direct solvent extraction with diethyl ether. Fifteen different compounds including esters, alcohols and aldehydes were identified. Methyl benzoate was the major ester aroma compound with a relative concentration of 81.9%. Z-3-hexenol was the major alcohol with a relative concentration of 2.2%. Z-hex-3-enal was the major aldehyde with a relative concentration of 2.1% (Shaw et al., 1990).

A comparison of the volatile composition in fresh feijoa fruit with that in feijoa aroma condensate, the volatile composition in the feijoa aroma condensate showed a higher proportion of alcohol group compounds, a lower proportion of ester and aldehydes groups, and no ketones. Methyl benzoate, ethyl benzoate and ethyl butanoate have characteristic feijoa-like aroma qualities and contribute significantly to the flavour of feijoa and feijoa juice (Shaw et al., 1983).

Table 4.2 presents the aroma value of individual components in the feijoa condensate. The aroma value indicates the intensity and importance of the aroma compound in the condensate product. Though relative concentrations of esters in the condensate were low, methyl benzoate, ethyl butanoate, ethyl benzoate and linalool were the main compounds contributing to feijoa aroma flavour.

4.1.2 Boysenberry

The volatile compounds in boysenberry aroma condensate isolated by SPE and direct solvent extraction, and identified by GC-MS and GC. The gas chromatogram of boysenberry aroma condensate is presented in Figure 4.2. Fourteen compounds were confirmed by GC retention time, using a mixed standard solution containing fourteen volatile compounds as listed on Table 4.3. All compounds except ethyl butanoate, nerol and 2-heptanol were identified by GC-MS. For the fourteen compounds identified, their approximate concentrations and relative concentrations determined using an internal standard, ethyl octanoate, are also shown in Table 4.3. In Table 4.4, the aroma threshold values, aroma values and properties of each aroma compound identified in boysenberry aroma condensate is presented.

Aliphatic and terpene alcohols made up 85% and 3%, respectively, the total aroma composition. Esters contributed to 12% of the total aroma composition. Ethanol was qualitatively the major compound present with a relative concentration of 81.5%. The next major aliphatic alcohol was 3-methyl butanol with a relative concentration of 1.6%. Linalool was the major terpene alcohol present with a relative concentration of 2%. α-terpinerol, geraniol and nerol were quantified with relative concentrations of 0.3%, 0.3% and 0.1%, respectively. The terpene alcohols contribute to the characteristic flavour of boysenberry (Porter, 1988; Allen et al., 1996)

Porter (1988) identified the volatile composition of fresh boysenberry fruit using two techniques, these were by headspace sampling or by distillation. The results from each technique were found to be different. The relative concentration of linalool was found to be much higher after sampling by the headspace technique than by the distillation technique. The relative concentration of aliphatic alcohols such as ethanol, 2- heptanol, E-2-hexenol was much higher by the distillation sampling technique than by headspace analysis.

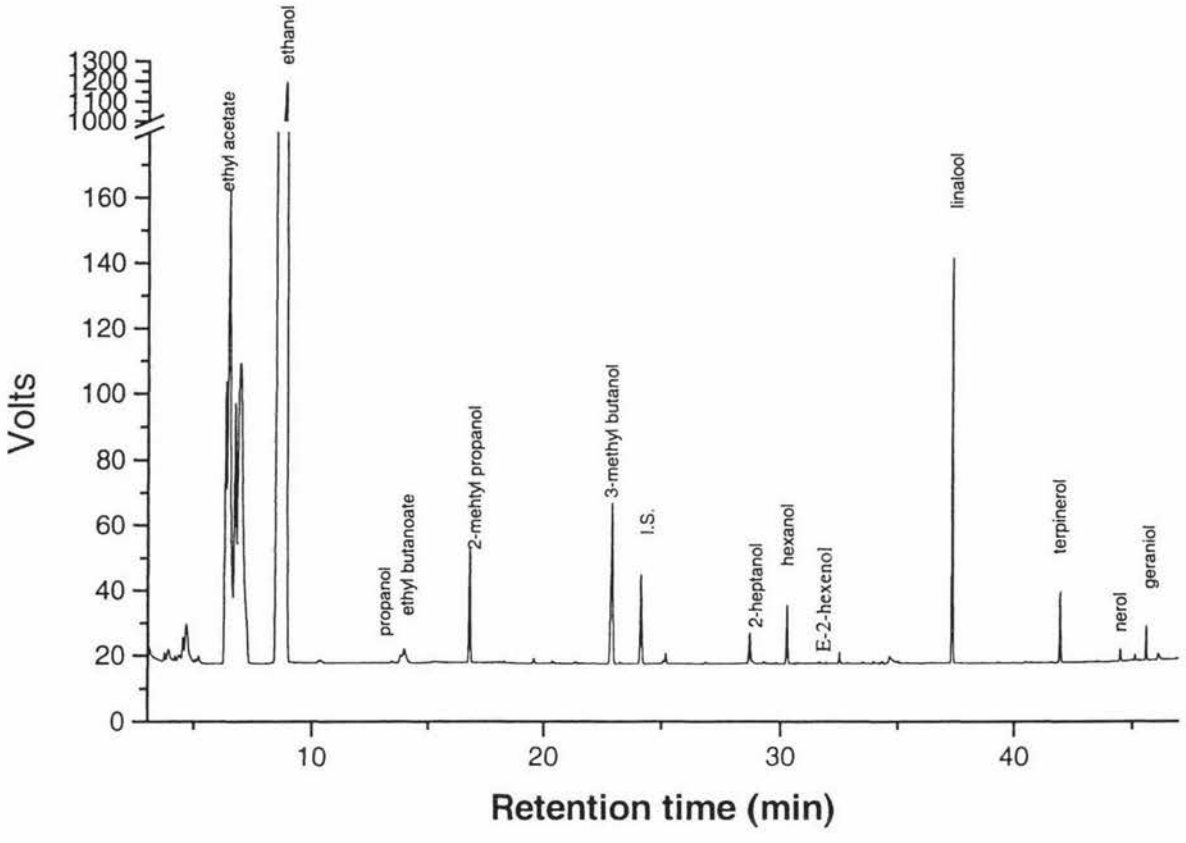

Figure 4.2 Gas chromatogram of boysenberry aroma condensate (feed sample). I.S.= Intenal Standard.

Table 4.3 The volatile compounds in boysenberry aroma condensate

Compounds	Identification method	Retention time (min.)[a]	Concentration (ug/g)	Relative concentration (%)
Ethyl acetate	MS,RT	6.40	1267 ± 60	12.2
Ethanol	MS,RT	8.66	20000 ± 456	81.5
Propanol	MS,RT	13.85	9 ± 3	0.1
Ethyl butanoate	RT	14.00	37 ± 2	0.4
2-methyl propanol	MS,RT	16.77	92 ± 4	0.9
3-methyl butanol	MS,RT	22.95	173 ± 7	1.7
E-2-hexenal	MS,RT	23.27	1.5 ± 0.0	0.0
2-heptanol	RT	28.69	24 ± 1	0.2
Hexanol	MS,RT	30.27	37 ± 2	0.4
E-2-hexenol	MS,RT	32.49	7.2 ± 0.3	0.1
Linalool	MS,RT	37.34	205 ± 12	2.0
Terpinerol	MS,RT	41.95	34 ± 2	0.3
Nerol	RT	44.49	13.4 ± 0.1	0.1
Geraniol	MS,RT	45.58	26 ± 1	0.3

MS: Mass spectrometer coupled with GC.

RT: Comparison of the GC retention time with a mixed external standard solution.

a: Retention times obtained on a DB-WAX column.

Table 4.4 Aroma threshold value, aroma value and properties of aroma compounds identified and studied in the boysenberry condensate

Compound	ATV[a]	AV[b]	MW[c] (g/mol)	BP[d] (°C)	WS[e] (mg/l)	LogP[f]	VP[g] (Pa)
Ester							
Ethyl acetate	1.0	1267	74.1	34.5	6.0×10^{4}	0.89	7.0×10^{4}
Ethyl butanoate	1×10^{-5}	3.6×10^{6}	102.0	92.3	2.1×10^{3}	2.03	6.8×10^{3}
Aldehyde							
E-2-hexenal	0.1	13	98.5	146.5	5.2×10^{3}	1.58	79.0
Aliphatic alcohol							
Ethanol	NF	NF	46.1	78.3	1.0×10^{6}	-0.31	7.8×10^{3}
Propanol	NF	NF	60.1	97.2	1.0×10^{6}	0.25	2.8×10^{3}
2-methyl propanol	NF	NF	74.1	107.9	8.5×10^{4}	0.75	1.3×10^{3}
3-methyl butanol	NF	NF	88.2	128.0	2.9×10^{4}	1.29	4.1×10^{2}
2-heptanol	NF	NF	116.0	159.0	3.3×10^{3}	2.31	1.6×10^{2}
Hexanol	0.1	375	102.0	157.1	5.9×10^{3}	2.03	1.2×10^{2}
E-2-hexenol	0.5	14.5	NF	NF	NF	NF	NF
Terpene alcohol							
Linalool	0.005	4×10^{4}	154.0	196.0	1.53×10^{3}	2.97	21.0
Terpinerol	NF	NF	154.0	222.3	1.9×10^{3}	3.33	4.1
Nerol	NF	NF	NF	NF	NF	NF	NF
Geraniol	0.005	5×10^{3}	154	229	1.0×10^{2}	3.47	4.0

a: Aroma threshold value; date sourced from Larsen et al (1992).
b: Aroma value obtained from the ratio of concentration of aroma/ aroma threshold value.
c: Molecular weight (g/mol).
d: Boiling point (°C).
e: Water solubility at 25°C (mg/l).
f: Hydrophobicity constant.
g: Vapour pressure at 25°C (mmHg).
c,d,e,f,g, sourced from Howard & Meylan (1997)

NF: Published information not found.

Allen et al. (1996) identified 32 volatile constituents of ripe boysenberry fruit isolated by vacuum steam distillation. Aliphatic alcohols and terpene alcohols comprised 63% and 33% of the total aroma compounds, respectively. Aliphatic alcohol mainly contained ethanol with a relative concentration of 54%. The relative concentrations of E-2-hexenol, 2-heptanol, 3-methyl butanol was 2.2%, 2.4% and 2.1%, respectively. Terpene alcohols mainly contained linalool with a relative concentration of 24%.

Compared with the volatile composition of fresh fruit, the boysenberry aroma condensate had a higher relative concentration of ethanol, and a lower relative concentration of terpene alcohols such as linalool, terpinerol, nerol and geraniol. According to the aroma values shown in Table 4.4, ethyl butanoate, linalool and geraniol contributes to the main flavour of boysenberry aroma condensate. The reports on boysenberry flavour sniffer port analysis confirmed that linalool, nerol and geraniol have sweet, floral and rose-like aroma attributes and were considered important contributors to boysenberry aroma (Porter, 1988; Allen et al., 1996).

4.2 Membrane evaluation

Three pervaporation membranes were evaluated with regard to their ability to recover or enrich feijoa or boysenberry aromas by pervaporation. The membrane evaluation was based on individual aroma selectivity, mass partial flux of the different components, and the aroma composition of final permeates. In this study, the permeate pressure was maintained at 100 Pa absolute pressure to maximize driving force for mass transfer across the membrane. The feed flow rate was set at 1.4×10^{-5} $m^3 s^{-1}$. It was assumed that the overall mass transfer coefficient will be mainly dependent on the membrane properties, therefore, boundary layer resistance on the feed side and permeate side were ignored.

Three membranes were evaluated using a 5% (w/w) ethanol solution as the feed. The total flux and enrichment factor for different membranes are presented in Table 4.5. It can be seen that the total flux for GFT1060 membrane was much higher than for both GFT1070 and PEBA membranes; the total flux for GFT1070 membrane was higher than for PEBA membrane. The enrichment factor of ethanol using GFT1070 membrane was much higher than with GFT1060 and PEBA membranes. This is because GFT 1070 membranes have added hydrophobic silicalite, thus it was more selective to ethanol than ordinary PDMS membranes (GFT1060) (Dotremont et al., 1995). The enrichment factor of ethanol for PEBA membrane was lower than for GFT1060 membrane.

Table 4.5 The influence of membrane type on total flux and enrichment factor for 5% (w/w) ethanol solution after pervaporation at a feed temperature of 30°C, feed flow rate of 1.4×10^{-5} $m^3 s^{-1}$ and permeate pressure of 100 Pa absolute pressure.

Membrane type	Total flux ($\times 10^{-5}$ $kgm^{-2}s^{-1}$)	Enrichment factor
GFT1060	5.5 ± 0.2	4.4
GFT1070	1.6 ± 0.1	5.6
PEBA	1.1 ± 0.1	2.8

4.2.1 Feijoa

Three membranes were tested using feijoa aroma condensate as the feed solution, at the same operating conditions.

The total flux, pervaporation experiment duration and total yield for the three different membranes are presented in Table 4.6. As can be seen, the total flux for GFT1060 membrane was much higher than for GFT1070 and PEBA membranes. The total flux with GFT1070 membrane was higher than with PEBA membrane. The total flux for the feijoa aroma condensate or for 5% ethanol solution was of the same order for the three different membranes

Table 4.6. Yield, pervaporation experiment duration and total flux for feijoa aroma solution after pervaporation at a feed temperature of 30°C, feed flow rate of 1.4 $\times 10^{-5} m^3 s^{-1}$ and permeate pressure of 100 Pa absolute pressure.

Membrane type	Yield (%)	Experiment duration (h)	Total flux ($\times 10^{-5}$ kg $m^{-2} s^{-1}$)
GFT1060	0.4	7.00	4.0 ± 0.1
GFT1070	0.4	21.0	1.5 ± 0.0
PEBA	0.4	30.5	1.0 ± 0.0

The individual concentrations of aroma compounds in the feed, retentate and permeate for the three membranes are shown in the Table 4.7. PEBA membrane produced permeates with the highest concentrations of ethyl butanoate, methyl benzoate, ethyl benzoate, hexanol, Z-3-hexenol and linalool. The concentrations of these compounds were less in permeates from GFT1070 and GFT1060 membranes. GFT1070 membrane produced permeates with the highest concentration of ethyl acetate and E-2-hexenal. Ethanol was highest in permeates obtained from GFT1060 and GFT1070 membranes. The concentration of total aroma compounds increased 13-15 fold based on the original aroma condensate.

The relative concentrations of aroma compounds in the feed and permeates obtained from

Table 4.7 The influence of different pervaporation membranes on the individual concentrations of aroma compounds in the feed, retentate and permeate for feijoa aroma pervaporation at a feed temperature of 30°C, feed flow rate of $1.4\times10^{-5}m^3s^{-1}$ and permeate pressure of 100 Pa absolute pressure. Each mean was obtained from 8 samples.

Aroma compounds	Concentration (ug/g)												
			GFT 1060				GFT1070				PEBA		
	Feed[a]		Retentate		Permeate		Retentate		Permeate		Retentate		Permeate	
	mean	SE	mean	SE	mean	SE	mean	SE	mean	SE	mean	SE	mean	SE
Ester														
Ethyl acetate	58.0	0.5	57.1	0.7	435	8	46.0	0.7	826	4	49	2	285	30
Ethyl butanoate	4.5	0.0	0.0	0.0	104.9	0.5	0.0	0.0	189	2	0.0	0.0	221	13
Methyl benzoate	87.1	0.2	16.5	0.2	2958	32	7.1	0.0	4529	13	2.5	0.2	7832	309
Ethyl benzoate	8.0	0.0	1.2	0.0	223	5	0.0	0.0	361	1	0.0	0.0	707	40
Aldehyde														
E-2-hexenal	5.5	0.0	0.00	0.0	110.9	0.5	3.9	0.0	188	2	3.8	0.0	114.6	0.2
Alcohol														
Ethanol	1246	21	907	16	12565	25	835	4	10616	11	1038	37	5776	1241
Hexanol	25.8	0.2	12.2	0.2	1168	3	11.3	0.0	1708	8	11.5	0.2	1940	5
Z-3-hexenol	75.2	0.2	46.7	0.4	2230	4	51.9	0.1	3552	7	49.8	0.6	3630	20
Linalool	6.7	0.1	1.8	0.1	172	2	1.2	0.0	288	1	0.0	0.0	539	23
Total aroma (mg/g)	1.5				20.1				22.5				22.7	

a: Feijoa aroma condensate Batch 2.

the three different membranes are presented in Table 4.8. The concentration of total aroma compounds and the relative aroma composition in the permeate were altered from that in the feed after pervaporation. The relative concentration of ethanol decreased, and the relative concentration of esters increased. There was a large difference in aroma composition of the permeates obtained from each different membrane. This also can be seen in their gas chromatograms (Appendix Figure A1, A2 and A3). The permeate obtained from PEBA membrane had the highest relative concentration of ethyl butanoate, methyl benzoate and ethyl benzoate. These aroma compounds have been identified to contribute to the feijoa-like flavour of feijoa (Shaw et al., 1983).

The partial fluxes of aroma compounds for the three membranes are presented in Table 4.9. The partial fluxes of aroma compounds for all three membranes are related to the original aroma concentrations in the feed. The aroma which was present in higher concentration in the feed, exhibited higher aroma partial fluxes. For both GFT1060 and GFT1070 membranes, ethanol which had the highest concentration in the feed, had the highest aroma partial flux. Methyl benzoate which had the second highest concentration in the feed, exhibited the second highest partial flux. Ethyl butanoate which had the lowest concentration in the feed, had the lowest partial flux. The order of the partial fluxes of aroma compounds follows the order of the concentrations of aroma compounds in the feed. For PEBA membrane, however, methyl benzoate had the highest partial flux, and ethanol had the second highest partial flux. This indicates that the PEBA membrane is strongly selective toward methyl benzoate rather than toward ethanol. This is because PEBA membranes exhibit high selectivity and permeability towards aromatic compounds (Djebbar et al., 1998).

The partial fluxes of all aroma compounds, except methyl benzoate, ethyl benzoate and linalool, decreased in the order of GFT1060, followed by GFT1070, and followed by PEBA. The order was the same as found for total fluxes for each membrane. Methyl

Table 4.8 The influence of membrane type on relative concentrations of aroma compounds in the permeate obtained from feijoa aroma pervaporation, at a feed temperature of 30°C, feed flow rate of 1.4×10^{-5} m^3s^{-1} and permeate pressure of 100 Pa.

Aroma Compound	Relative concentration of aroma compounds (%)				
	Fresh fruit[a]	Feed	Permeate with GFT1060	Permeate with GFT1070	Permeate with PEBA
Ester					
Ethyl acetate	NF	3.8	2.2	3.7	1.4
Ethyl butanoate	0.3	0.1	0.5	0.8	1.1
Methyl benzoate	81.9	5.7	14.5	20.1	32.6
Ethyl benzoate	0.5	0.5	1.1	1.6	2.9
Aldehyde					
E-2-hexenal	1.7	0.4	0.6	0.9	0.5
Alcohol					
Ethanol	NF	81.9	62.6	47.1	33.2
Hexanol	0.2	1.7	5.8	7.6	8.6
Z-3-hexenol	NF	4.9	11.0	15.8	15.9
Linalool	NF	0.4	0.8	1.3	2.2

a: Data sourced from Shaw et al. (1990)

NF: Published information not found

Table 4.9 The influence of membrane type on the partial flux of aroma compounds for feijoa aroma pervaporation, at a feed temperature of 30°C, feed flow rate of 1.4×10^{-5} m^3s^{-1} and permeate pressure of 100 Pa absolute pressure.

Aroma compounds	Feed concentration (ug/g)	Partial flux ($\times10^{-8}$ kg m^{-2} s^{-1})		
		GFT1060	GFT1070	PEBA
Ester				
Ethyl acetate	58	1.7 ± 0.0	1.3 ± 0.0	0.3 ± 0.0
Ethyl butanoate	4.5	0.4 ± 0.0	0.3 ± 0.0	0.2 ± 0.0
Methyl benzoate	87	11.8 ± 0.3	7.0 ± 0.0	7.8 ± 0.2
Ethyl benzoate	8.0	1.0 ± 0.0	0.6 ± 0.0	0.7 ± 0.0
Aldehyde				
E-2-hexenal	5.5	0.4 ± 0.0	0.3 ± 0.0	0.1 ± 0.0
Alcohol				
Ethanol	1246	50 ± 1	16.3 ± 0.5	6 ± 1
Hexanol	25.8	4.7 ± 0.0	2.7 ± 0.0	1.9 ± 0.0
Z-3-hexenol	75	8.9 ± 0.0	5.5 ± 0.0	3.6 ± 0.0
Linalool	6.7	0.7 ± 0.0	0.5 ± 0.0	0.5 ± 0.0

benzoate, ethyl benzoate and linalool had higher aroma partial fluxes in the PEBA membrane than in the GFT1070 membrane.

The mass transfer coefficient gives a measure of the permeability of the aroma compound across membrane. The mass transfer coefficients of individual aroma compounds for the three different membranes are presented in Figure 4.3. Mass transfer coefficients were calculated using eqaution 2.2. For ethyl acetate, ethyl butanoate, E-2-hexenal, ethanol, hexanol and Z-3-hexenol, the mass transfer coefficients for each membrane decreased in the order of GFT1060, followed by GFT1070, and followed by PEBA. For methyl benzoate, ethyl benzoate and linalool, the mass transfer coefficients with GFT1060 and PEBA membranes were the same, but both coefficients were higher than those with GFT1070 membrane. It was found that, for PEBA membrane, the mass transfer coefficient significantly increased as the molecular weight of the aroma compound increased. This agreed with the work of Groβ & Heintz (1999). The sorption isotherms of seven aromatic compounds in PEBA membrane were investigated by Groβ & Heintz (1999). They concluded that the solubility of aroma compounds in PEBA membrane depends significantly on the molecular weight of the aromatic compound (Groβ & Heintz, 1999).

The enrichment factor indicates the selectivity of the membrane for individual permeated aroma compounds. The enrichment factors are presented in Figure 4.4. For ethyl butanoate, methyl benzoate, ethyl benzoate, hexanol and linalool, pervaporation with the PEBA membrane yielded the highest enrichment factors, followed by GFT1070 and GFT1060 membranes. This result agreed with earlier studies in which PEBA membrane had increased selectivity to aromatic hydrocarbons (Böddeker & Bengtson, 1990). For ethanol and ethyl acetate, pervaporation with GFT1070 membrane produced the highest enrichment factors, followed by GFT1060 and PEBA membranes. This is because silicalite-filled PDMS membranes preferentially separate small or unbranched organics (Dotremont et al., 1995). For Z-3-hexanol, enrichment factors due to pervaporation were higher with PEBA and GFT1070 membrane. For E-2-hexenal, pervaporation with GFT1060 and GFT1070 membranes produced higher enrichment factors than PEBA membrane.

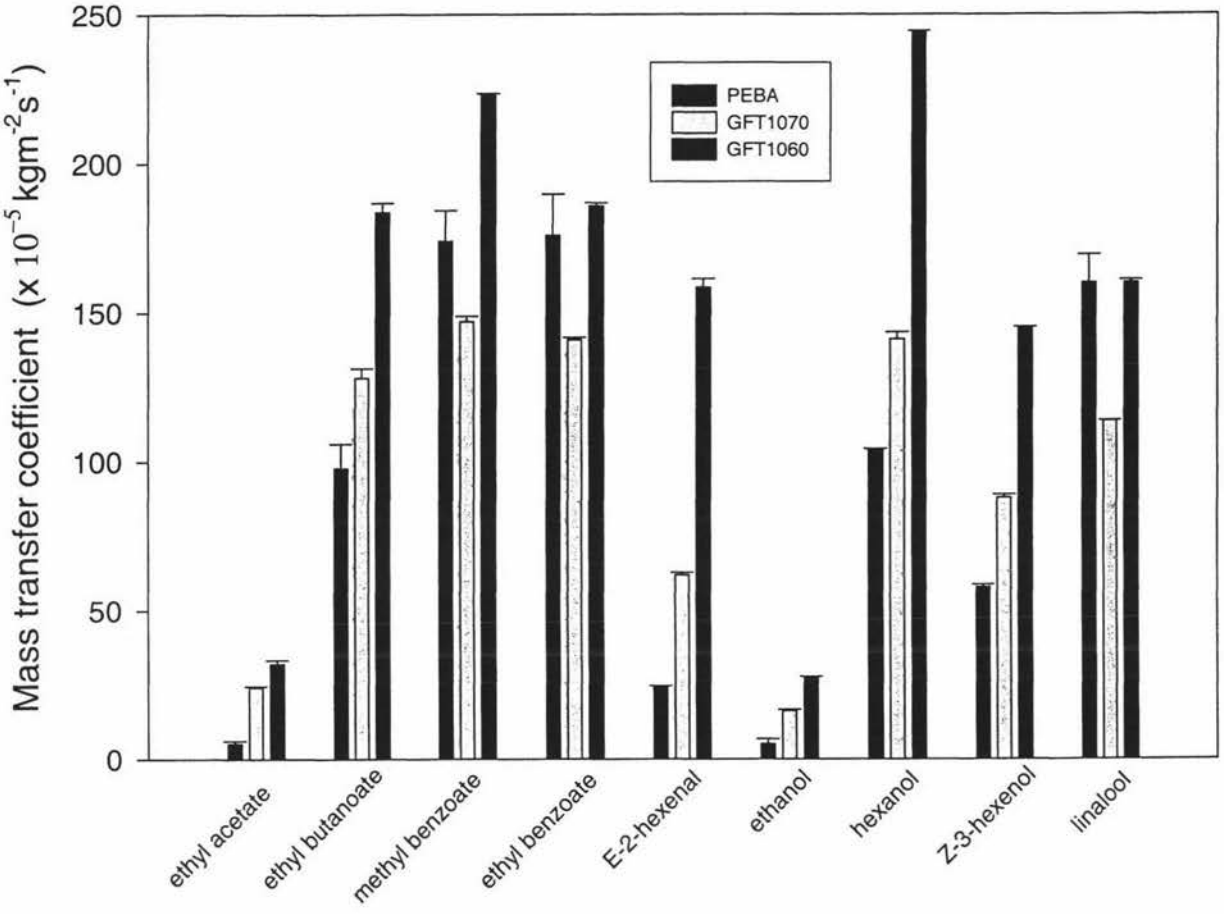

Figure 4.3 Mass transfer coefficients of aroma compounds for feijoa aroma pervaporation with membranes: GFT1060, GFT1070 and PEBA; at a feed temperature of 30°C, feed flow rate of 1.4×10^{-5} m^3 s^{-1} and permeate pressure of 100 Pa absolute pressure.

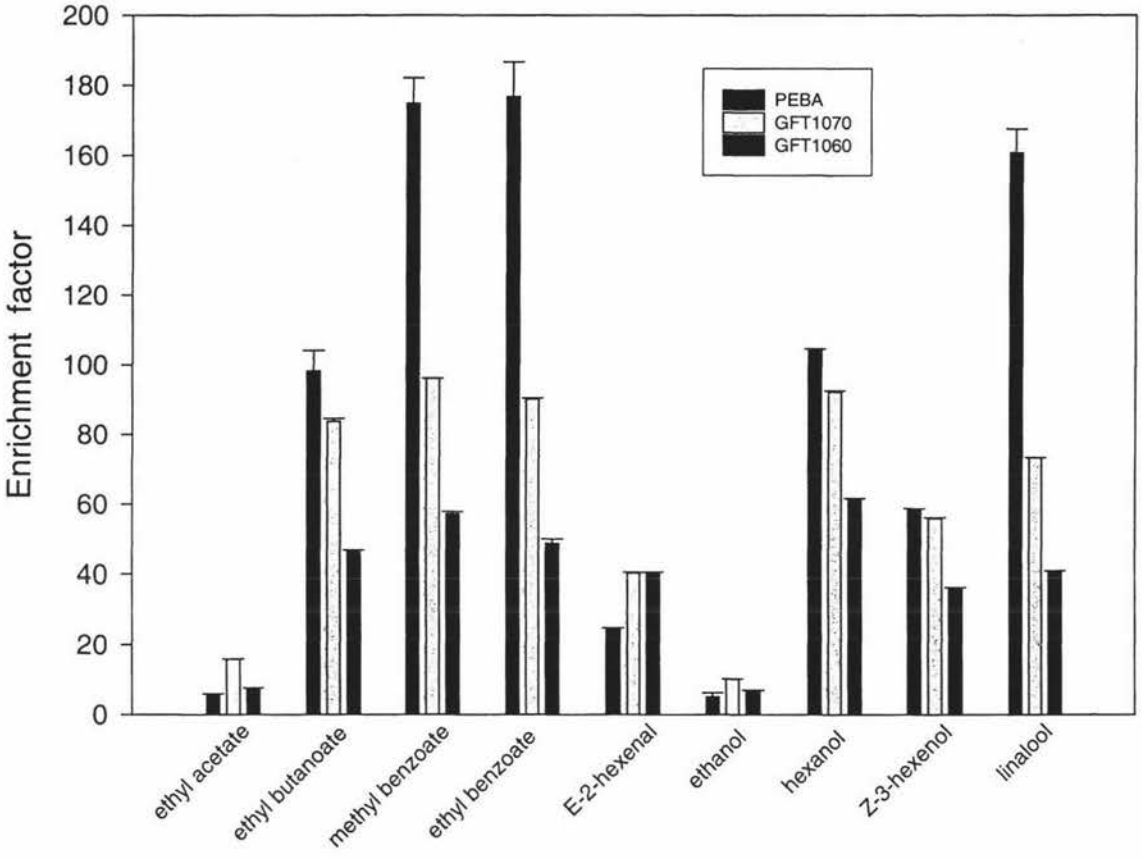

Figure 4.4 Enrichment factors of aroma compounds of feijoa aroma after pervaporation using three different membranes; GFT1060, GFT1070 and PEBA, at a feed temperature of 30°C, feed flow rate of a 1.4×10^{-5} m^3 s^{-1} and permeate pressure of 100 Pa absolute pressure.

4.2.2 Boysenberry

Three membranes were evaluated with boysenberry aroma condensate as the feed solution at the same operating conditions.

The yield, pervaporation experiment duration, and total flux for the three different membranes are presented in Table 4.10. The total flux after pervaporation with GFT1060 membrane for recovery of boysenberry aroma was much higher than with GFT1070 and PEBA membranes. The total flux with GFT1070 membrane was higher than with PEBA membrane.

Table 4.10 Yield, pervaporation experiment duration and total flux for boysenberry aroma solution after pervaporation at a feed temperature of 30°C, feed flow rate of 1.4×10^{-5} m^3s^{-1} and permeate pressure of 100 Pa absolute pressure.

Membrane type	Yield (%)	Experiment duration (h)	Total flux ($\times 10^{-5}$ $kgm^{-2}s^{-1}$)
GFT1060	0.5	7.7	5.9 ± 0.2
GFT1070	0.5	20.0	2.0 ± 0.1
PEBA	0.5	31.5	1.2 ± 0.0

The concentrations of aroma compounds in the feed, retentate and permeate are shown in Table 4.11. The concentration of aroma compounds in the retentate and the permeate for the three different membranes were different. Terpene alcohols such as linalool, terpinerol, nerol and geraniol had the highest concentrations in the permeates obtained with the PEBA membrane. Esters such as ethyl acetate and ethyl butanoate, and aliphatic alcohols, ethanol, propanol, 2-methyl propanol, 3-methyl butanol, 2-heptanol, hexanol, and E-2-hexenol had the highest concentrations in the permeate obtained through the GFT1070 membrane. The total aroma compounds had been concentrated 6-12 fold based on the original aroma condensate.

Table. 4.11 The influence of membrane type on the concentrations of aroma compounds in the feed, retentate and permeate for boysenberry aroma pervaporation at a feed temperature of 30°C, feed flow rate of 1.4×10^{-5} m^3s^{-1} and permeate pressure of 100 Pa absolute pressure. Each mean was obtained from 8 samples.

Aroma compounds	Concentration (ug/g)													
	Feed		GFT1060				GFT1070				PEBA			
			Retentate		Permeate		Retentate		Permeate		Retentate		Permeate	
	mean	SE	mean	SE	mean	SE	mean	SE	mean	SE	mean	SE	mean	SE
Ester														
Ethyl acetate	1267	60	515	41	58216	1230	505	8	67000	3535	859.4	0.5	25664	289
Ethyl butyrate	37	1	30	1	274	5	43.3	0.6	396	47	37	1	277	7
Aldehyde														
E-2-hexenal	1.0	0.0	0.0	0.0	150.0	0.3	0.0	0.0	158	5	0.0	0.0	181	0
Aliphatic alcohol														
Ethanol	20000	456	19000	987	115870	9990	19000	1567	152807	7664	19000	1236	70000	987
Propanol	9	3	9	2	103	8			167	2	7.6	0.0	111	1
2-methyl propanol	92	4	75	5	1182	53	80	1	1839	52	79	7	963	4
3-methyl butanol	173	7	129	8	3682	187	133	2	10592	301	135	12	3895	27
2-heptanol	24	1	10.3	0.3	1032	49	8.3	0.3	2170	87	8.2	0.3	1858	59
Hexanol	37	2	21	1	1334	56	19.5	0.3	2653	95	18	1	2435	74
E-2-hexenol	7.2	0.3	4.9	0.4	190	7	4.9	0.1	353	11	4.4	0.3	367	10
Terpene alcohol														
Linalool	205	12	73	6	7899	635	50	2	18110	614	22	2	20769	726
Terpinerol	34	2	20	2	493	48	20.1	0.7	1035	9	11	1	1965	76
Nerol	13.4	0.1	6.9	0.4	222	24	6.4	0.2	517	2	7.0	0.7	1040	33
Geraniol	26	1	15	1	275	31	14.3	0.7	733	5	7.0	0.7	1736	52
Total aroma(mg/g)	21.9				190.0				258.0				131.0	

The permeates obtained from GFT1070 membrane had the highest total concentration, this was followed by permeates from GFT1060 and PEBA membranes. The permeates obtained from GFT1070 and GFT1060 membranes did not freeze at –18°C due to the high ethanol and aliphatic alcohol concentration. The relative aroma composition in the permeates were altered in comparison with the feed as shown in Table 4.12 The relative concentration of important aroma compounds; linalool, terpinerol, nerol and geraniol, were increased in the permeate. The permeates obtained through PEBA membrane had the highest relative concentration of linalool, terpinerol, nerol and geraniol. The relative aroma composition of the terpene alcohols in the permeate obtained through PEBA membrane was very similar to the relative aroma composition of fresh fruit. . The gas chromatograms of three permeates obtained from the three different membranes are shown in the Appendix (Figure A4, A5, A6).

The partial fluxes of aroma compounds for the three different membranes are presented in Table 4.13. For the three membranes, the partial fluxes of the aroma compounds were related to the concentration of aroma compounds in the original feed as was found for feijoa aroma. The aroma that had the higher concentration in the feed would yield higher partial fluxes during pervaporation. There were large differences in partial fluxes of individual aroma compounds between the three different membranes as can be seen in Table 4.13. Partial fluxes for all of the aroma compounds with the exception of terpinerol, nerol and geraniol followed the decreasing order of GFT1060, followed by GFT1070, followed by PEBA membranes. For geraniol, PEBA membrane had the highest aroma partial flux. The aroma partial flux for terpinerol and nerol was greatest in GFT1060 membranes, followed by PEBA and GFT1070 membranes.

The mass transfer coefficients of individual aroma compounds for the three different membranes are presented in Figure 4.5. For all aroma compounds with the exception of terpinerol, nerol and geraniol, mass transfer coefficients for each membrane are in the decreasing order of GFT1060, followed by GFT1070, and then by PEBA membranes. For

Table 4.12 The influence of membrane type on the relative concentrations of aroma compounds in the permeate obtained from boysenberry aroma pervaporation at a feed temperature of 30°C, feed flow rate of 1.4×10^{-5} m^3s^{-1} and permeate pressure of 100 Pa absolute pressure.

Aroma Compound	Relative concentration of aroma compounds (%)				
	Fresh fruit[a]	Feed	Permeate with GFT1060	Permeate with GFT1070	Permeate with PEBA
Ester					
Ethyl acetate	0.4	12.2	25.9	23.3	26.2
Ethyl butyrate	0.9	0.4	0.2	0.2	0.3
Aldehyde					
E-2-hexenal	0.1	0.0	0.1	0.1	0.2
Aliphatic alcohol					
Ethanol	54.1	81.4	64.5	61.5	39.5
Propanol	0.7	0.1	0.1	0.1	0.1
2-methyl propanol	0.0	0.9	0.7	0.7	1.0
3-methyl butanol	0.7	1.7	2.2	4.1	3.8
2-heptanol	2.4	0.2	0.6	0.9	1.8
Hexanol	1.5	0.4	0.8	1.1	2.3
E-2-hexenol	2.2	0.1	0.1	0.1	0.3
Terpene alcohol					
Linalool	23.7	2.0	4.4	7.1	20.0
Terpinerol	5.1	0.3	0.3	0.4	1.9
Nerol	0.9	0.1	0.1	0.2	1.0
Geraniol	2.4	0.3	0.2	0.3	1.7

a: Data sourced from Allen et al. (1996).

Table 4.13 The influence of membrane type on the partial fluxes of aroma compounds for boysenberry aroma pervaporation at a feed temperature of 30°C, feed flow rate of 1.4×10^{-5} $m^3 s^{-1}$ and permeate pressure of 100 Pa absolute pressure.

Aroma Compounds	Feed concentration (ug/g)	Partial flux ($\times 10^{-8}$ kg m^{-2} s^{-1})		
		GFT1060	GFT1070	PEBA
Ester				
Ethyl acetate	1267	343 ± 62	122 ± 2	30.0 ± 0.7
Ethyl butyrate	37	1.6 ± 0.0	0.8 ± 0.0	0.3 ± 0.0
Aldehyde				
E-2-hexenal	1.0	0.9 ± 0.0	0.3 ± 0.0	0.2 ± 0.0
Aliphatic alcohol				
Ethanol	20000	688 ± 41	301 ± 20	82 ± 2
Propanol	9	0.6 ± 0.1	0.3 ± 0.0	0.1± 0.0
2-methyl propanol	92	7.0 ± 0.2	3.6 ± 0.1	1.1 ± 0.0
3-methyl butanol	173	21.9 ± 0.5	21 ± 1	4.6 ± 0.0
2-heptanol	24	6.1 ± 0.1	4.3 ± 0.2	2.2 ± 0.1
Hexanol	38	8.0 ± 0.2	5.2 ± 0.2	2.8 ± 0.1
E-2-hexenol	7.2	1.1 ± 0.0	0.7 ± 0.0	0.4 ± 0.0
Terpene alcohol				
Linalool	205	47 ± 2	35 ± 2	24.3 ± 0.8
Terpinerol	34	2.9 ± 0.2	2.0 ± 0.2	2.3 ± 0.0
Nerol	13	1.3 ± 0.1	1.0 ± 0.0	1.2 ± 0.0
Geraniol	26	1.6 ± 0.1	1.4 ± 0.0	2.0 ± 0.0

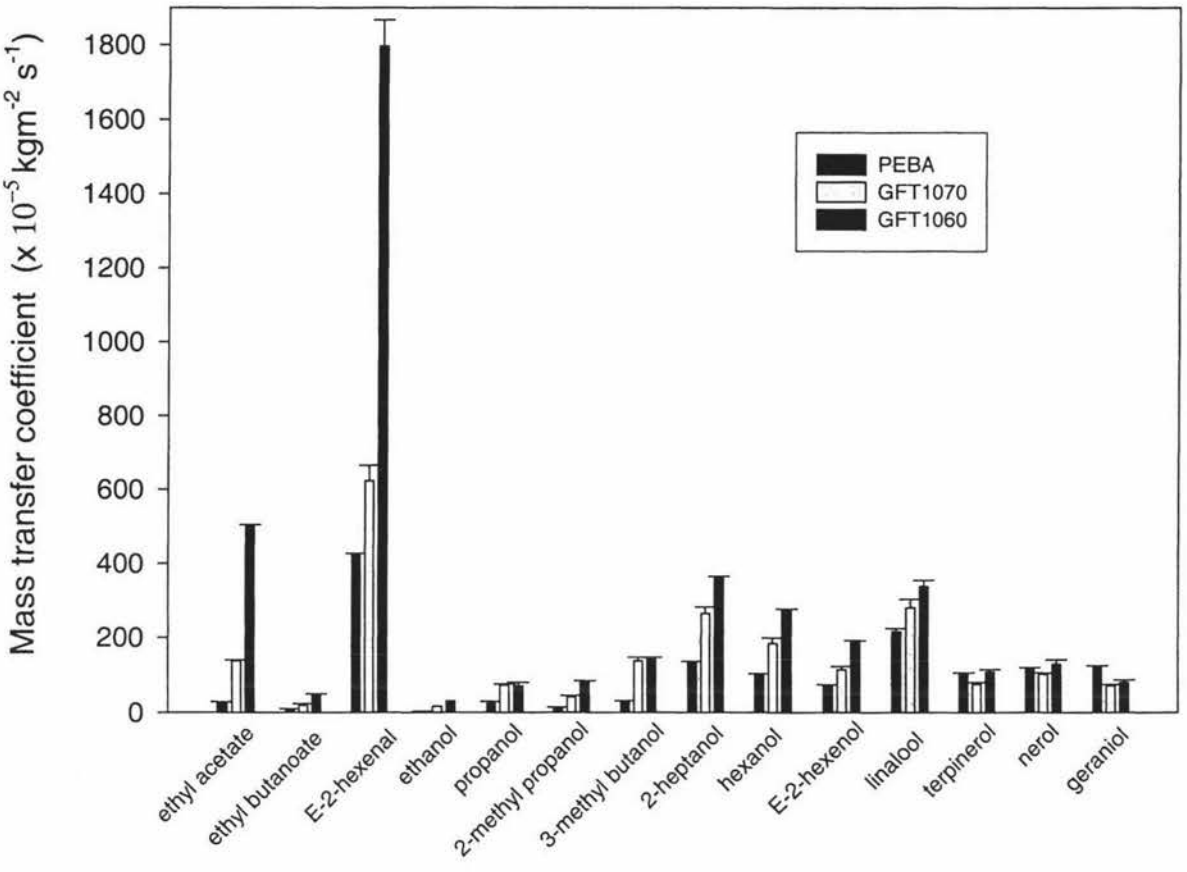

Figure 4.5 Mass transfer coefficients of aroma compounds for boysenberry aroma pervaporation with membranes: GFT1060, GFT1070 and PEBA, at a feed temperature of 30°C, feed flow rate of 1.4×10^{-5} m^3 s^{-1}, permeate pressure of 100 Pa absolute pressure.

terpinerol, nerol and geraniol, the mass transfer coefficients with the GFT1060 and PEBA membranes were similar, but were higher than with GFT1070 membrane.

The enrichment factors of aroma compounds for three different membranes are shown in Figure 4.6. For ethyl acetate, pervaporation with GFT1060 membranes yielded the highest enrichment factor. For aliphatic alcohols with low molecular weight such as ethanol, propanol, 2-methyl propanol, and 3-methyl butanol, pervaporation with GFT1070 membranes yielded highest enrichment factors. For aliphatic alcohols with high molecular weight such as hexanol and E-2-hexenol, pervaporation with PEBA and GFT1070 membranes yielded similar enrichment factors, which were higher than with GFT1060 membrane. For terpene alcohols, pervaporation with PEBA membranes yielded highest enrichment factors, followed by GFT1070 and GFT1060 membranes. For aldehydes, PEBA membranes gave the highest enrichment.

4.2.3 Discussion

The aroma compounds were highly concentrated by pervaporation for both feijoa and boysenberry. The relative aroma composition was altered to improve the proportion of more desirable aroma compounds present in the final permeate product.

The separation ability of pervaporation membranes was influenced by the molecular structures and the physico-chemical properties of membrane polymers, and by the affinity relationship between the membrane polymers and the solutes in the feed. The membrane polymer type, thickness, presence of zeolites and particles, and manufacturing technique affected the pervaporation performance, when the feed solution was constant (Djebbar et al., 1998).

From the experimental results, pervaporation with PDMS membranes (GFT1060 and GFT1070) produced much higher total fluxes than with PEBA membranes. It was observed that the diffusion of organic compounds in PDMS membranes was much higher than in

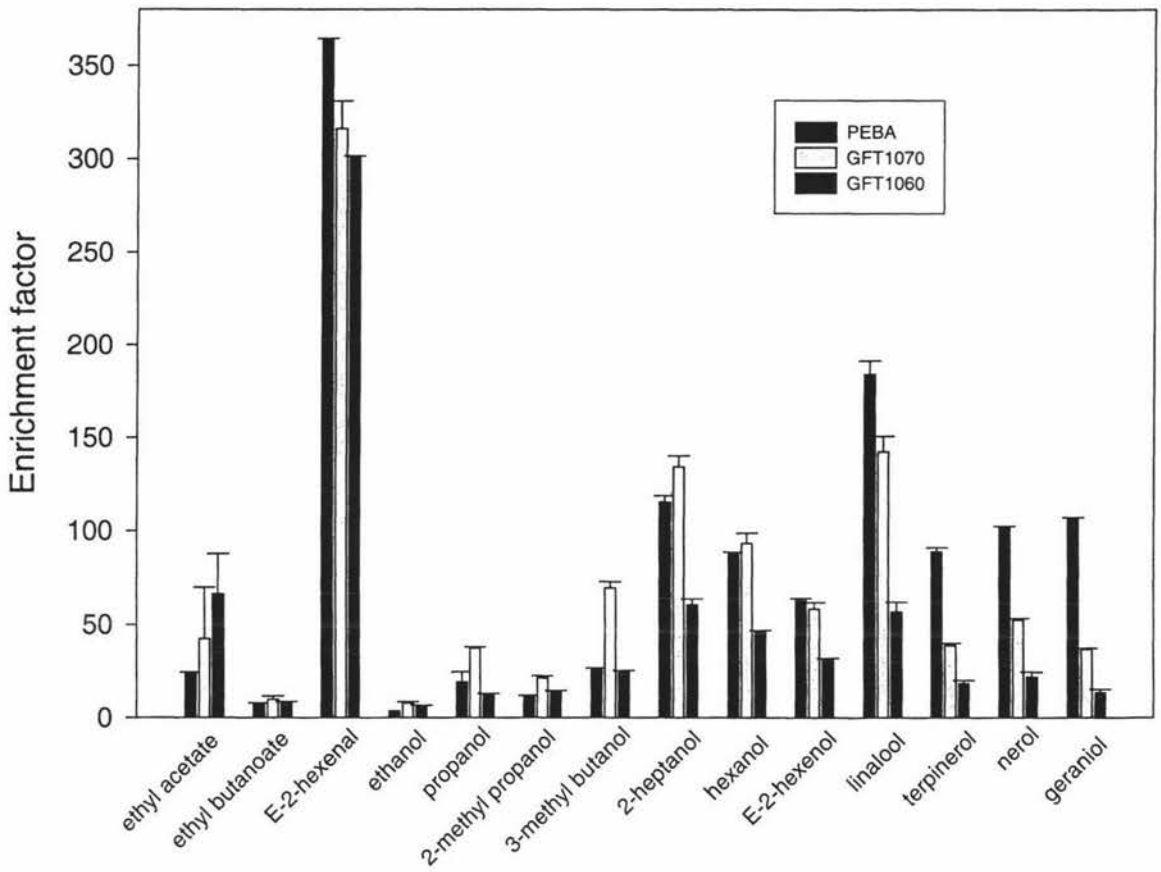

Figure 4.6 Enrichment factors for aroma compounds of boysenberry aroma after pervaporation using three different membranes; GFT1060, GFT1070 and PEBA, at a feed temperature of 30°C, feed flow rate of 1.4×10^{-5} m^3 s^{-1} and permeate pressure of 100 Pa absolute pressure.

PEBA membranes. This is because the PDMS polymer chains are more flexible than PEBA chains (hydrocarbon chains) (Djebbar, 1998). In PDMS membranes, there is high diffusivity of organic compounds and a low activation energy requirement for organic molecule transport (Djebbar, 1998). PEBA membranes produced the highest enrichment factors and mass transfer coefficients for terpene alcohols, linalool, terpinerol, nerol, geraniol, which are important aroma compounds for boysenberry flavour. Compared to the aliphatic alcohols, terpene alcohols have higher molecular weight, higher boiling point and are more hydrophobic. This result is similar to that reported of Baudot & Marin (1996). PEBA membranes were much more selective than the PDMS membranes for the extraction of methylthiobutanoate from water, whereas they are much less selective in the extraction of diacetyl than the PDMS membranes. Methylthiobutanoate has high molecular weight, high boiling point and is more hydrophobic than diacetyl (Baudot & Marin, 1996).

PEBA membranes also produced the highest enrichment factors and mass transfer coefficients for the aromatic esters such as methyl benzoate and ethyl benzoate which are important aroma compounds for feijoa flavour. This agreed with the conclusions of Baudot & Marin (1997), that the PEBA membranes are more effective in the extraction of aromatic organic compounds than PDMS membranes. The PDMS membranes exhibit high selectivity and permeability toward non-aromatic compounds (compounds without a benzene ring in their structure) (Baudot & Marin, 1997).

The relative aroma composition of permeates obtained from PEBA membranes approach the relative aroma compositions of fresh feijoa fruit and boysenberry fruit, more so than that of permeates obtained from PDMS membranes. Therefore, PEBA membranes are good membranes for recovery of feijoa and boysenberry aroma by pervaporation.

PDMS membrane generally shows high fluxes for organics but with lower selectivity. Silicalite has a porous structure and a very high hydrophobic character. Silicalite –filled PDMS membranes reduce the water sorption and improve the organic sorption, especially for small or unbranched apolar organic compounds (Dotremont et al., 1995). Compared to

GFT1060 membranes, GFT1070 membranes, due to the presence of the silicalite, had lower total flux, but had higher enrichment factors for all of aroma compounds, especially for aliphatic alcohol compounds.

4.3 Influence of permeate pressure

In this study, the permeate pressure were set at 100 Pa and 1000 Pa absolute pressure. The effect of the permeate pressure on pervaporation performance was examined using the 5% (w/w) ethanol solution with GFT1060 membranes at a feed temperature of 30°C and feed flow rate of 0.83×10^{-5} m^3 s^{-1}. Table 4.14 shows the fluxes and enrichment factors obtained. The flux at 1000 Pa was significantly less than the flux at 100 Pa ($P<0.025$). There was no difference in enrichment factor going from 100 Pa to 1000 Pa absolute pressure on the permeate side. Hickey et al. (1992) observed a permeate flux decline from 1.1×10^{-4} kg m^{-2} s^{-1} to 1.1×10^{-5} kg m^{-2} s^{-1}, as the permeate pressure was increased from 132 Pa to 5263 Pa for a 5% ethanol solution using poly-1-trimethyl silyl-1-propyne (PTMSP) pervaporation membranes, at a feed temperature of 30°C. There was no significant difference in the ethanol selectivity as the permeate pressure was increased from 132 Pa to 1320 Pa (Hickey et al., 1992).

Table 4.14 The effect of permeate pressure on the total flux and enrichment factor for 5% (w/w) ethanol solution after pervaporation with GFT1060 membranes at a feed temperature of 30°C, feed flow rate of 0.83×10^{-5} m^3 s^{-1}.

Absolute Permeate pressure (Pa)	Total flux ($\times10^{-5}$ kg $m^{-2}s^{-1}$)	Enrichment factor
100	5.5 ± 0.0	4.4
1000	4.9 ± 0.1	4.4

4.3.1 Feijoa aroma

The effect of the permeate pressure on pervaporation performance was examined using the feijoa aroma condensate at a temperature of 30°C. The results are presented in Table 4.15. The total flux at 1000 Pa absolute pressure was 10% less than the flux at 100 Pa absolute pressure, this was a significant reduction in the total flux ($P< 0.025$).

Table 4.15 Yield, pervaporation experiment duration and total flux for feijoa aroma solution after pervaporation with GFT1060 membranes at feed temperature of 30°C, feed flow rate of 0.83 $\times 10^{-5}$ m^3s^{-1}.

Absolute permeate pressure (Pa)	Yield (%)	Experiment duration (h)	Total flux ($\times 10^{-5}$ $kgm^{-2}s^{-1}$)
100	1.0%	21	4.4 ± 0.1
1000	1.0%	24	4.0 ± 0.0

The concentrations of aroma compounds in the feed, retentate, and permeate for the permeate pressures of 100 Pa and 1000 Pa absolute pressure are presented in Table 4.16. The concentrations of aroma compounds in the permeate collected at the 100 Pa were not significantly different ($P>0.025$) to the concentration of aroma compounds collected at 1000 Pa, except for ethyl acetate, E-2-hexenal, hexanol and Z-3-hexenol. There was a significant decrease in the concentrations of E-2-hexenal, hexanol and Z-3- hexenol in the permeate, as the permeate pressure was increased from 100 Pa to 1000 Pa ($P<0.025$). However, the concentration of ethyl acetate in the permeate increased significantly as the permeate pressure was increased from 100 Pa to 1000 Pa ($P< 0.025$).

The partial fluxes of aroma compounds obtained at the permeate pressures of 100 Pa and 1000 Pa absolute pressure are presented in Table 4.17. The enrichment factors of aroma compounds for the permeate pressures of 100 Pa and 1000 Pa absolute pressure are presented in Table 4.17.

Table 4.16 The effect of permeate pressure on the individual concentrations of aroma compounds in the feed, retentate and permeate for feijoa aroma pervaporation, with GFT1060 membrane at a feed temperature of 30°C, feed flow rate of 0.83×10^{-5} m^3s^{-1}. Each mean was obtained from 8 samples.

Aroma compounds	Concentration (ug/g)									
			Permeate pressure of 100 Pa				Permeate pressure of 1000 Pa			
	Feed[a]		Retentate		Permeate		Retentate		Permeate	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
Ester										
Ethyl acetate	52.0	0.5	33.5	0.4	350	2	25	2	499*	32
Ethyl butanoate	3.3	0.0	0.0	0.0	78	2	0.0	0.0	68	3
Methyl benzoate	64.2	0.2	1.7	0.0	1675	52	2.3	0.1	1657	75
Ethyl benzoate	5.0	0.0	0.0	0.0	76	3	0.0	0.0	70	8
Aldehyde										
E-2-hexenal	3.6	0.0	0.0	0.0	142	1	0.0	0.0	131*	2
Alcohol										
Ethanol	872	21	786	36	17043	135	806	56	16422	256
Hexanol	20.0	0.2	5.4	0.2	1238	12	6.6	0.1	1108*	7
Z-3-hexenol	58.5	0.2	34.5	0.7	2841	11	37	1	2313*	29
Linalool	5.4	0.1	0.0	0.0	174.1	0.6	0.0	0.0	172	12
Total aroma (mg/g)	1.1				23.6				22.3	

a: Feijoa aroma condensate Batch1.

*: Significantly different to permeate concentration at 100 Pa (97.5% confidence).

Table 4.17 The effect of permeate pressure on the partial fluxes and enrichment factors of aroma compounds for feijoa aroma pervaporation, with GFT1060 membranes at a feed temperature of 30°C, feed flow rate of 0.83 $\times 10^{-5}$ m^3 s^{-1}. Each mean was obtained from 8 samples.

Aroma compounds	Feed concentration (ug/g)	Partial flux (kg m^{-2} s^{-1}) $\times 10^{-8}$		Enrichment factor	
		100Pa	1000Pa	100Pa	1000Pa
Ester					
Ethyl acetate	52	1.5 ± 0.4	1.9 ± 0.0	8.8 ± 0.8	10 ± 1
Ethyl butanoate	3.3	0.3 ± 0.1	0.3 ± 0.0	47 ± 3	57 ± 2
Methyl benzoate	64.2	7.2 ± 0.5	7.0 ± 0.1	52 ± 4	54 ± 10
Ethyl benzoate	5	0.3 ± 0.0	0.3 ± 0.0	31 ± 3	28 ± 6
Aldehyde					
E-2-hexenal	3.6	0.6 ± 0.0	0.5 ± 0.0*	79 ± 1	73 ± 9
Alcohol					
Ethanol	872	73 ± 4	63.5 ± 0.5*	11 ± 1	14.8 ± 0.5
Hexanol	20	5.3 ± 0.1	4.3 ± 0.1*	98 ± 1	83 ± 2*
Z-3-hexenol	58.5	12.2 ± 0.2	9.0 ± 0.1*	61.1 ± 0.5	49 ± 2*
Linalool	5.4	0.7 ± 0.0	0.7 ± 0.0	64 ± 1	64 ± 9

*: Value at 100 Pa significantly different to value at 1000 Pa (97.5% confidence).

4.3.2 Boysenberry:

The effect of permeate pressure was also studied using boysenberry aroma condensate. The total flux at a permeate pressure of 1000 Pa absolute pressure was significantly less ($P<0.025$) than at 100 Pa absolute pressure by 10%, as can be seen in Table 4.18.

Table 4.18 Yield, pervaporation experiment duration and total flux for boysenberry aroma solution after pervaporation with GFT1060 membranes at feed temperature of 30°C, feed flow rate of 0.83×10^{-5} m^3s^{-1}.

Absolute permeate pressure (Pa)	Yield (%)	Experiment duration (h)	Total flux ($\times 10^{-5}$ $kgm^{-2}s^{-1}$)
100	2.0%	34	5.1 ± 0.1
1000	2.0%	39	4.6 ± 0.0

The concentrations of aroma compounds in the feed, retentate and permeate for different permeate pressures of 100 Pa and 1000 Pa absolute pressure are presented in Table 4.19. The concentration of the majority of the aroma compounds in the permeate collected at 100 Pa were not significantly different ($P> 0.025$) to the concentration of aroma compounds collected in the permeate at 1000 Pa, except for ethanol, 3-methyl butanol, hexanol, E-2-hexenol and terpinerol. There was a significant increase in the concentration of the ethanol in the permeate, as the permeate pressure was increased from 100 Pa to 1000 Pa ($P<0.025$). There was a significant decrease in the concentrations of 3-methyl butanol, hexanol, E-2-hexenol and terpinerol, as the permeate pressure was increased from 100 Pa to 1000 Pa ($P<0.025$).

The partial fluxes of aroma compounds for permeate pressures of 100 Pa and 1000 Pa absolute pressure are present in Table 4.20. The enrichment factors of aroma compounds for permeate pressure of 100 Pa and 1000 Pa was also provided in Table 4.20.

Table 4.19 The effect of permeate pressure on the concentration of aroma compounds in the feed, retentate and permeate for boysenberry aroma pervaporation, with GFT1060 membranes at feed temperature of 30°C, feed flow rate of 0.83×10^{-5} m^3s^{-1}. Each mean was obtained from 8 samples.

Aroma compounds	Concentration (ug/g)									
	Feed		Permeate pressure of 100Pa				Permeate pressure of 1000Pa			
			Retentate		Permeate		Retentate		Permeate	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
Ester										
Ethyl acetate	1267	60	207	23	28620	4876	210	25	41775	2024
Ethyl butyrate	37	1	29.0	0.0	329	16	35	3	334	22
Aldehyde										
E-2-hexenal	1	0.0	0.0	0.0	78	2	0.0	0.0	84	4
Aliphatic alcohol										
Ethanol	20000	456	19000	230	89500	354	19000	56	95000*	707
Propanol	9	3	10.7	0.2	87	5	9.0	0.0	87	13
2-methyl propanol	92	4	69.2	0.2	1340	1	65.9	0.5	1376	26
3-methyl butanol	173	7	93.8	0.2	3790	17	95.6	0.5	3656*	42
2-heptanol	24	1	0.0	0.0	727	10	4.2	0.4	741	23
Hexanol	38	3	7.4	0.0	1126	12	11.3	0.0	1063*	14
E-2-hexenol	7.2	0.3	2.7	0.0	189	1	3.6	0.0	159*	1
Terpene alcohol										
Linalool	205	12	11.2	0.3	5134	83	28.7	0.1	5837	324
Terpinerol	34	2	10.7	0.1	480	2	18.6	0.1	421*	16
Nerol	13.4	0.1	10.0	0.0	188	8	6.0	0.0	187	10
Geraniol	26	1	7.8	0.5	277	18	14.4	0.2	248	12
Total aroma (mg/g)	21.9				131.5				143.7	

*: Significantly different to permeate concentration at 100 Pa (97.5% confidence).

Table 4.20 The effect of permeate pressure on the partial flux and enrichment factor of aroma compounds for boysenberry aroma pervaporation with of GFT1060 membranes at feed temperature of 30°C, feed flow rate of 0.83 $\times 10^{-5}$ m^3 s^{-1}.

Aroma compounds	Feed concentration (ug/g)	Partial flux (kg m^{-2} s) *10^{-8}		Enrichment factor	
		100Pa	1000Pa	100Pa	1000Pa
Ester					
Ethyl acetate	1267	148 ± 20	191 ± 11	39 ± 2	56 ± 2
Ethyl butyrate	37	1.6 ± 0.0	1.5 ± 0.1	10.± 1	9.3 ± 0.8
Aldehyde					
E-2-hexenal	1	0.4 ± 0.0	0.4 ±0.0	156 ± 9	167 ± 6
Aliphatic alcohol					
Ethanol	20000	461 ± 6	435 ± 8*	4.6 ± 0.0	4.9 ± 0.0
Propanol	9	0.4 ± 0.0	0.4 ± 0.0	8.8 ± 0.6	13.± 1
2-methyl propanol	92	6.9 ± 0.0	6.3 ± 0.0*	16.6 ± 0.0	17.4 ± 0.0
3-methyl butanol	173	19.3 ± 0.2	16.7 ± 0.0*	28.4 ± 0.2	27.3 ± 0.2
2-heptanol	24	3.7 ± 0.1	3.4 ± 0.1	60.5 ± 0.4	53 ± 2
Hexanol	38	5.8 ± 0.1	4.9 ± 0.1*	50.2 ± 0.7	43.5 ± 0.7*
E-2-hexenol	7	1.0 ± 0.0	0.7 ± 0.0*	38.3 ± 0.3	29.4 ± 0.2*
Terpene alcohol					
Linalool	205	26.5 ± 0.9	27 ± 2	47 ± 2	50 ± 3
Terpinerol	34	2.5 ± 0.0	1.9 ± 0.1*	21.7 ± 0.0	16.2 ± 0.6*
Nerol	14	1.0 ± 0.0	0.9 ± 0.1	16.1 ± 0.7	19 ± 1
Geraniol	26	1.4 ± 0.1	1.1± 0.1	16.5 ± 0.6	12.4 ± 0.5

*: Value at 100 Pa significantly different to value at 1000 Pa (97.5% confidence).

4.3.3 Discussion

Several authors had tried to predict and model the mass transfer performance as a function of permeate pressure (Böddeker & Bengtson, 1990; Böddeker et al., 1990; Baudot & Marin, 1996; Lamer et al., 1996; Baudot et al., 1999). Böddeker et al. (1990) investigated the effect of permeate pressure on the performance of pervaporation with PDMS membranes (thickness 50μm) for recovery of n-butanol which has a boiling point (bp) at 117.7°C and tert-butanol (bp 82.5°C). The pervaporation was carried out at a feed temperature of 50°C and feed concentration of 1wt. %. Böddeker et al. (1990) found that the permeation rate of the high boiling point n-butanol increased significantly as the permeate pressure was reduced from 10000 Pa to 10 Pa, while the permeation rate of the low boiling tert-butanol was only slightly affected. The n-butanol enrichment factor improved moderately with decreasing permeate pressure, whereas the tert-butanol enrichment factor dramatically declines with decreasing permeate pressure. Böddeker & Bengtson (1990) studied pervaporation of low volatility aromatics from water using PEBA 40 membranes at a feed temperature of 44.4°C. It was observed that water permeability depends little on permeate pressure, whereas for phenol (bp 182°C), its enrichment factor increased as the pressure was lowered from 1000 Pa to 100 Pa absolute pressure. Baudot & Marin (1996) found that the total flux and the aroma partial flux for pervaporation of dairy aroma compounds e.g. methyl thiobutanoate (bp 142°C), with PDMS1070 and PEBA 40 membranes, decreased as permeate pressure was increased from 250 Pa to 2500 Pa absolute pressure. Lamer et al. (1996) found that the flux of benzaldehyde (bp 179°C) during pervaporation with PDMS membranes decreased as the permeate pressure was increased from 35 Pa to 700 Pa absolute pressure. Baudot et al. (1999) investigated the effect of permeate pressure on the selectivity of four different aroma compounds during pervaporation. These different compounds included diacetyl (bp 99°C), ethyl acetate (bp 77°C), S-methyl thiobutanoate (bp 142°C) and r- decalactone (bp 281°C). It was observed that the pervaporation of low boiling compounds, such as diacetyl and ethyl acetate, was independent of permeate pressure, whereas the high boiling methyl thiobutanoate was

highly dependent on the permeate pressure. High boiling r-decalactone flux was found to be not affected by permeate pressure.

The conclusion from literature was that the influence of permeate pressure was dependent on the physical-chemical properties of aroma compounds such as boiling point, hydrophilic/hydrophobic properties and saturated vapour pressure (Baudot et al., 1999). The mass transfer performance of high boiling point aroma compounds was more sensitive to permeate pressure than that of low boiling point aroma compounds. For aroma compounds with large molecules and low volatility, desorption resistance is the permeation rate limiting step (Baudot & Marin, 1997).

During the pervaporation of feijoa and boysenberry aroma condensates the effect of permeate pressure on selectivity of alcohols can be related to the boiling points of the individual alcohols. The selectivities of higher boiling alcohols, such as hexanol (bp 157°C), Z-3-hexenol (bp 156°C) and terpinerol (bp 229°C), increased significantly, as the permeate pressure was decreased. Whereas, the selecitvities of low boiling compounds, such as 2-methyl propanol (bp 107°C), propanol (bp 97°C) and ethanol (bp 78°C), were not affected by permeate pressure. This agreed with the published literature which also found higher boiling point aroma compounds were more sensitive to permeate pressure.

However, for high boiling terpene alcohols such as linalool (bp 195°C) and geraniol (bp 229°C), their fluxes were not affected by permeate pressure.

The partial fluxes of esters, including the high boiling methyl benzoate (bp 199°C) and ethyl benzoate (bp 211°C), did not decrease as permeate pressure was increased from the 100 Pa to 1000 Pa. The permeation of esters was dominated by the resistance in the boundary layer on the feed side of membrane, but not by the resistance in the membrane, whereas, the permeation of alcohols was dominated by the resistance in the membrane (Olsson & Trägårdh,1999). Wijmans et al. (1996) also found that the fluxes of benzene, toluene, ethyl benzene and xylenes were not reduced by increasing the permeate pressure

from 1300 Pa to 9100 Pa, though the water flux reduced as the permeate pressure was increased. The explanation was that boundary layer effects dominated the pervaporation of volatile organic compounds with high enrichment factor.

For feijoa, the pervaporation of three important aroma compounds, methyl benzoate, ethyl benzoate and ethyl butanoate, was not effected by permeate pressure in the studied permeate pressure range. For boysenberry, the pervaporation of three important aroma compounds, linalool, nerol and geraniol, was also not improved by decreasing the permeate pressure from 1000 Pa to 100 Pa.

4.4 Influence of feed flow rate

Feed flow rate is an important operating parameter for the pervaporation, especially when the feed solution is very dilute (Beaumelle et al., 1992).

The effect of feed flow rate was evaluated by feijoa aroma condensate with GFT1060 membranes at a feed temperature of 30°C, permeate pressure of 100 Pa absolute pressure and feed flow rates of 1.1×10^{-5} m^3s^{-1} and 1.4×10^{-5} $m^3 s^{-1}$. The results are presented in Table 4.21.

Table 4.21 Yield, experiment duration and total flux for feijoa aroma after pervaporation with GFT1060 membranes, at a feed temperature of 30°C, permeate pressure of 100 Pa absolute pressure.

Feed flow rate (m^3s^{-1})	Yield (%)	Experiment duration (h)	Total flux ($\times 10^{-5}$ $kgm^{-2}s^{-1}$)
1.1×10^{-5}	1.0%	20.5	4.4 ± 0.0
1.4×10^{-5}	1.0%	20.5	4.4 ± 0.0

There was no difference in the total fluxes between the two feed flow rates of 1.1×10^{-5} m^3s^{-1} and 1.4×10^{-5} m^3s^{-1} ($P > 0.025$). This agreed with the results of Karlsson & Trägårdh (1993a). The total flux was relatively constant with increasing feed flow rate, when they studied the resistance in the boundary layer during pervaporation, using a multicomponent aroma model solution, consisting of 2-methyl-propanal, 2-methyl-butanal, 1-pentene-3-ol, trans-2-hexenal and linalool.

The concentrations of aroma compounds in the feed, the retentate and the permeate for the different feed flow rates are presented in Table 4.22. The concentrations of methyl benzoate, ethyl benzoate, hexanol, Z-3-hexenol and linalool in the permeate increased significantly ($P<0.025$) as the feed flow rate increased from 1.1×10^{-5} m^3s^{-1} to 1.4×10^{-5} m^3s^{-1}.The ethanol concentration in the permeate decreased significantly ($P<0.025$) with

increasing feed flow rate from 1.1×10^{-5} m^3s^{-1} to 1.4×10^{-5} m^3s^{-1}. The concentration of ethyl acetate, ethyl butanoate and E-2-hexenal in the permeates collected between the two feed flow rates of 1.1×10^{-5} m^3s^{-1} and 1.4×10^{-5} m^3s^{-1} were not significantly different ($P>0.025$).

The partial fluxes of aroma compounds are presented in Table 4.23. The enrichment factors of aroma compounds for feed flow rates of 1.1×10^{-5} m^3s^{-1} and 1.4×10^{-5} m^3s^{-1} are also presented in Table 4.23.

4.4.1 Discussion

The resistance to mass transfer in the boundary layer of the feed side due to concentration polarization must be considered (Borjesson et al., 1996). The concentration polarization is strongly dependent on the feed flow rate and on the hydraulic diameter. Increasing feed flow rate decreases the resistance in boundary layer in the feed side (Dotremont et al., 1994).

Karlsson & Trägårdh (1993a) found the effect of feed flow rate was different for different aroma compounds such as 2-methyl-propanal, 2-methyl-butanal, 1-pentene-3-ol, trans-2-hexenal and linalool. Dotremont et al. (1994) found that as the feed flow rate was decreased, the chlorinated hydrocarbons (Cl-HC) with a high permeability showed a considerable flux decline, while for organic compounds with low permeability, like propanol, the decrease in flux was negligible. Wijmans et al. (1996) found that the flux of BTEX (a mixture of benzene, toluene, ethylbenzene and xylenes) was influenced by the boundary layer effect. Schnabel et al (1998) found that the concentration polarization effect was weak for the butanol pervaporation but was strong for chloroform pervaporation, because butanol had a lower activity coefficient in water and a lower affinity for silicone than chloroform. Olsson & Trägårdh (1999) found that increasing the feed flow velocity did not significantly increase the recovery of the limiting alcohols, whereas it increased the ester recovery. In summary, the combination of low concentration of organic compounds in the aqueous feed solution and the high selectivity values of the membrane can result in

Table 4.22 The effect of feed flow rate on the individual concentration of aroma compounds in the feed, retentate and permeate for feijoa aroma pervaporation with GFT1060 membranes at feed temperature of 30°C, permeate pressure of 100Pa. Each mean was obtained from 8 samples.

Aroma compounds	Concentration (ug/g)									
			Feed flow rate of 1.1×10^{-5} m^3s^{-1}				Feed flow rate of 1.4×10^{-5} m^3s^{-1}			
	Feed[a]		Retentate		Permeate		Retentate		Permeate	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
Ester										
Ethyl acetate	58.0	0.5	41	3	465	90	38	10	415	10
Ethyl butanoate	4.5	0.0	0.0	0.0	107	19	0.0	0.0	112	1
Methyl benzoate	87.1	0.2	2.5	0.4	2797	130	1.4	0.0	3613*	47
Ethyl benzoate	8.0	0.0	0.0	0.0	202	3	0.0	0.0	292*	4
Aldehyde										
E-2-hexenal	5.5	0.0	0.0	0.0	133.8	0.1	0.0	0.0	143	5
Alcohol										
Ethanol	1246	21	977	797	27359	575	1087	12	10044	39
Hexanol	25.8	0.2	6.0	0.2	1260	36	5.8	0.3	1437*	4
Z-3-hexenol	75.2	0.2	35.2	0.2	2777	45	36	2	3107*	4
Linalool	6.7	0.1	0.0	0.0	238	6	0.0	0.0	295*	1
Total aroma (mg/g)	1.5				35.2				23.1	

a: Feijoa aroma condensate Batch 2.

*: Value is significantly different to value in permeate collected at a feed flow rate of 1.1×10^{-5} m^3s^{-1} (97.5% confidence).

Table 4.23 The effect of feed flow rate on the partial fluxes and enrichment factors of aroma compounds for feijoa aroma after pervaporation with of GFT1060 membranes, at a feed temperature of 30°C, permeate pressure of 100 Pa.

Aroma compounds	Feed concentration (ug/g)[a]	Partial flux ($\times 10^{-8}$ kg m^{-2} s)		Enrichment factor	
		1.1×10^{-5} m^3 s^{-1}	1.4×10^{-5} m^{-3} s^{-1}	1.1×10^{-5} m^3 s^{-1}	1.4×10^{-5} m^3 s^{-1}
Ester					
Ethyl acetate	58.0	2.0 ± 0.5	1.8 ± 0.0	9.5 ± 0.5	9 ± 1
Ethyl butanoate	4.5	0.4 ± 0.0	0.5 ± 0.0	47 ± 2	49.± 2
Methyl benzoate	87.1	12.1 ± 0.9	15.4 ± 0.3*	62 ± 3	81 ± 10*
Ethyl benzoate	8.0	0.9 ± 0.0	1.2 ± 0.0*	50 ± 3	73 ± 6*
Aldehyde					
E-2-hexenal	5.5	0.6 ± 0.0	0.6 ± 0.0	48± 1	52 ± 1
Alcohol					
Ethanol	1246	118 ± 4	42.9 ± 0.2*	15 ± 1	8.6 ± 0.5
Hexanol	25.8	5.4 ± 0.2	6.1 ± 0.0*	79 ± 1	91.0 ± 0.8
Z-3-hexenol	75.2	11.9 ± 0.2	13.2 ± 0.0*	50 ± 1	56 ± 2
Linalool	6.7	1.0 ± 0.0	1.2 ± 0.0*	70.9 ± 0.5	87 ± 6*

a: Feijoa aroma condensate Batch 2.

*: Value at the feed flow rate of 1.4×10^{-5}m^3 s^{-1} is significantly different to value at the feed flow rate of 1.1×10^{-5}m^3 s^{-1} (97.5% confidence).

mass transfer limitations due to concentration polarization phenomena occurring at the liquid boundary layer.

Feijoa aroma condensate as the feed solution was a very dilute solution (total aroma concentration of 1.52 mg/g). The water was the quantitative major component in the feed (99.8%). Compared with water, the aroma compounds generally exhibited very high permeability in the polymer materials used for the separation process (Schnabel et al, 1998). Water was the non-preferentially permeating component due to its low permeability. The partial fluxes of aroma compounds may be controlled by the boundary layer on the feed side, whereas water flux is independent of the boundary layer on the feed side (Schnabel et al., 1998). Therefore, the overall total fluxes did not decrease as the feed flow rate was decreased. This agreed with the work of Schnabel et al (1998) who found pure water pervaporation fluxes were the same for the different feed flow rates.

During pervaporation of feijoa aroma, as the feed flow rate was decreased, the partial fluxes of methyl benzoate, ethyl benzoate, hexanol, Z-3-hexenol and linalool decreased significantly, and the enrichment factors of methyl benzoate, ethyl benzoate and linalool decreased significantly. The explanation for this is that methyl benzoate, ethyl benzoate and linalool are preferentially permeating components, and their pervaporation was dominated by resistant in the boundary layer in the feed side of membrane.

The decrease in partial flux of ethanol as feed flow rate was increased has not been reported elsewhere. This may be due to the coupling transfer between the compounds.

Consequently, for feijoa aroma, the pervaporation performance for recovery and enrichment aroma compounds can be improved by increasing the feed flow rate by 27%.

4.5 Comparison between the vacuum distillation and pervaporation

Vacuum distillation, which is based on the principle of the liquid-vapour equilibrium, is the most popular technique for aroma recovery or concentration. The recovery or enrichment of aroma compounds from aqueous solutions depends on the relative volatility of aroma compounds related to water. The selectivity depends on the volatility difference (Chardon et al., 1990).

The selectivity of pervaporation, given constant operating conditions, is affected by the intrinsic selectivity of membrane and the selectivity difference of the liquid-vapour equilibrium (Wijmans et al.,1993)

4.5.1 Feijoa

Vacuum distillation was used to recover aroma from feijoa aroma condensate. The vacuum distillation was carried out at a feed temperature of 30°C and a yield of 5% was obtained. The gas chromatogram of aroma concentrate is presented in the Appendix (Figure A7). The concentration of aroma compounds in the feed, retentate and aroma concentrate are presented in Table 4.24. Comparison of the relative concentrations of aroma compounds between the permeate obtained from pervaporation and aroma concentrate obtained from vacuum distillation is shown in Table 4.25. The relative concentration of ethanol was much higher in the aroma concentrate obtained by vacuum distillation than by pervaporation. The relative concentration of methyl benzoate, ethyl benzoate in the aroma concentrate was much higher after pervaporation than after vacuum distillation.

From concentration factors for vacuum distillation presented in the Table 4.26, it was noted that the concentration factor of aroma compounds was affected by the physical or chemical

Table 4.24 The individual concentration of aroma compounds in the feed, retentate and aroma concentrate for feijoa aroma vacuum distillation at 30°C and yield of 5%.

Aroma compounds	Concentration (ug/g)					
	Feed[a]		Retentate		Aroma concentrate	
	Mean	SE	Mean	SE	Mean	SE
Ester						
Ethyl acetate	52.0	0.5	32.7	0.2	146	3
Ethyl butanoate	3.3	0.0	2.5	0.0	0.0	0.0
Methyl benzoate	64.2	0.2	38.9	0.6	58.8	0.1
Ethyl benzoate	5.0	0.0	3.1	0.0	3.5	0.0
Aldehyde						
E-2-hexenal	3.6	0.0	2.9	0.0	0.0	0.0
Alcohol						
Ethanol	872	21	541.5	0.4	3254	33
Hexanol	20.0	0.2	14.1	0.1	37.2	0.5
Z-3-hexenol	58.5	0.2	44.1	0.6	106.9	0.6
Linalool	5.4	0.1	3.6	0.0	7.6	0.0
Total aroma (mg/g)	1.1				3.6	

a: Feijoa aroma condensate Batch 1

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Table 4.25 The relative concentrations of aroma compounds in the feijoa aroma concentrate obtained by pervaporation (PV) and by vacuum distillation (VD).

Aroma Compound	Relative concentration of aroma compounds (%)			
	Fresh fruit[a]	Feed	Aroma concentrate (PV)	Aroma concentrate (VD)
Ester				
Ethyl acetate	NF	3.8	2.2	4.0
Ethyl butanoate	0.3	0.	0.5	0.0
Methyl benzoate	81.9	5.7	14.5	1.8
Ethyl benzoate	0.5	0.5	1.1	0.1
Aldehyde				
E-2-hexenal	1.7	0.4	0.6	0.0
Alcohol				
Ethanol	NF	81.9	62.6	90.0
Hexanol	0.2	1.7	5.8	1.0
Z-3-hexenol	NF	4.9	11.0	3.0
Linalool	NF	0.4	0.8	0.2

a: Data sourced from Shaw et al. (1990)

NF: Published information not found

Table 4.26 The concentration factors of aroma compounds for the feijoa aroma pervaporation and vacuum distillation with a 5% yield.

Aroma compounds	Concentration factor[a]		Concentration factor of PV/VD[c]
	Pervaporation[b] (PV)	Vacuum distillation (VD)	
Ester			
Ethyl acetate	1.4	2.8	0.5
Ethyl butanoate	4.8	0.0	
Methyl benzoate	5.2	0.9	5.7
Ethyl benzoate	3.1	0.7	4.4
Aldehyde			
E-2-hexenal	7.9	0.0	∞
Alcohol			
Ethanol	3.9	3.7	1.1
Hexanol	12.4	1.9	6.7
Z-3-hexenol	9.7	1.8	5.3
Linalool	6.5	1.4	4.6

a: Concentration factor was defined as the ratio of aroma compound concentration in the aroma concentrate to its concentration in the original aroma condensate.

b: Pervaporation achieved 1% yield, in order to compare methods, concentrations were divided by 5 in order to compare concentration at 5% yield by vacuum distillation. This permeate was obtained from the feijoa aroma pervaporation with GFT1060 membranes at feed temperature of 30°C, feed flow rate of 0.83×10^{-5} m^3 s^{-1} and permeate pressure of 100Pa.

c: Ratio of pervaporation concentration factor (PV) to vacuum distillation concentration factor (VD).

properties of aroma compounds. The low boiling point compounds, such as ethanol and ethyl acetate, had higher concentration factors, whereas, the high boiling point aroma compounds such as linalool, methyl benzoate, ethyl benzoate had lower concentration factors. This result was opposite to the concentration factors for pervaporation. The concentration factor of ethanol for pervaporation was much lower than that of higher boiling point aroma compounds such as the hexanol, Z-3-hexenol, and linalool. The concentration factors of esters after pervaporation, for the high boiling point and high hydrophobic ester aroma compounds such as methyl benzoate, ethyl benzoate were much higher than the lower boiling point compounds such as ethyl acetate and ethyl butanoate. From the ratio of the pervaporation concentration factor to the vacuum distillation concentration factor, pervaporation was much more selective than vacuum distillation for the extraction of all aroma compounds except ethyl acetate and ethanol. This agreed with the review of Baudot and Marin (1997). Pervaporation was more selective than vapour-liquid equilibrium for compounds such as the methyl benzoate, ethyl benzoate and linalool which are highly hydrophobic, have small relative volatility and are high molecular weight (Baudot and Marin, 1997).

4.5.2 Boysenberry

Vacuum distillation was used to recover aroma from boysenberry aroma condensate at a temperature of 30°C. The gas chromatogram of aroma concentrate is presented in Appendix (Figure A8). The concentration of aroma compounds in the feed, retentate and aroma concentrate for a yield of 5% and 10% are present in Table 4.27. The concentration of aroma compounds in the aroma concentrate obtained with a yield of 5% were significantly higher than from a yield of 10% ($P<0.025$). The relative concentrations of aroma compounds in the aroma concentrate obtained by pervaporation and vacuum distillation are present in Table 4.28. The relative concentration of ethanol in the aroma concentrate obtained by vacuum distillation was much higher than by pervaporation, whereas the relative concentration of linalool in the aroma concentrate obtained by vacuum distillation was much lower than by pervaporation.

Table 4.27 The individual concentration of aroma compounds in the feed, retentate and aroma concentrate for boysenberry aroma vacuum distillation with yields of 5% and 10% at feed temperature of 30°C. Each mean was obtained from 8 samples.

Aroma compounds	Concentration (ug/g)									
			Yield of 5%				Yield of 10%			
	Feed		Retentate		Product		Retentate		Product	
	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
Ester										
Ethyl acetate	1267	60	1061	12	1978	37	963	62	1459*	48
Ethyl butyrate	36.9	0.9	39	4	59.7	0.4	34	1	45*	6
Aldehyde										
E-2-hexenal	1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Aliphatic alcohol										
Ethanol	20000	456	19000	355	34762	1246	19000	234	25000*	706
Propanol	9	2	5.7	0.0	22.2	0.1	8	1	15*	3
2-methyl propanol	92	4	82	2	184.8	0.1	82.9	1.0	129*	2
3-methyl butanol	173	7	152	4	356	5	155	2	247*	2
2-heptanol	24	1	20.0	0.1	51	1	20.6	0.1	32.1*	0.4
Hexanol	38	3	32.5	0.7	79	2	33.0	0.2	52*	2
E-2-hexenol	7.2	0.3	6.5	0.2	13.6	0.2	6.6	0.1	9.7*	0.3
Terpene alcohol										
Linalool	205	12	164.2	0.1	374	3	162	2	181*	7
Terpinerol	34	2	28.3	0.9	41.5	0.4	28.6	0.1	27.3*	0.6
Nerol	13.4	0.1	10.8	0.3	17.7	0.1	10.7	0.0	9.7*	0.1
Geraniol	26	1	21.7	0.6	27.6	0.0	22.0	0.1	18.5*	0.1
Total aroma (mg/g)	21.9				37.6				26.9*	

*: Value is significantly different to the value in permeate collected with yield of 5% (97.5% confidence).

Table 4.28 The relative concentrations of aroma compounds in boysenberry aroma concentrate obtained by pervaporation (PV) and by vacuum distillation (VD) with 5% yield.

Aroma Compound	Relative concentration of aroma compounds (%)			
	Fresh fruit[a]	Feed	Aroma concentrate (PV)	Aroma concentrate (VD)
Ester				
Ethyl acetate	0.4	12.2	25.9	5.2
Ethyl butyrate	0.9	0.4	0.2	0.1
Aldehyde				
E-2-hexenal	0.1	0.0	0.1	0.0
Aliphatic alcohol				
Ethanol	54.1	81.4	64.5	92.5
Propanol	0.7	0.1	0.1	0.1
2-methyl propanol	0.0	0.9	0.7	0.5
3-methyl butanol	0.7	1.7	2.2	1.0
2-heptanol	2.4	0.2	0.6	0.1
Hexanol	1.5	0.4	0.8	0.1
E-2-hexenol	2.2	0.1	0.1	0.0
Terpene alcohol				
Linalool	23.7	2.0	4.4	1.0
Terpinerol	5.1	0.3	0.3	0.1
Nerol	0.9	0.1	0.1	0.0
Geraniol	2.4	0.3	0.2	0.1

a: Data sourced from Allen et al. (1996)

From concentration factors of individual aroma compounds for vacuum distillation presented in Table 4.29, it was obvious that concentration factors of aliphatic alcohols were higher than the concentration factors of terpene alcohols by vacuum distillation. Vacuum distillation was preferred to enrich aliphatic alcohols. This result was different from that obtained with pervaporation. In pervaporation, the terpene alcohols yielded higher enrichment factors than aliphatic alcohols. From the ratio of pervaporation concentration factor to vacuum distillation concentration factor presented in Table 4.29, pervaporation is much more selective than vacuum distillation for the extraction of aroma compounds of boysenberry except ethyl acetate, ethanol and propanol. This agreed with the results of Ferreira (1998). Ferreira (1998) found that the enrichment factor of pervaporation was less than that of evaporation for extraction of ethyl acetate, ethanol and propanol.

4.5.3 Discussion

For the important aroma compounds of feijoa and boysenberry; methyl benzoate, ethyl benzoate, linalool, nerol and geraniol, the pervaporation concentration factor was much greater than the vacuum distillation concentration factor. The aroma profile of the final aroma concentrates obtained by pervaporation were closer to the aroma profile of the fresh fruit than the aroma concentrate obtained by vacuum distillation. Consequently, pervaporation with hydrophobic membranes provided a significant improvement to the recovery and concentration of feijoa and boysenberry aroma condensate.

Table 4.29 The concentration factors of aroma compounds for boysenberry aroma pervaporation and vacuum distillation with a 5% yield.

Aroma compounds	Concentration factor[a]		Concentration factor of PV/VD[c]
	Pervaporation[b] (PV)	Vacuum distillation (VD)	
Ester			
Ethyl acetate	1.3	1.5	0.9
Ethyl butyrate	1.8	1.6	1.1
Aldehyde			
E-2-hexenal	15.6	0.0	∞
Aliphatic alcohol			
Ethanol	0.9	1.7	0.5
Propanol	1.9	2.4	0.8
2-methyl propanol	2.9	2.0	1.5
3-methyl butanol	4.4	2.1	2.1
2-heptanol	6.1	2.2	2.8
Hexanol	6.0	2.2	2.8
E-2-hexenol	5.2	1.9	2.7
Terpene alcohol			
Linalool	5.0	1.8	2.8
Terpinerol	2.9	1.2	2.4
Nerol	2.8	1.3	2.2
Geraniol	2.2	1.1	2.0

a: Concentration factor was defined as the ratio of aroma compound concentration in the aroma concentrate to its concentration in the original condensate.

b: Pervaporation achieved 1% yield, in order to compare methods, concentrations were divided by 5 in order to compare concentration at 5% yield by vacuum distillation. This permeate was obtained from the feijoa aroma pervaporation with GFT1060 membranes at feed temperature of 30°C, feed flow rate of 0.83×10^{-5} m^3 s^{-1} and permeate pressure of 100Pa.

c: Ratio of pervaporation concentration factor to vacuum distillation concentration factor.

4.4 Mass balances during pervaporation

The percentages of feijoa and boysenberry aroma compounds recovered in the permeate and retentate after the different pervaporation experiments are shown in Table 4.30 and Table 4.31, respectively.

From the Table 4.30 and Table 4.31, it can be seen that there were losses of aroma compounds, especially aromatic esters, such as methyl benzoate and ethyl benzoate. The losses could have occurred during the pervaporation process or during the GC analysis process. During the pervaporation, aroma compounds may be lost through the vacuum pump, evaporated from the feed tank, and adsorbed on the membrane material. During analysis aroma compounds may have been lost during the solvent extraction process. The greatest losses were observed with methyl benzoate and ethyl benzoate compounds.

Table 4.30 Percent recovery of feijoa aroma compounds in permeate and retentate after different pervaporation experiments under the same operating conditions: feed temperature of 30°C, feed flow rate of 1.4×10^{-5} m^3 s^{-1} and permeate pressure of 100Pa.

Aroma compounds	Recovery of aroma compounds (%)											
	GFT 1060 Yield 1.0 %			GFT1060 Yield 0.4%			GFT1070 Yield 0.4%			PEBA Yield 0.4%		
	P	R	T	P	R	T	P	R	T	P	R	T
Ester												
Ethyl acetate	8	64	72	2	90	92	5	81	86	2	89	91
Ethyl butanoate	28	0	28	8	0	8	15	0	15	18	0	18
Methyl benzoate	28	4	32	11	19	30	19	8	27	29	3	32
Ethyl benzoate	21	0	21	9	15	24	16	0	16	27	0	27
Aldehyde												
E-2-hexenal	21	56	77	7	69	76	13	71	84	7	69	76
Alcohol												
Ethanol	16	81	87	3	78	81	3	67	70	2	87	89
Hexanol	41	24	65	15	48	63	24	44	68	25	43	78
Z-3-hexenol	35	47	82	14	63	77	17	69	86	16	65	81
Linalool	30	0	30	8	28	36	16	18	34	26	4	30

P: permeate; R: retentate; T: total.

Table 4.31 Percent recovery of boysenberry aroma compounds in permeate and retentate after different pervaporation experiments under the same operating conditions: feed temperature of 30°C, feed flow rate of 1.4×10^{-5} m^3 s^{-1} and permeate pressure of 100Pa.

Aroma compounds	Recovery of aroma compounds (%)											
	GFT1060 yield 2%			GFT1060 yield 0.5%			GFT1070 yield 0.5%			PEBA yield 0.5%		
	P	R	T	P	R	T	P	R	T	P	R	T
Ester												
Ethyl acetate	74	19	93	19	45	64	22	41	63	8	68	76
Ethyl butyrate	17	82	99	4	83	87	6	90	96	3	95	98
Aldehyde												
E-2-hexenal	86	0	86	87	0	87	75	0	75	75	0	75
Aliphatic alcohol												
Ethanol	6	50	56	3	95	98	4	95	99	1	95	96
Propanol	25	65	90	6	59	65	9	80	89	5	82	87
2-methyl propanol	31	69	100	7	75	84	9	86	95	4	75	79
3-methyl butanol	44	56	100	11	68	79	29	71	100	9	68	77
2-heptanol	68	15	83	23	41	64	43	36	79	33	32	65
Hexanol	61	30	91	19	50	69	34	51	85	28	32	60
E-2-hexenol	46	50	96	14	61	75	23	67	90	22	55	77
Terpene alcohol												
Linalool	64	14	78	20	32	52	42	23	65	44	9	53
Terpinerol	28	56	84	7	55	62	14	57	71	26	36	62
Nerol	32	44	76	8	47	55	17	45	62	33	58	92
Geraniol	22	57	79	5	51	56	13	51	64	29	31	60

P: permeate; R: retentate; T: total.

Chapter Five

Conclusions and Recommendations

5.1 Conclusions

1.The aroma composition in the feijoa aroma condensate was altered to that found in fresh feijoa fruit. In the aroma condensate, the proportion of alcohols had increased, while the proportion of esters had decreased. Methyl benzoate, ethyl benzoate, ethyl butanoate and linalool are the main compounds contributing to feijoa aroma flavour.

2. The aroma composition in boysenberry aroma condensate was different to the aroma composition in fresh boysenberry fruit. The proportion of aliphatic alcohols had increased, while the proportion of terpene alcohols had decreased. Ethyl butanoate, linalool, terpinerol, nerol, geraniol are the main compounds contributing to boysenberry aroma.

3. Pervaporation with the three commercial membranes investigated (PDMS GFT1060, PDMS GFT1070, PEBA GKSS) highly enriched both feijoa and boysenberry aroma by 13-15 fold and 6-12 fold based on the original aroma condensate, respectively. The relative composition of the aroma compounds in the permeate was altered and thus improved the proportion of desirable aroma compounds. PEBA membranes proved to have the best performance for feijoa and boysenberry aroma recovery due to the higher enrichment factors and mass transfer coefficients for the important aroma compounds.

4. The permeate pressure was found to have a significant effect on the total flux for both feijoa and boysenberry aroma pervaporation. Increasing permeate pressure was found to significantly decrease the flux of high boiling alcohols such as hexanol, Z-3-hexenol and terpinerol, whereas there was no effect on the flux of low boiling alcohol such as ethanol,

propanol, 2-methyl propanol. The permeate pressure was also found to have no effect on the flux of ester compounds.

5. Increasing the feed flow rate had no influence on total flux of feijoa aroma pervaporation, but increased significantly the partial flux of aroma compounds which were preferentially permeating compounds such as methyl benzoate, ethyl benzoate and linalool.

6. The resistance to mass transfer of methyl benzoate, ethyl benzoate and linalool was dominated by the boundary layer effects. The mass transfer resistances of high boiling aliphatic alcohols such as the hexanol, Z-3-hexenol and E-2-hexenol was influenced by the permeate pressure.

7. For important aroma compounds of both feijoa and boysenberry, pervaporation provided 2 - 6 times the concentration factor achieved in vacuum distillation. Pervaporation produced aroma concentrates that had closer aroma profiles to the natural fresh fruit aromas than vacuum distillation.

5.2 Recommendations

1. In order to identify the unknown aroma components in the aroma condensates by GC and GC-MS, it is suggested to obtain a higher extraction of aroma compounds, before analysis.

2. Evaluate other pervaporation membranes suitable for feijoa and boysenberry aroma recovery, e.g. polyoctylmethyl siloxane membrane (POMS), which may have better performance than the three membranes investigated.

3. Investigate the effect of permeate pressure and feed flow rate on the performance of pervaporation with PEBA membranes. Extend the investigated permeate pressure range and feed flow rate range.

4. Investigate the effect of operating temperature on the performance of pervaporation for feijoa and boysenberry aroma recovery and concentration.

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Appendix

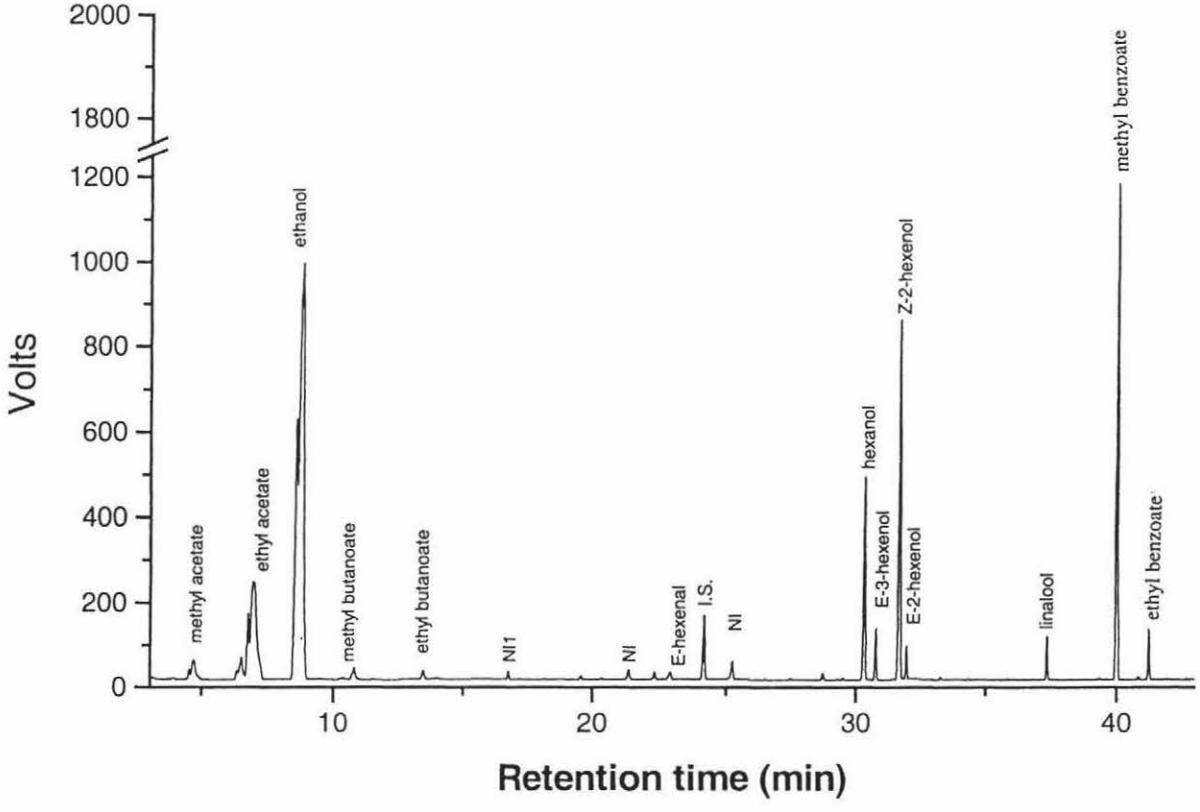

Figure A1 Gas chromatogram of the feijoa aroma permeate after pervaporation with GFT1060 membranes at a feed temperature of 30°C, permeate pressure of 100 Pa, feed flow rate of 1.4×10^{-5} m^3 s^{-1}. I.S.= Internal Standard. NI= Not identified

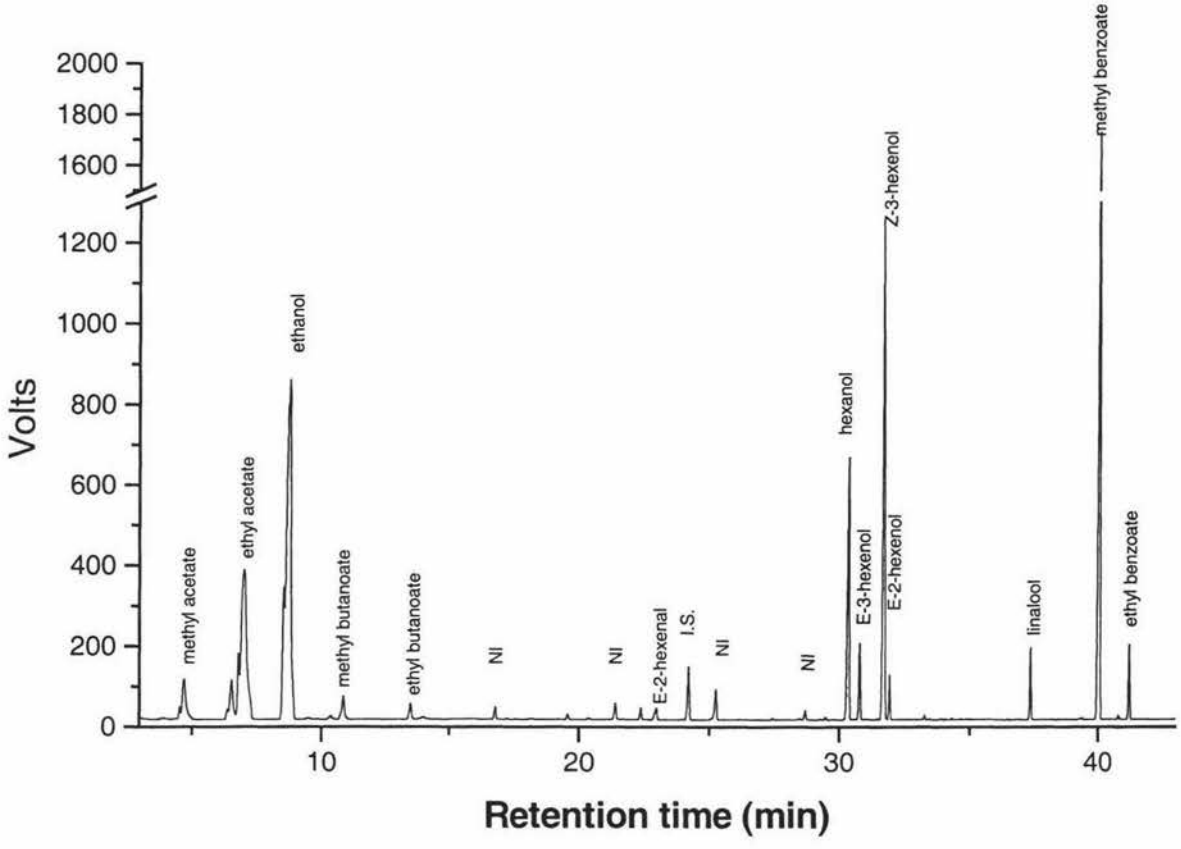

Figure A2 Gas chromatogram of the feijoa aroma permeate after pervaporation with GFT1070 membranes at a feed temperature of 30°C, permeate pressure of 100 Pa, feed flow rate of 1.4×10^{-5} m^3 s^{-1}. I.S.= Internal Standard, NI= Not identified

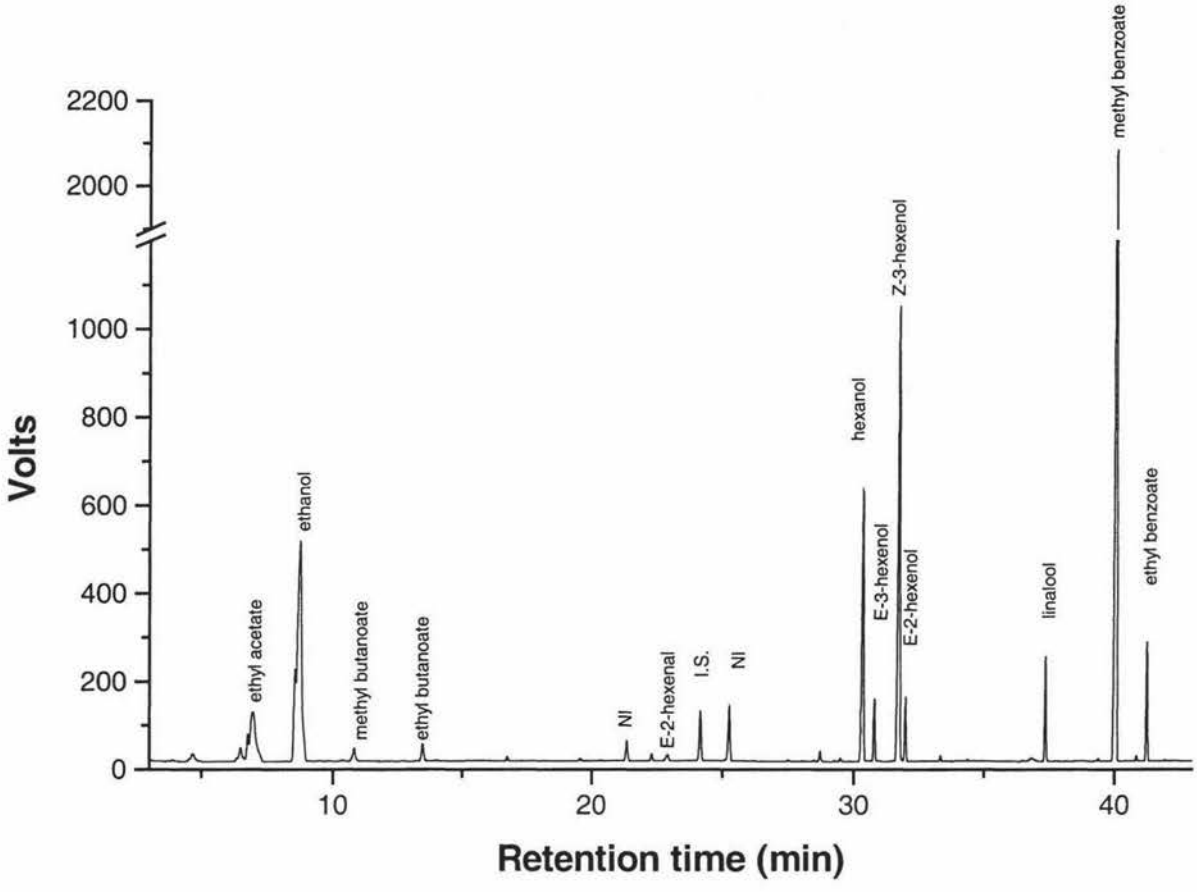

Figure A3 Gas chromatogram of the feijoa aroma permeate after pervaporation with PEBA membranes at a feed temperature of 30°C, permeate pressure of 100 Pa, feed flow rate of 1.4×10^{-5} m^3 s^{-1}. I.S.= Internal Standard, NI = Not identified

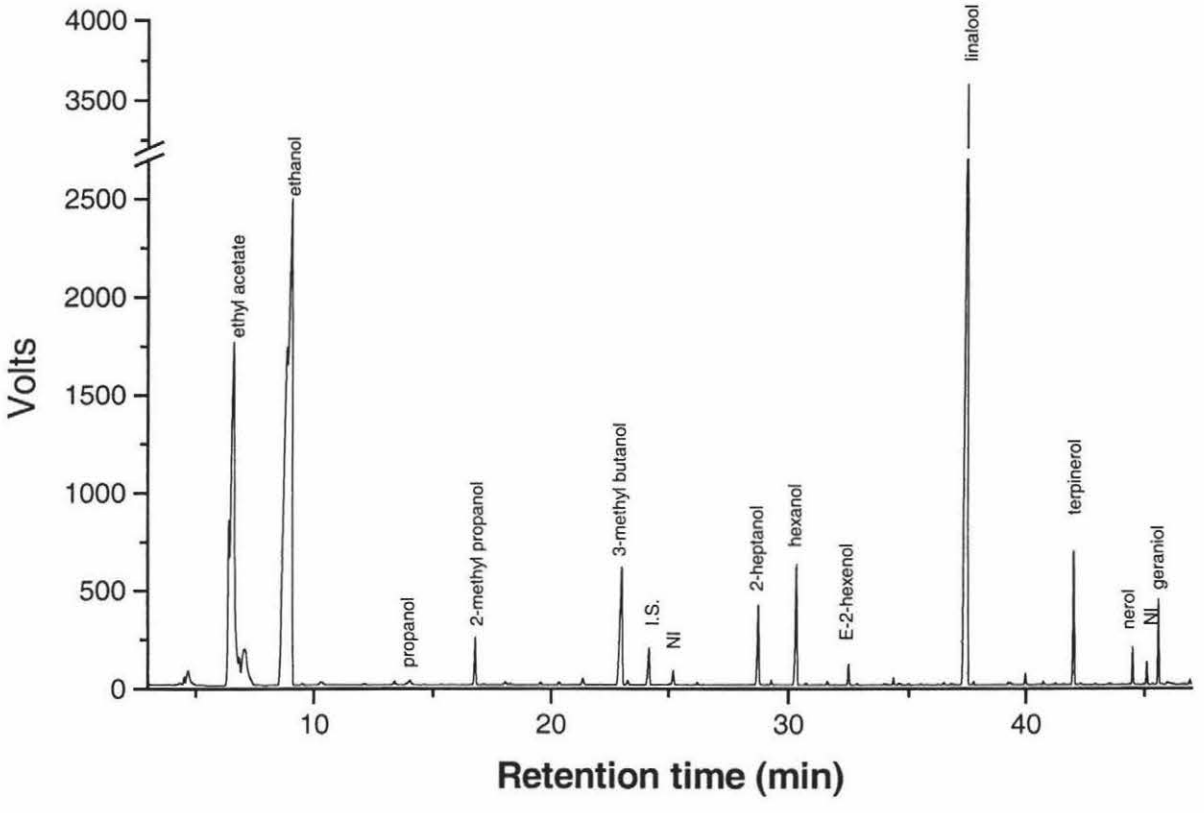

Figure A4 Gas chromatogram of the boysenberry aroma permeate after pervaporation with GFT1060 membrane, at feed temperature of 30°C permeate pressure of 100 Pa, feed flow rate of 1.4×10^{-5} m^3 s^{-1}. I.S.= Internal Standard.

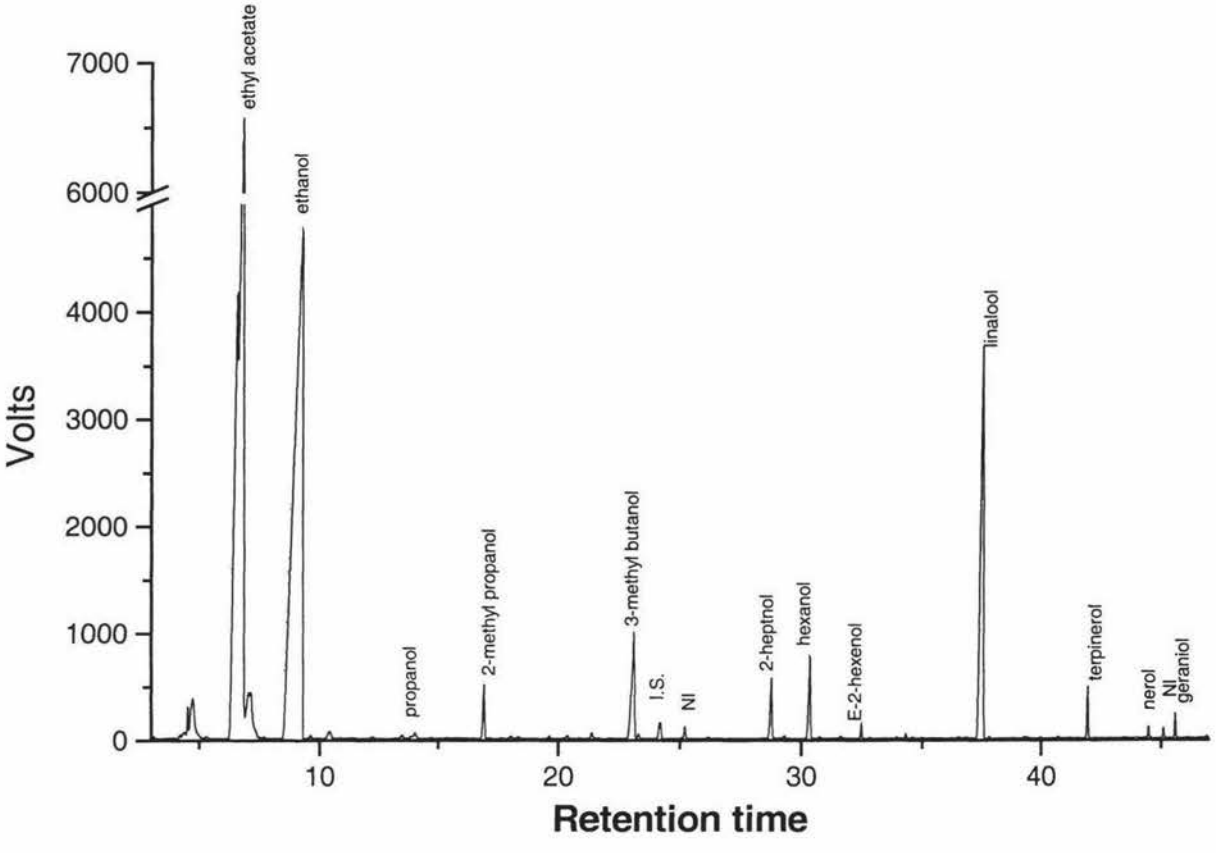

Figure A5 Gas chromatogram of boysenberry aroma permeate after pervaporation with GFT1070 membrane at a feed temperature of 30°C. permeate pressure of 100 Pa, feed flow rate of 1.4×10^{-5} m^3 s^{-1}. I.S.= Internal Standard.

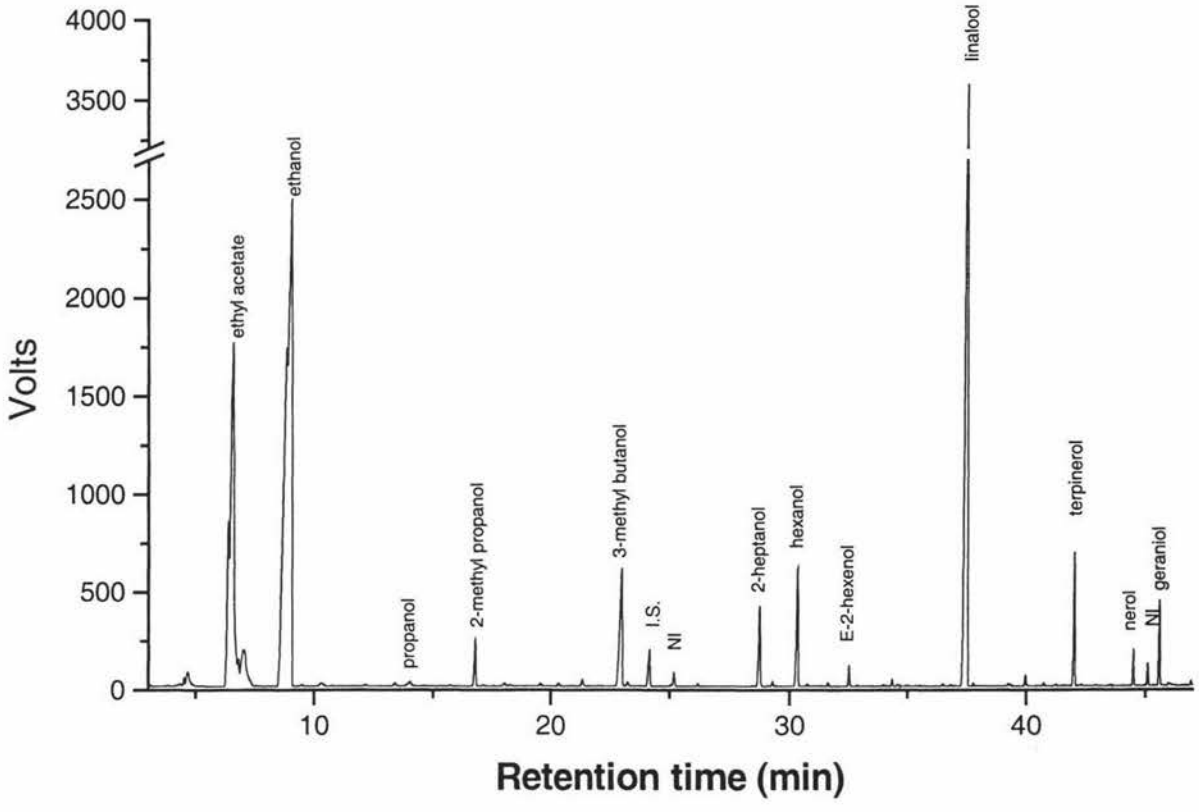

Figure A6 Gas chromatogram of boysenberry aroma permeate after pervaporation with PEBA membranes at feed temperature of 30°C, permeate pressure of 100 Pa, feed flow rate of 1.4×10^{-5} m^3 s^{-1}. I.S.= Internal Standard . NI = Not identified

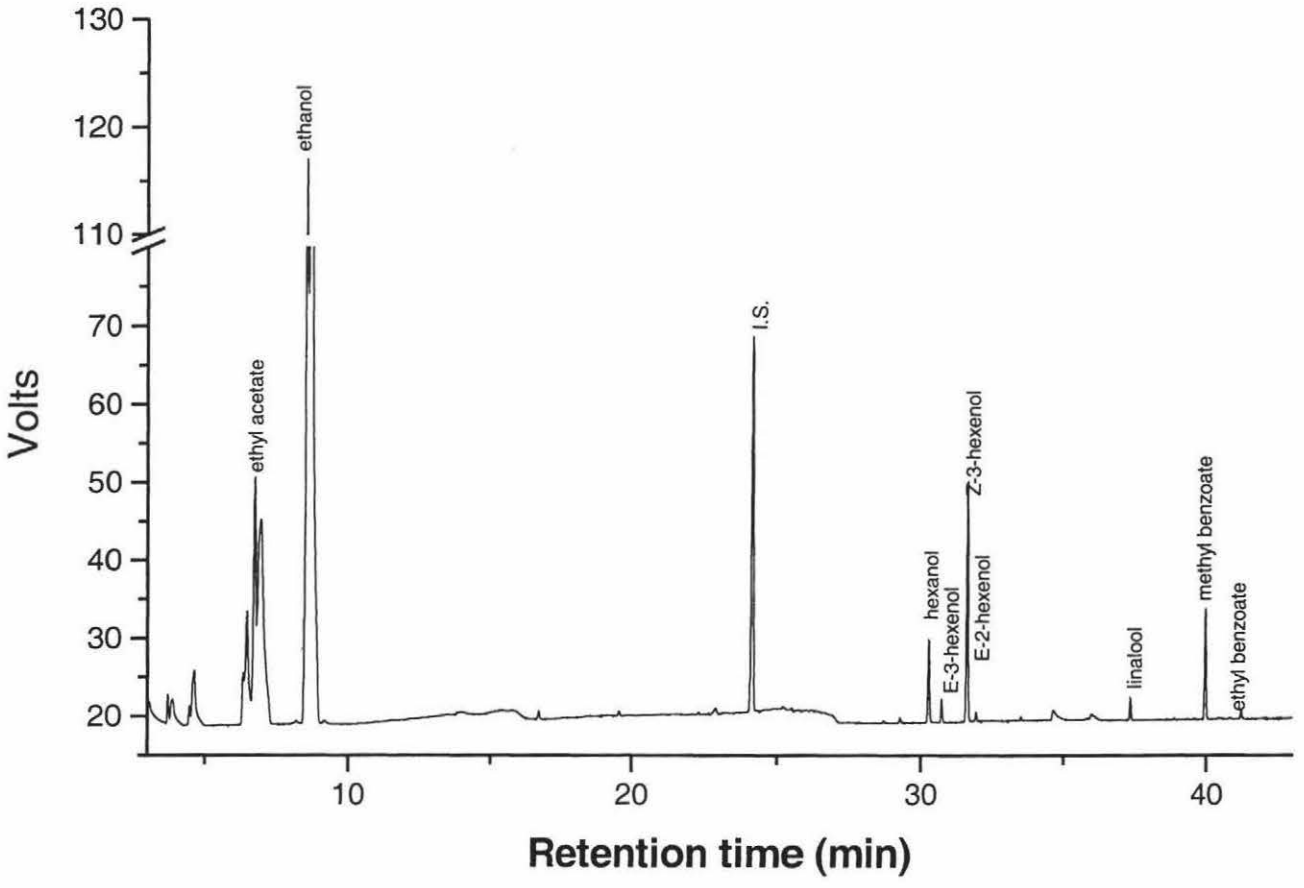

Figure A7 Gas chromatogram of the feijoa aroma concentrate concentrated by vacuum distillation at 30°C.

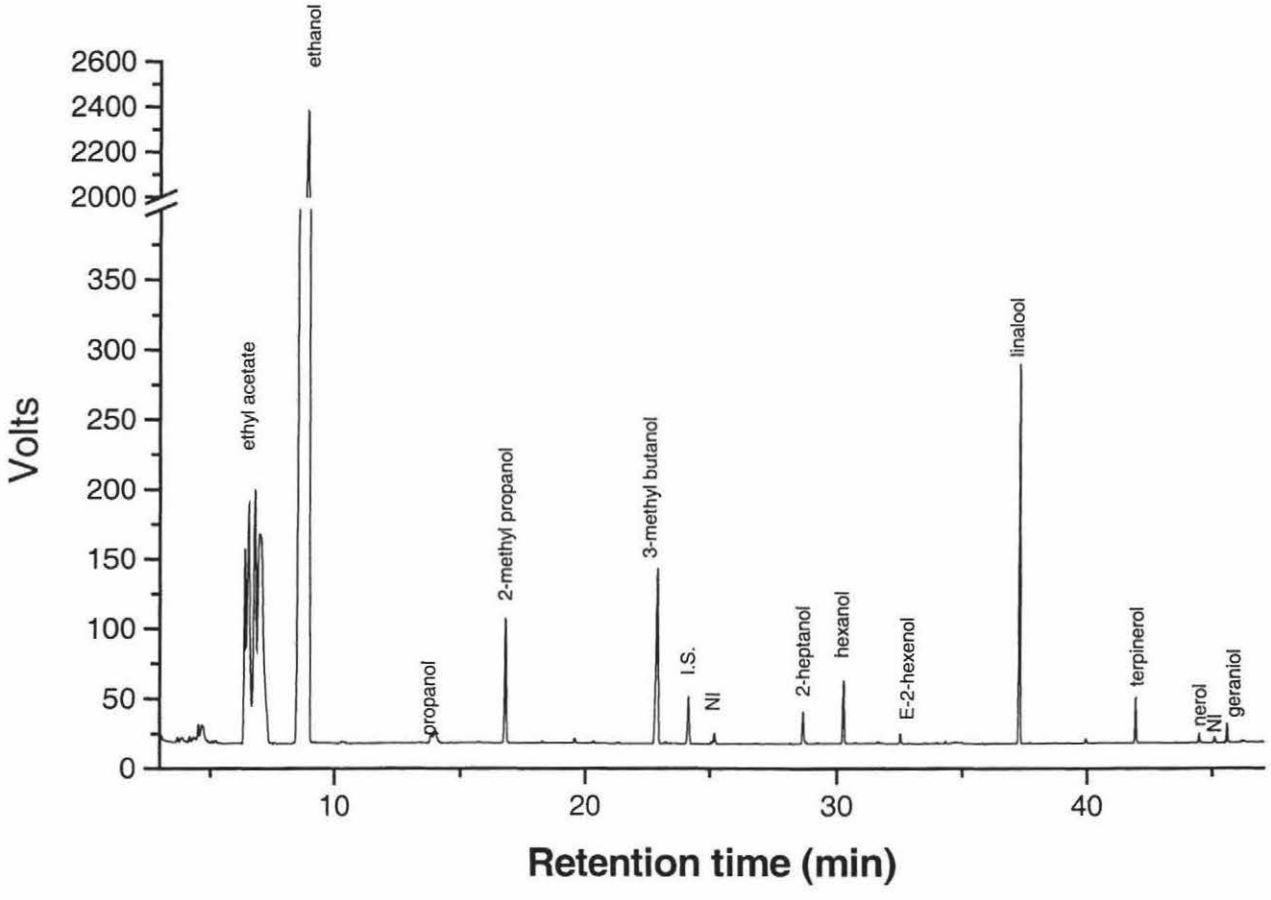

Figure A8 Gas chromatogram of boysenberry aroma concentrate by vacuum distillation at 30°C