Recovery of Volatile Aroma Compounds by Membranes

by

Susan Davari

A thesis
presented to the University of Waterloo
in fulfillment of the
thesis requirement for the degree of
Master of Applied Science
in
Chemical Engineering

Waterloo, Ontario, Canada, 2024

Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

This research investigates the potential application of poly(ether block amide) (PEBA) membranes for the separation of volatile aroma compounds from wine and the effect of non-volatile components on the separation performance using the pervaporation process.

The study examined the selective retrieval of two aroma compounds (4-ethyl guaiacol and 4-ethyl phenol) from binary dilute aqueous solutions through pervaporation utilizing the PEBA 2533 membrane. It was observed that this membrane effectively recovers hydrophobic aroma compounds. The influence of feed concentration and temperature on aroma recovery was also analyzed. The performance of PEBA 2533 for aroma recovery was assessed, and experimental data were analyzed using a batch pervaporation model.

It was discovered that both the flux of aroma compounds and their selectivity were notably influenced by the concentration of aroma compounds in the feed. The permeation flux and their selectivity in separating the volatile aroma compound in a binary solution followed the sequence of 4-ethyl phenol > 4-ethyl guaiacol, showing an inverse relationship with their molecular size. Generally, the permeation flux of aroma was found to be directly proportional to the concentration of aroma compounds in the solution within the tested concentration range (10-110 ppm). The impact of temperature on permeation flux followed an Arrhenius-type relationship and 4-EG with larger molecular size showed higher apparent activation energy than 4-EP and water.

It was observed that the recovery of 4-Ethyl guaiacol from its dilute aqueous solution was affected by non-volatile wine components (sugar, yeast, and salt) and alcohol. Specifically, the presence of glucose as a model sugar and NaCl as a model salt in the feed solution did not notably affect the pervaporative performance of 4-EG, maybe because of their low contents in the feed mixture and low interactions with aroma. The addition of agar initially increased the permeate flux

of 4-EG due to its insolubility and ability to absorb water molecules, boosting the concentration of 4-EG and enhancing the driving force. However, at higher agar concentrations, precipitation formed a thick layer of swollen agar in the tank, trapping 4-EG molecules and reducing their concentration in the solution. This led to a peak flux followed by a decline, reaching a maximum turning point at a specific agar concentration. Finally, the presence of ethanol as a model alcohol in the binary solution of 4-ethyl guaiacol was found to significantly reduce the permeation of 4-ethyl guaiacol. However, the total flux of the mixture considerably increased. The presence of ethanol affected the partitioning and activity coefficients of the components in the mixture as well as membrane swelling and plasticization, which ultimately affected the solubility and diffusivity properties of the membrane.

Acknowledgments

First and foremost, I extend my deepest gratitude to my supervisor, Dr. Xianshe Feng for their invaluable guidance, unwavering support, and scholarly wisdom throughout my master's journey at the University of Waterloo. Dr. Feng's mentorship has been instrumental in shaping my research endeavors and academic growth. Their dedication, encouragement, and insightful feedback have continuously inspired me to strive for excellence. I am truly fortunate to have had Dr. Feng as my supervisor, and I am indebted to them for their mentorship, patience, and expertise. Their guidance has been instrumental in helping me navigate through the complexities of my research and academic pursuits. I am immensely grateful for Dr. Feng's commitment to my success and for their profound impact on my scholarly development. I am truly grateful for his investment of time, patience, ideas, and financial support, which have significantly contributed to the productivity and enrichment of my experience.

I extend my sincere gratitude to the members of my thesis committee: Prof. Ali Elkamel and Prof. Elisabeth Prince. Their invaluable suggestions, insightful questions, and encouraging comments have greatly enriched my work. I am truly appreciative of their guidance and support throughout this endeavor.

I am deeply grateful to my esteemed teachers, Prof. Croiset, Prof. Li, and Prof. Penlidis at the University of Waterloo. Their dedication to excellence in teaching and mentorship has been truly inspiring. Their expertise and guidance in my academic pursuits have been invaluable, instilling in me a passion for the subject matter and pushing me to achieve my fullest potential.

I express heartfelt gratitude to my family for their unwavering love, support, and understanding throughout my academic journey. Their encouragement has been my pillar of strength, propelling me through challenges and triumphs alike. Their sacrifices and belief in my

abilities have fueled my determination to succeed. I am profoundly grateful for their constant presence, guidance, and unwavering belief in my dreams. To my family, your support has been the cornerstone of my achievements, and I am forever indebted to you.

Research support from the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

Dedication

I would like to dedicate this thesis to my beloved family.

Table of Contents

List of Figures

List of Tables

List of Symbols

A	Effective membrane area, m^2
a	Chemical activity
C	Permeate concentration, mol/m^3
D	Diffusivity or diffusion coefficient in membrane, m^2/s
D_o	Pre-exponential factor for diffusivity, m^2/s
E_D	Activation energy for diffusion, J/mol
E_J	"Apparent" activation energy for permeation, J/mol
E_P	"Intrinsic" activation energy for membrane permeability, J/mol
H	Henry's sorption constant, $Pa/(mol \cdot m^{-3})$
ΔH	Heat of evaporation, J/mol
J	Permeation flux, $g/(m^2 \cdot h)$
J_o	Pre-exponential factor for permeation flux, $g/(m^2 \cdot h)$
L	Membrane thickness, m
m	Weight, g
M	Molecular weight, g/mol
P'	Permeability coefficient, m^2/s
P, P^G	Permeability coefficient, Barrer
$p_{i,o}$	Partial pressure of component i in equilibrium with the feed solution, Pa
$p_{i,L}$	Partial pressure of component i in the permeate, Pa
p_p	Permeate pressure, Pa

p^{sat}	Saturated vapor pressure, Pa
pK_a	Logarithmic of acid dissociation constant
R	Universal gas constant, 8.314 J/mol.K
S_o	Pre-exponential factor for solubility, mol/(m^3·Pa)
T	Temperature, K
t	Time, s
V	Feed solution volume, L
X, x	Molar fraction of permeant in the feed
Y	Molar fraction of permeant in the permeate

Greek symbols

α	Separation factor
β	Enrichment factor
γ	Activity coefficient
γ^{∞}	Activity coefficient in dilute solution
λ_{max}	Maximum absorption wavelength, nm

Chapter 1

Introduction

1.1 Background

Red wine, beyond its indulgent taste, holds a profound significance in the realm of culinary and health sciences due to its complex array of volatile aroma compounds. During winemaking, these compounds are extracted from the grapes and further developed through processes like fermentation, maceration, and aging in oak barrels. From fruity esters like ethyl acetate and isoamyl acetate to floral terpenes such as linalool and geraniol and spicy phenols like eugenol and guaiacol, these volatile compounds not only tantalize the senses but also play a pivotal role in the overall sensory experience of wine consumption [1]. Their volatile nature allows them to evaporate easily, releasing aromatic molecules that contribute to the overall sensory experience of wine tasting. Beyond the hedonistic pleasure they provide, these compounds possess potential health benefits, with studies suggesting their antioxidant properties and potential cardiovascular protective effects [2]. Moreover, the volatile aroma compounds in red wine have been linked to the enhancement of food pairing experiences, enriching the nuances of culinary delights. Not only is there a great deal of research [3, 4] but also many books have dealt with red wine technology [5, 6].

The separation of volatile aroma compounds in wine holds pivotal importance across various domains of winemaking and sensory analysis. Firstly, this separation enables precise identification and quantification of individual compounds, allowing for a comprehensive understanding of the

wine's aroma profile. Each compound contributes uniquely to the overall sensory experience, and by isolating them, winemakers can fine-tune blends and optimize flavor profiles to achieve desired characteristics. Moreover, the separation of these volatile compounds aids in quality control processes, allowing producers to detect and mitigate off-flavors or faults that may arise during fermentation or aging. For instance, compounds like 4-EG and 4-EP are associated with undesirable smoky or medicinal aromas, which can be minimized through careful management of fermentation conditions [7-9].

Additionally, the analysis of volatile aroma compounds plays a crucial role in authenticity verification and wine classification. Certain compounds, such as vanillin or linalool that are of commercial importance, may be indicative of specific grape varieties or winemaking techniques, providing insights into the wine's origin and production methods [10]. Finally, research into the separation and characterization of volatile compounds contributes to advancements in sensory science, deepening our understanding of aroma chemistry and perception. This knowledge fosters innovation in winemaking practices, allowing for the development of new techniques to enhance aroma complexity and diversity.

Traditionally, aroma compounds are concentrated by solvent extraction, distillation, partial condensation, and gas stripping [11, 12]. Thermal processes like distillation and condensation offer simplicity and scalability for separating volatile aroma compounds though their limitations in terms of selectivity, potential loss of delicate aromas, and energy consumption have made them economically inefficient [13]. Solvent extraction method is another traditional method which can be employed to separate a wide range of aroma compounds and the possibility of using various solvents would allow the operation is highly selective to a specific class of aroma compounds. However, if not properly removed, solvent residues may remain in the extracted

sample, posing health risks or interfering with subsequent analyses. This can cause environmental concerns, especially in the case of the food industry where traces of toxic solvents can lead to serious health issues [10]. Gas stripping offers advantages such as selective and rapid extraction of volatile aroma compounds but may also suffer from drawbacks including loss of compounds, lack of selectivity, equipment complexity, inefficiency in the case of low volatile compounds, and sensitivity to operating conditions. Filtration techniques like ultra- and nano-filtration and reverse osmosis also can be used but they are inefficient for the separation of organic compounds in dilute solutions.

Pervaporation, a comparatively recent method of separation, has garnered attention as a viable substitute for conventional aroma retrieval technologies. This process entails the selective passage of components in a liquid mixture through a membrane, yielding a vapor stream downstream, which can then be condensed and gathered as a liquid. When aiming to recover aroma compounds from aqueous solutions, membranes with an affinity for organic compounds are employed, allowing aroma compounds to permeate through the membrane more readily than water, thus generating a permeate enriched in aroma [14]. Comparing this technique with the traditional methods clarifies that pervaporation has several potential advantages. For example, since it removes the risk of secondary contamination, it can be applicable to the food industry. Moreover, the selectivity of this process is so high that numerous hydrophobic aroma compounds have the potential to be concentrated in the permeate beyond their solubility thresholds. As a result, significantly higher purity levels can be attained in the organic phase during the subsequent phase separation of the permeate. It can also be conducted in mild temperatures so the quality of products prone to thermal degradation can be easily preserved. Moreover, recovery or concentration or separation of organic compounds in dilute solution can be easily performed due to the affinity of

hydrophobic membranes with hydrophobic species in the feed solution [15]. Finally, energy consumption is relatively lower than other processes, which makes it a cost-effective process.

Despite extensive research on pervaporation for aroma recovery, the lack of industrial-scale units for this application persists, partly due to inadequate understanding of the sensory profiles of the permeate and limited knowledge regarding the long-term performance of membranes. Another concern arises from the potential interaction between aroma compounds when the feed solution contains multiple components. This issue becomes more intricate when the feed mixture includes non-volatile components such as salts, sugar, yeast extract, and protein commonly found in wine fermentation products. Although these non-volatile components typically do not permeate through pervaporation membranes, they may still interact with aroma compounds, influencing the pervaporation behavior of aromas or causing fouling. While many researchers utilize binary aroma-water solutions to investigate the pervaporation process without complicating factors, the permeation performance with real dairy solutions may not consistently align with results obtained from model feeds.

So far, many studies have been done to evaluate the availability of the volatile aroma compounds in red wine, focusing on the performance of pervaporation process of variety solutions from binary to the real models of wine under different operating conditions. Besides, many researchers evaluated production of alcohol-free beverages. Moreover, recently vanillin production from wine fermentation has attracted huge attention. Although a wide range of volatile aroma compounds and their different multicomponent mixtures have been the subject of many studies, the presence of two specific volatile organic compounds (VOCs) in red wine seems to need more investigation.

4-ethyl guaiacol (4-EG) and 4-ethyl phenol (4-EP) are two aroma compounds commonly found in red wine, contributing to its characteristic aroma profile. These compounds are formed during the fermentation process through the metabolism of yeast and bacteria, particularly certain strains of Brettanomyces yeast. The presence of 4-EG and 4-EP in red wine is primarily attributed to the metabolic activities of yeast and bacteria during fermentation, as well as the influence of oak aging. While these compounds can contribute to the aroma complexity of red wine at low levels, excessive concentrations may lead to undesirable off-flavors like barnyard, particularly if dominated by Brettanomyces-derived aromas. Winemakers carefully monitor fermentation conditions and aging processes to control the formation of these compounds and achieve the desired aroma profile in the final wine. However, complete removing the bacteria/yeast is difficult and traces can grow fast, especially in low-alcohol media, enhancing the enzymatic reactions of ethyl phenols production.

Currently, the most common method to alleviate this problem is dilution of the spoiled wine with clean wine. However, it may serve only as a temporary solution because more spoilage may occur in future. Solvent absorption using activated carbons, polyaniline nanoparticles, or suberin have undergone several examinations but these approaches can enhance risk of nanoparticle contamination. Recently, in one study, the efficiency of the pervaporation process in the separation of ethyl phenols from red wine fermentation headspace using fractional concentrations was examined [16]. However, the separation was performed at ambient temperature and its focus was mainly on the modelling and optimization of the condensers' temperature to the maximum recovery of the species. Thus, a comprehensive study regarding the potential of pervaporation technique to reduce the off-flavor components in red wine would be worthwhile.

PEBA 2533 is a type of poly(ether block amide) (PEBA) membrane commonly used in pervaporation processes for various applications, including aroma recovery from liquid matrices such as wine or dairy products. PEBA membranes are composed of alternating polyether and polyamide segments, providing a balance of mechanical strength, flexibility, and chemical resistance. PEBA 2533 specifically has a distinct composition optimized for pervaporation applications. PEBA 2533 membranes exhibit selective permeability to certain compounds based on differences in molecular size, polarity, and solubility. This selectivity allows for the preferential permeation of target volatile aroma compounds while rejecting non-volatile components present in the liquid matrix. PEBA 2533 membranes are designed to withstand the rigors of pervaporation operations, including exposure to organic solvents, elevated temperatures, and mechanical stress. However, proper handling and maintenance are essential to ensure membrane integrity and longevity over time. The performance of PEBA 2533 membranes in pervaporation processes depends on various factors, including membrane thickness, and operating conditions such as temperature, and feed composition. Optimization of these parameters is necessary to achieve desired separation efficiency and aroma enrichment in the permeate.

1.2 Research objectives

The aim of this study was to study pervaporation as a method of separating ethyl phenols from dilute binary aqueous solutions using PEBA membranes. The specific objectives of this project were:

(1) To determine the effects of operating conditions (i.e., feed aroma concentration and feed temperature) on the pervaporation of each aroma compound in binary aroma-water feed solutions;

(2) To identify the effects of non-volatile components (e.g., salt, sugar, yeast extract) in feed solutions on pervaporative separation of off-flavor 4-EG;

(3) To investigate the effect of ethyl alcohol as a non-aroma volatile compound in feed solutions on pervaporative separation of off-flavor 4-EG;

1.3 Thesis structure

This thesis comprises five chapters, structured as outlined below:

Chapter 1 offers an introduction to the background of the subjects, encompassing an examination of existing research within the field and areas warranting further investigation. It also outlines the research objectives.

Chapter 2 conducts a comprehensive literature review, addressing the objectives of off-flavor reduction, along with recent advancements in associated technologies. Pervaporation, emerging as a viable alternative to conventional methods, receives detailed scrutiny. The discussion covered the mechanism of mass transport, various types of membranes suitable for pervaporation in volatile aroma compounds, and several factors that could impact the separation performance.

Chapter 3 presents the experimental findings of pervaporation conducted with dilute binary model aroma-water feed solutions utilizing the PEBA 2533 membrane. The research delved into investigating the influence of feed aroma concentration and temperature on parameters such as permeation flux, permeability, and enrichment factor.

In Chapter 4, the impact of ethanol and non-volatile components including NaCl, glucose, and agar, on the recovery of aroma compounds through pervaporation is discussed. The chapter

explores the relationship between the interaction of these compounds with both aroma compounds and membranes.

Chapter 5 summarizes the general conclusions of this research, and future work for further studies was recommended.

Chapter 2

Literature review

2.1 Introduction

Volatile aroma compounds, known as odorants, aromas, fragrances, or flavors are volatile molecules that, in order to be perceived, have to be transmitted via the air from the food or beverage and must reach the olfactory receptors in the upper part of the nose [17]. Food and beverages contain over 10,000 volatile compounds with molecular weights below 290 Da [18]. However, while a compound must be volatile enough to be perceived nasally, only a small fraction of these molecules contributes to the overall aroma of food. So far, approximately 230 volatiles have been recognized as "key food odorants" (KFO) [19]. For example, there are only three compounds with distinct butter aromas including diacetyl, (R)-δ-lactone, and butyric acid. These three compounds are found in butter at concentrations above their odor threshold values (OTV), representing the chemical odor code for a buttery aroma [17].

2.2 Volatile phenols

Being originated from the aromatic amino phenylalanine, volatile phenols like phenylpropanoid and benzoid compounds are biosynthesized via the shikimate/arogenate pathway. These volatile compounds contribute to the aroma of several economically important plant-derived foods like herbs, spices, and fruits. [17]. They are essential to the odor and flavor of beverages like wine or roasted coffee. Historically, the application of wood smoke was a useful way to prevent

food from spoiling and smoked food is appealing concerning both taste and the fine state of preservation [20].

Volatile phenols that consist of about 10% of all known KFOs are about 21 compounds including mono-, di-, and trihydroxylated derivatives. The structure of some more frequent compounds in this category, as well as their trivial names, the type of odor, their use, and the frequency of their occurrence in percent in 227 food samples, are listed in **Table 2-1**.The top five odor-active phenols in food are vanillin, guaiacol, 4-vinyl guaiacol, 4-ethylguaiacol (4-EG), and eugenol [17].

Table 2-1 Structure of some volatile phenolic compounds as well as their trivial names, the type of their odor, their, and the frequency of their occurrence in percent in 227 food samples.

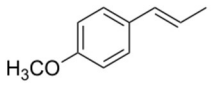
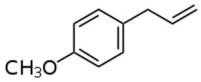
Name	**Structure**	**Odor**	**Use**	**Frequency of occurrence (%) [17]**
(a): mono-				
Trans-Anethole		Sweet (13 times sweeter than sugar)	Flavors, antibacterial and antifungal agent, pharmaceuticals	2.6
Estragole (Methylchavicol)		Phenolic and liquorice	Perfume industry	3.5

Table 2-1 Continued.

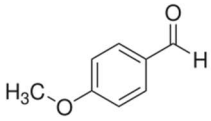
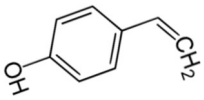
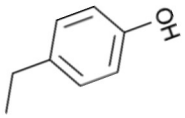
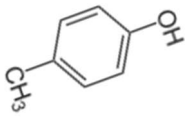
Name	Structure	Odor	Use	Frequency of occurrence (%) [17]
4-anisaldehyde		Sweet, floral	Fragrances, flavors, perfumes, and pharmaceuticals	2.6
4-vinylphenol		Medicinal, band-aid, mousy, barnyard	Fragrance, and flavor industry	2.2
4-EP		Medicinal, band-aid, mousy, barnyard	Phenol resin production	3.1
Cresol		Phenolic, coal tar-like	Plastics, pesticides, pharmaceuticals	6.2

Table 2-1 Continued.

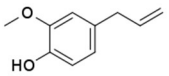
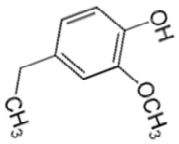
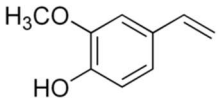
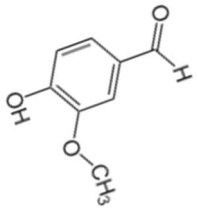
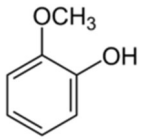
Name	Structure	Order	Use	Frequency of occurrence (%) [17]
(b): di-				
Eugenol		Pleasant spicy, clove-like	Flavors, aroma ingredients, cosmetics, essential oils, insecticide, pain-relief	8.4
4-EG		Smoky, spicy, bacon-and clove-like	Fragrances and Flavorings	11.0
4-vinyl guaiacol		apple, spicy, peanut, wine-like or clove and curry	Fragrances and flavorings	13.7
Vanillin		Vanillin, sweet, creamy	Food industry, fragrances, and flavorings	27.8

Table 2-1 Continued.

Name	Structure	Order	Use	Frequency of occurrence (%) [17]
Guaiacol		Smoky	Flavorings, intermediate for vanillin synthesis	23.8

It is clear that the human body's olfactory receptors (ORs) have a significant role in perceiving odors. According to studies on structure-activity relationships of a specific type of human receptors called OR10G, these receptors are highly tuned to volatile phenols [21]. It is conceived once an odor is perceived by a receptor, in addition to the odor activity, the small molecules of the odor can biologically affect the human body, and after ingestion, they may pass through cellular barriers and reach other target tissues. Recently, research indicated that low molecular-weight metabolites from polyphenols are able to attenuate neuroinflammation and prevent cardiovascular diseases [22, 23].

2.3 Generation of volatile phenols

Volatile phenols can be generated via three main methods: 1- De Novo biosynthesis in planta, 2- microbial formation of volatile phenols, and 3- thermal formation of volatile phenols during food processing [17].

2.3.1 De Novo biosynthesis in planta

In this method, volatile phenols are produced in planta from phenylalanine that yields the C_6C_3 building block of all phenylpropanoids [24, 25]. The key enzyme is phenylalanine ammonia lyase (PAL) that is well-characterized and controls the flux through this pathway [26]. Generation of vanillin from ferulic acid is a special case in this category in which some byproducts like vanillic acid, vanillyl alcohol, and guaiacol are generated during the biosynthesis process [13].

2.3.2 Microbial formation of volatile phenols

During food processing by fermentation, microorganisms degrade non-volatile phenylpropanoids to volatile, highly odorous phenols. Yeast-mediated formation of ethyl- and allyl-phenols by decarboxylation reduction during the alcoholic fermentation is so common in the wine and beer industry [20, 27]. However, if degradation highly yields to the formation of products at excessively high concentrations, aroma defects, like a “horse sweat” note in wine, can develop. For instance, while the presence of 4-EG sounds attractive to red wine, its occurrence with 4-ethylphenol (4-EP) causes a defect which is known to “wine fault” [7].

2.3.3 Thermal formation of volatile phenols during food processing

During thermal treatment of food, volatile phenols can be produced from labile precursors [28]. During coffee roasting, the green smell of the raw coffee converts into the pleasant aroma characteristic of the Arabica coffee in which volatile phenols including 4-vinyl guaiacol, 4-EG, and vanillin contribute as key odorant compounds [29]. Moreover, the pyrolysis of wood generates a variety of volatile phenols with antioxidative and aromatic properties of smoke, which is used for food preservation by smoking [30] and aromatizing wine by storage in toasted oak barrels [3, 31].

2.4 Red wine making

The winemaking process starts with the harvest of grapes and then in the second stage, they are prepared for primary ferment. Red wine is produced by fermenting grapes pulp, and the grape skins are responsible for the red wine's color that may vary from rosy to red, and finally purple. At this stage, yeast may be added to the container or naturally produced during the fermentation and converts the sugar to ethanol. Thereafter, free run wine is pumped off into the tank and whatever remained from skins are pressed and its extracted juice and wine are added to the tank, for further fermentation in a warm place [5].

Malolactic fermentation (MLF) is the next process in the making of red wine, a process in which microorganisms like bacteria or yeast convert malic acid to soft, creamy lactic acid, giving a pleasant taste to the wine [32]. Being transferred to oak barrels, red wine is kept for several weeks or months to mature while gradually oak aromas and some tannin penetrate to the wine. Finally, after being settled and clarified and adjusted, it is ready to bottle [33]. During barrel ageing, the organoleptic quality of wine increases through increment of aromatic complexity as well as stability improvement in the wine. In this complex process, volatile and polyphenol compounds are extracted in the barrels, which is dependent to factors such as wood and wine compositions as well as the contact time between the wine and wood [5].

However, barrel age contributes to a remarkable decrease of volatile substances after continuous usage of the barrels. While pores of the wood gradually are plugged, less oxygen can penetrate into the wine which reduces oxidation rate of polyphenol in turn. Used barrels are also at the risk of being contaminated by the B.B. yeasts which are responsible for the nasty appearance like horsy sweat, animal, leather, phenol in wine. Although disinfection of barrels is a promising

way to hygiene the barrels especially used ones [34], remaining traces of microorganisms can make a problem during wine ageing in roasted oak barrels [35].

2.4.1 Volatile composition of red wine

Volatile compounds in red wine can be classified into those extracted from oak wood and those generated during aging in barrels. These compounds can be categorized based on their chemical structure in furanic compounds, lactones, phenolic aldehydes, and volatile phenols. The extraction of the chemical compounds from oak and their subsequent transformations can be influenced by some factors like the wood composition, the contact time between wine and barrel, the age of the barrel, and the wine compositions. The perception threshold of some of these components are provided in Table 2-2.

Furanic aldehydes (furfural, 5-methylfurfural, 5-hydroxymethylfurfural) are extracted from oak to wine and then during the wine maturation they are biologically reduced to furanic alcohols (furfuryl alcohol, 5-methylfurfuryl alcohol, 5-hydroxymethylfurfuryl alcohol). Except for 5-hydroxymethylfurfural that is odorless, the rest give bitter almond aroma to wine [36]. Among them furfural is the most abundant and easily reducible compound that is converted to the furfuryl alcohol with an aroma like hay, and the longer the contact time between wine and the barrel, the higher the concentration of this alcohol in wine [37]. It is revealed that the perception threshold of the furanic aldehydes are so high (more than 20 mg/l) which means they are not perceived in wine [38]. In general, short-term extraction results in increment of increase in furanic compounds. Nonetheless, as time passes, they are reduced to their corresponding alcohols and their concentrations decrease below their threshold perceptions so that their aroma characteristics can no longer be perceived [3].

Table 2-2 Data of perception thresholds of the extracted volatile compounds of oak, volatile compounds in red wine, and generated compounds during barrel aging.

	Perception threshold (μg/l)
Furanic compounds [36]	
Furfural	20000
5-methyl furfural	45000
Phenolic aldehydes [36]	
Vanillin	320
Syringaldehyde	50000
Volatile phenols [36]	
Eugenol	500
Guaiacol	65
4-methyl guaiacol	75
Volatile ethyl phenols [39]	
4-EG	33-135
4-EP	230-650

Two main phenolic aldehydes are vanillin and syringaldehyde. Vanillin contributes to the vanilla aroma to wine as its perception threshold is about 320 μg/l and though syringaldehyde is not perceived by nasal olfactory system, it helps boost the flavor of vanillin. According to research [4], although vanillin concentration would reach its highest level after approximately 10-12

months, it gradually decreases in longer barrel aging. Next group is volatile phenols including eugenol, guaiacol, 4-methylguaiacol, phenol, m-cresol, and p-cresol. While eugenol confers clove aroma, guaiacol and 4-methylguaiacol give smoky and toast aroma. The smell of ink is attributed to phenol and cresols contribute to pharmaceutical aroma in wine. Compared to the two previous groups (furanic compounds and phenolic aldehydes), volatile phenols are more stable and do not undergo chemical or biological reduction during aging. Indeed, their concentrations are significantly dependent on their extraction rate. For instance, it takes about 3 months for 4-methyl guaiacol to reach its highest concentration while this time would be around 9 months for guaiacol [40].

2.4.2 Volatile ethyl phenols in wine aged in oak barrels

Generation of volatile ethyl phenols in red wine often decreases the quality of the wine, especially its freshness and fruitiness [35]. The precursors of volatile ethyl phenols are hydroxycinnamic acids, p-coumaric and ferulic acids, which constitute natural components of grapes and wines [34, 41]. These cinnamic acids can exist in wine in the form of tartaric esters including caftaric, coumaric and fertaric acids as well as in the free form or esterified with anthocyanins [42] and ethanol [43]. Usually, these phenolic acids can convert into volatile phenols through two sequential enzymatic reactions in the presence of the contaminating Dekkera/Brettanomyces Bruxellensis yeasts [35, 44-46]. In the first reaction, the hydroxycinnamic acid is decarboxylated and yields vinyl derivative. In this stage 4-EP is generated from p-coumaric acid and 4-vinyl guaiacol is produced from ferulic acid. Then, in the second step, a reductase transforms the vinyl phenol into 4-EP and 4-EG (Figure 2-1) [41].

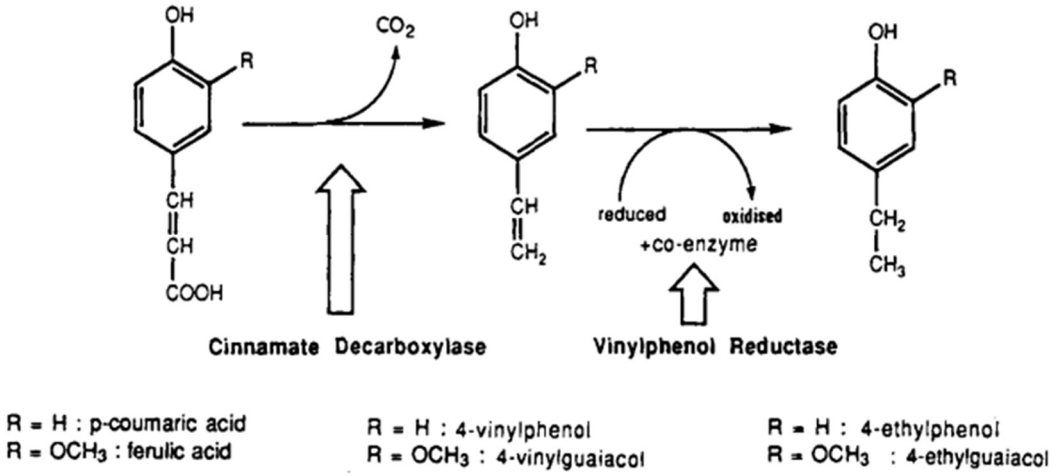


Figure 2-1 Biosynthesis of ethyl phenols in wine by B.B yeast *[39]*

4-EG is a phenolic compound with the molecular formula $C_9H_{12}O_2$. Extracted from natural wood oil, 4-EG is a colorless to slightly yellow liquid with a condimental smell and distinctive soy scent. 4-EG can be used as spices in various ways like foodstuff, feed, cosmetics, and daily commodities. 4-EG can contribute bacon, spice, clove, or smoky aromas to the wine and these characteristics can be quite pleasant in the wine. It has the function of antisepsis and deoxidization and prevention of hypersensitive skin. With a strong soy scent, 4-EG can preserve wine and soy sauce for lasting longer without decaying. Yet, it can remain aromatic even after heating [47].

However, the formation of 4-EG usually coincides with the production of 4-EP whose aromas are so aggressive, and this can confer a horsy defect to the wine [35]. The mixture of 4-EG and 4-EP in the wine can be so prejudicial especially when their concentrations are greater than their limit perception threshold. In overall, it is obvious that production of 4-EG and 4-EP in the red wines is highly dependent to the presence of their precursors and yeast [48]. Moreover, concentrations of 4-EG and 4-EP are higher in the barrels with lower concentration of ethanol. It

is because of the disinfection characteristic of ethanol that would hinder the microbial growth and subsequent generation of volatile ethyl phenols.

2.5 Removal of volatile ethyl phenols from red wine

In spite of many efforts to remove this yeast [49-51] or stabilize it [52-54], its so well-adapted and resistant characteristic to harsh conditions [55] cause even too scarce amount of this yeast in red wine can remain in the barrels before bottling and then exponentially grow during ageing, eventuating in the production of high amount of 4-EP and 4-EG [35].

The wild yeast *Dekkera/Brettanomyces* (*Dekkera* is the sporulating, sexual form, *Brettanomyces* the non-sporulating, asexual form) is omnipresent in the vineyard as well as in wineries and various winery equipment like pumps or gaskets [56]. The production of ethyl phenols mainly occurs in fermented wine, especially during barrel aging, when the reductive conditions of the fermentation gradually change to a more and more oxidative environment. The resistance of *Brettanomyces* to alcohol is as high as 14.5% vol. and is able to produce volatile phenols even at low residual sugar contents less than 275 mg/L [57]. Especially barreled wines are more susceptible to *Brettanomyces* metabolites, in particular after malolactic fermentation, where SO_2 loses its anti-microbiological effectivity as a result of the pH shift and due to the porous surface of the barrels providing constant oxidative conditions. The yeast can exist at 8 mm depth in barrel staves, making it difficult to remove *Brettanomyces* from a once contaminated barrel and therefore, there is always a danger of contaminating wines during its subsequent employment [58].

Concentration of volatile ethyl phenols can vary depending on many factors including the type of grape, the irrigation water, time and method of harvesting, fermentation medium, time of maturation, type of oak barrels, and aging [5, 57]. According to the literature, 4-ethylphenol

concentration can vary from 17.7 µg/l in 21-month Q. Robur wine in Spanish barrel [59] to 1850 µg/l in a combination of Tempranillo and Cabernet Sauvignon stored in a French Oak barrel [33]. The least amount of concentration of 4-ethylguaiacol was reported 5 µg/l belonging to a 1998 Shiraz wine stored in American oak barrel after 4 times use [60] and highest value was 3250 µg/l attributed to Roboso Piave wine after 9 months of aging in acacia wood barrel [61].

Although minimum odor perception threshold of 4-EP and 4-EG, each one in the absence of another, are reported 230 µg/l and 33 µg/l, respectively, when both exist in red wine, this parameter can decrease [62]. Thus, in order to reduce volatile phenols concentration several remedies have been examined. The simplest way is mixing spoiled wine with clean wine but it is temporary and not professional and since microorganisms still remain in the mixture, they are able to grow and cause more loss [9]. Other remedies are reverse osmosis (RO) technology, sorption, and pervaporation.

2.5.1 Reverse osmosis and nanofiltration processes

Commercial reverse osmosis (RO) and nanofiltration (NF) membranes are made of a dense polyamide layer on a porous support layer like polysulfone and can reject NaCl up to 99% separation efficiency. Accordingly, they can also be used for removal of volatile phenols. RO and NF membranes are permeable to low molecule compounds, such as small molecules as water and these processes are not very selective, separation of these compounds is conducted at the cost of losing other valuable aromatic compounds [63]. Ugarte et al. [64] utilized a two-stage process including an RO module coupled by hydrophobic adsorptive resin to remove ethyl phenols in wine. They also mentioned that the removal of other aroma compounds was unavoidable. Furthermore,

based on their perception threshold, these ethyl phenols are usually generated in the range of > 100 ppm for 4-EG and 44 to 150 ppm for 4-EP [45].

2.5.2 Sorption of ethyl phenols

Sorption of ethyl phenols on the yeast lees or yeast cell-walls have been evaluated in several studies [65, 66]. However, the sorption is highly influenced by the nature of the yeast strain, yeast wall nature and composition, the medium and mode of culture. Moreover, it is revealed that dry active yeast possesses a higher capacity to absorb ethyl phenols. However, this additional step can dramatically influence the cell wall composition which in turn affects sorption capacity.

Adsorption of ethyl phenols on polymers like molecularly imprinted polymers [67], cyclodextrin [68], polyaniline [9] and suberin which is a biopolymer extracted from cork [62] was investigated. Additionally, activated carbon has been studied for removal of off-odor ethyl phenols [69] and it was revealed that its adsorption capacity is greatly dependent on its physiochemical characteristics like Brunauer-Emmett-Teller surface area, surface area of mesopores, total volume of pores, micropore volume, average pore diameter, and apparent density. Accordingly, a commercial type of activated carbon from coconut shell with improved physiochemical characteristics was utilized to enhance adsorption capacity of ethyl phenols [8].

In spite of the fact that adsorption has been extensively evaluated for the removal of off-flavor ethyl phenols from red wine, its application has several downsides. First, some resins and activated carbon is not completely selective to ethyl phenols and, therefore, other compounds present in the fermentation broth can also be adsorbed, such as vanillic acid, vanillyl alcohol and guaiacol, as well as the substrate, ferulic acid [13]. Second, traces of adsorbent contaminants are difficult to avoid, requiring strict quality control of the recovered product [10].

2.5.3 Pervaporation

Pervaporation offers significant s advantages over other recovery processes because adsorbents are not required. The membrane is regarded as a non-miscible solid solvent and solute recovery is conducted by use of a reduced downstream pressure as a driving force. The desirable solute can then be trapped by condensation, which in the case of different volatile compounds can be done at different temperatures, depending on the melting and boiling points of the components, followed by condensation in a cold trap to capture the residual solute. Furthermore, its capability to hybridize with other separation techniques can make it a versatile process [70].

Among various volatile phenols, recovery of vanillin by pervaporation has been extensively studies by pervaporation [10, 13, 71, 72] and its efficiency of these method has been proved successfully. Removal of EPs from fermentation broth by pervaporation has not been examined, to the author's knowledge. Recently Brazinha et al. [16] used an integrated vapor permeation–fractionated condensation system, exhibited a good recovery of esters as well as reduce off-flavors from red wine fermentation headspace. They utilized organophilic polydimethylsiloxane (PDMS) membrane and concluded that 85% of 4-EP and 49% of 4-EG were removed from the permeating vapor. However, they used pervaporation at the ambient temperature and their work was based on modelling of fractional condensation and optimization of the first condenser's temperature to evaluate the percentage of the recovery of different species from the headspace. This means a comprehensive investigation concerning the operating condition of pervaporation process is lacking.

2.6 Effect of matrix composition on the volatility of volatile ethyl phenols

In many wine matrix, yeasts are responsible for non-volatile components (carbohydrates, proteins, and polyphenols) coming from the skin and pulp of the grapes and from the cell wall of the fermentation yeast.

In general, the release of volatiles from the food or liquid matrix into the vapor phase highly depends on their interaction with other compounds present in the food matrix, such as polysaccharides, proteins, and lipids [73]. In the case of red wine, these compounds can be other phenolic compounds, and alcohol, non-volatile compounds like salts and yeasts. In addition to the matrix composition of the wine, acidity would also influence the volatility of ethyl phenols [5].

2.6.1 Effect of polyphenols

Polyphenols are valuable constituents in red wine and secondary plant metabolites that are synthesized during the development of the grape berry under stressed conditions. Red wine polyphenols can be formed during growth of grapes or can be the products of reactions during the winemaking process and both types can make a significant contribution to the sensory properties and antioxidant activity of wines. Among them, the most important groups and their representatives are flavanols (catechin), stilbenes (*trans*-resveratrol), flavonols (quercetin) and hydroxybenzoic acids (gallic acid) [2].

Polyphenols can influence volatility and solubility of aromatic compounds in red wine through non-covalent interactions. Additionally, it was shown that hydrophobicity can be regarded as a driving force for bimolecular phenolic-aroma interactions [74]. Jung et al. used one- and two-dimensional NMR to study binding two phenols (gallic acid, naringin) with three aroma compounds (2-methylpyrazine, vanillin, and ethyl benzoate). They revealed that the interaction is

principally π-π stacking between the galloyl ring of gallic acid and the aromatic ring of the aroma compounds. Furthermore, the secondary hydrogen-bonding effects would help to stabilize the complex [75]. In general, these types of interactions can stabilize the presence of hydroxyl groups and the formation of hydrogen bonds. In one study, the effect of polyphenols on the volatility and sensory perception of volatile ethyl phenols demonstrated that interactions between polyphenols and volatile ethyl phenols significantly reduced the volatility of these aroma compounds [60].

2.6.2 Non-volatile compounds and their impact on separation performance

Non-volatile compounds are substances that do not readily evaporate at normal temperatures and pressures, remaining in the liquid or solid phase rather than transitioning to a gaseous state. These compounds typically have higher boiling points or lower vapor pressures compared to volatile compounds, making them less prone to evaporation. These non-volatile compounds play essential roles in various processes, including flavor development, texture, stability, and nutritional composition of foods and beverages.

Some examples of non-volatile compounds include sugars (e.g., glucose, fructose, sucrose, and lactose), salts (e.g., sodium chloride, potassium chloride, and calcium chloride), proteins (e.g., including albumin, casein, whey proteins, and globulins), fats and lipids (e.g., triglycerides, fatty acids, cholesterol, and phospholipids), minerals (e.g., calcium, magnesium, iron, zinc, and potassium), organic acids (e.g., citric acid, lactic acid, acetic acid, and tartaric acid), and flavor compounds with low volatility (e.g., certain flavor enhancers, colorants) or additives may have low volatility and remain non-volatile in food or beverage matrices).

Salts

Saltiness of the wine is attributed to mineral salts which originate from vineyards. Vineyards are planted in different soils with a range of natural components called soluble salts. Being spread out across the layers of soil, these components are subsequently absorbed by the roots of the vine. Grapes' sensitivity to salinity causes fresh grape yield dramatically decrease in grapevines as the salinity of the irrigation water increases [76]. Moreover, the higher the concentration of salts in irrigation water, the higher the risk of grapevine mortality. However, a certain level of salts is needed to maintain the mineral balance in the grapevine [77].

Ions that are indispensable for maintaining vine growth as well as providing a mineral balance for producing high-quality grapes are potassium, sodium, calcium, and magnesium. Potassium constitutes up to 3% of the dry weight of the grape and preserves the structure of non-woody parts of the plant and berries. Sodium, on the other hand, is accumulated in much lower amounts and generally accounts for less than 0.5% of the dry weight of the grape. Usually, between 2-4 grams of salt per liter can appear in wine.

In addition to the salts that are naturally available in the wine, salts can be added during wine processing for deacidification [5]. Potassium is usually added to wine in the form of tartrate while calcium is an additive in the form of its carbonate salt. Deacidification is conducted for two main reasons: to expedite the malolactic fermentation and to make the wine taste pleasant as wine acid enhances the perception of astringency.

Sugars

The presence of sugars in red wine can impact the volatility of ethyl phenols, key aroma compounds. High sugar levels can potentially mask the perception of ethyl phenols, reducing their

volatility and making them less detectable. Additionally, sugars may influence the sweetness perception of the wine, indirectly affecting how ethyl phenols are perceived. Sugars can participate in the Maillard reaction, generating volatile compounds, including ethyl phenols, which contribute to the wine's aroma complexity. However, sugars can also enhance the stability of ethyl phenols, protecting them from degradation or oxidation. Overall, the effect of sugar on ethyl phenols' volatility in red wine is intricate, involving interactions that shape the wine's flavor profile and aroma perception.

Yeast extracts

The yeast cell walls are capable of binding volatile compounds. Indeed, aroma substances and yeast walls interact with each other which can influence the volatility of these compounds. The impact of cell walls on the volatility of aroma depends on the physio-chemical nature of volatile compounds. Yeast walls cause vapor phase concentration of all aroma substances to reduce. The greater the hydrophobicity of volatile compounds, the higher the degree of binding of cell walls and aroma substances: ethyl octanoate and β-ionone. Binding capacity of yeast cell walls was partly explained by lipid matter and the insolubility of walls [78].

Acids

Acidity and pH are important variables in red winemaking. The pH of wine is strongly related to its microbiological and physiochemical stability. The outset and the behavior of malolactic fermentation may be affected by pH. Moreover, pH may be responsible for the natural selection of microorganisms during winemaking. Furthermore, it obviously directed the equilibrium of sulfur dioxide in wine. Finally, the color of red wine may be controlled by the pH.

The main organic acids in grape juice and wine are tartaric, malic, citric, succinic, and lactic acids. In normal winemaking conditions, even without specific acidification or deacidification processes, the acidity of wine fluctuates. However, unexpected variations in acidity may adversely affect the wine quality [5].

Alcohols

The ethanol content in wine also impacts the extraction of the analytes, because higher concentrations of this compound reduces extraction of volatile phenols [79]. According to the experimental studies that confirmed the theoretical results, the alcoholic grade in commercial samples may vary from 11.0 to 14.3% (v/v) [80]. Needless to say, the presence of ethanol and their interactions with volatile aroma compounds is also an important factor [10, 16, 81, 82].

Fouling and presence of non-volatile compounds

In the pervaporation process for the separation of VOCs from wine, membrane fouling may occur depending on the composition of the feed. Fouling tends to occur more frequently when fermentation broth is used directly without any pre-treatment. Nanofiltration of the fermentation broth is commonly employed to reduce fouling. It is important to investigate the fouling effects of common non-volatile compounds like proteins and yeast extracts to understand their impact on the process. These compounds may contribute to fouling due to their interactions with the membrane surface [83, 84].

2.7 Separation of VOCs by pervaporation

2.7.1 Solution-diffusion model

In pervaporation, the feed solution is introduced to one side of the membrane, and the other side is maintained at a sub-atmospheric pressure using a vacuum pump to induce the permeation. Different components (for example, water and ethyl phenols) pass through the membrane at different permeation rates due to different perm-selectivity. Figure 2-2 illustrates the pervaporation process. Currently, the most common application of pervaporation is dehydration of ethanol, which can produce a residue stream of almost pure ethanol and can be considered an effective replacement for distillation processes in which the separation is stopped at azeotropic point in the best case scenario [85]. Additionally, pervaporation is widely evaluated for separation of low concentration volatile organics from water for pollution control as well as for some food applications [86].

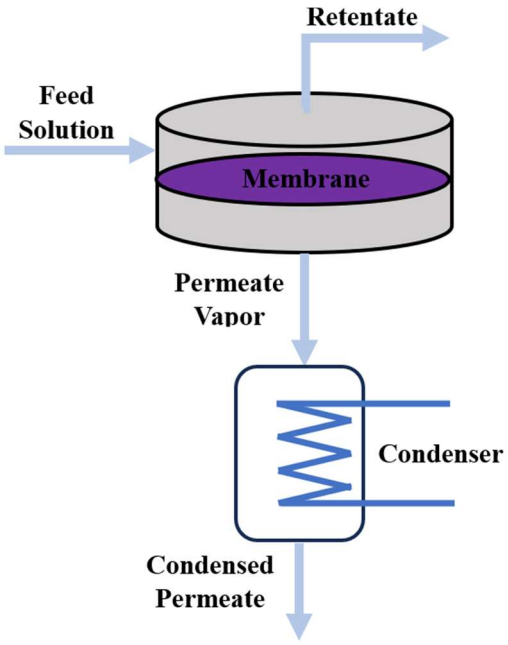


Figure 2-2 Schematic of pervaporative membrane separation process.

The pervaporation process with polymer membrane is described using the solution-diffusion mechanism. Pervaporation process is generally made up three sequential steps: permeant adsorption on membrane surface, diffusion through the membrane and desorption from the downstream side of the membrane, where the three steps are shown in **Figure 2-3.** Both the sorption and desorption steps are thought to occur very fast, and equilibria are built instantaneously on both sides of the membrane, and diffusion is the rate controlling step in pervaporation.

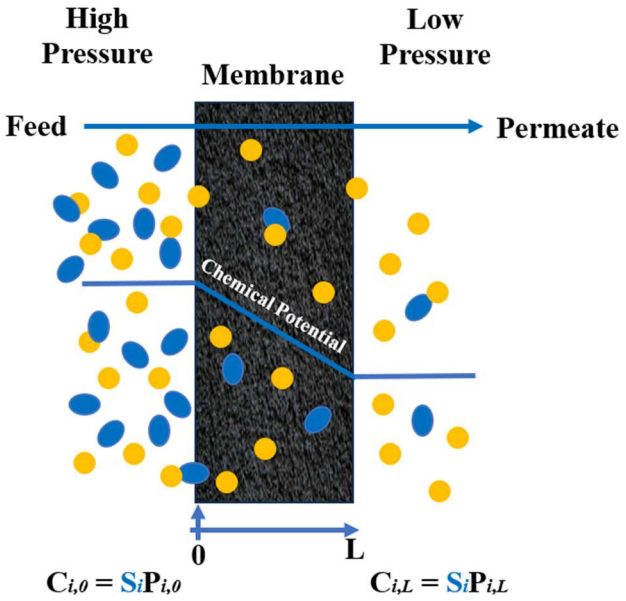


Figure 2-3 Schematic of pervaporation process based on the solution-diffusion model.

Fick's law equation which can be applied to describe the pervaporation process is defined as below:

$$J_i = -D_i \frac{dC_i}{dL} \tag{2-1}$$

where J_i is the permeation flux of component i (mol/(m^2·h)); D_i is the diffusion coefficient (m^2/s); L represents membrane thickness (m), and dC_i/dL is the concentration gradient across the

membrane (mol/m^4). It should be noted that C_i is the permeate concentration (mol/m^3) in the membrane, not the liquid concentration in the feed.

The concentrations at membrane surfaces can be described by the Henry's law:

$$C_{i.} = S_i p_i \tag{2-2}$$

where S_i is the Henry's solubility coefficient (mol/(m^3·Pa)), and pi is the partial vapor pressure of component i (Pa) in equilibrium with the feed liquid. If Henry's solubility coefficient is independent of concentration, by combing Equations (2-1) and (2-2), the below equation is obtained:

$$J_i = -D_i S_i \frac{dp_i}{dL} \tag{2-3}$$

Integrating Equation (2-3) over the thickness of the membrane gives:

$$J_i = D_i S_i \frac{p_{i,0} - p_{i,L}}{L} \tag{2-4}$$

And finally, defining the permeability coefficient, Pi, as D_iS_i:

$$J_i = P_i \frac{p_{i,0} - p_{i,L}}{L} \tag{2-5}$$

where P_i is the permeability coefficient of permeant i (customarily in units of Barrer), which equals to the product of diffusion coefficient D_i and solubility coefficient S_i. The subscripts 0 and L represent the positions of the feed and permeate interfaces, respectively. As indicated in Equation (2-4), the partial pressure difference across a membrane may be considered as the driving force for pervaporation. More specifically, Equation (2-4) can be further expressed as:

$$J_i = P_i \frac{X_i \gamma_i p_i^{sat} - Y_i P^p}{L} \tag{2-6}$$

where p_i^{sat} and γ_i represent the saturated vapor pressure and activity coefficient of permeation component i, respectively, and X_i and Y_i are the molar fractions of the permeate in feed and

permeate, respectively, and p^p is the pressure on the permeate side. The membrane permeability coefficient to a specific component can be calculated from permeation flux using Equation (2-5), where the saturated vapor pressure and the activity coefficient in the feed can be determined using a process simulator, (e.g., Aspen).

In this work, due to lack of data, it was impossible to calculate thermodynamic properties and activity coefficients of ethyl phenols using Aspen. But the trend of the change of the activity coefficients can be estimated. The activity coefficients of ethyl phenols at the ambient temperature in aqueous solution can be determined using the mutual solubility method [12]. This method is applicable only to highly hydrophobic compounds and involves measuring the concentration of the aroma compound in an aqueous phase that is in equilibrium with the organic compound phase (i.e. vanillin). If thermodynamic equilibrium is achieved, the activity of the aroma compound in the organic phase can be related to its activity in the aqueous phase as described by [13]:

$$\gamma_i^{org} \cong 1 \; and \; x_i^{org} \cong 1; \; \gamma_i^{\infty} = \frac{1}{x_i^{aqu}}$$

$$a_i^{aqu} = a_i^{org} \tag{2-7}$$

Assuming that the organic phase is almost pure compound then:

$$\gamma_i^{aqu} x_i^{aqu} = \gamma_i^{org} x_i^{org} \tag{2-8}$$

In the Equation (2-8) provided, a_i represents the chemical activity of compound i,, x_i denotes the molar fraction of compound i in a liquid phase, and γ_i^{∞} represents the activity coefficient at infinite dilution.

The permeability coefficient is normalized by membrane thickness, P_i/L, which is practically more useful, especially in the case of composite membranes and asymmetric membranes where

accurately measuring the effective membrane thickness is difficult. The permeability coefficient normalized by membrane thickness, P_i/L , is the permeance:

$$\frac{P_i}{L} = \frac{J_i}{X_i \gamma_i p_i^{sat} - Y_i P^p} \tag{2-9}$$

The membrane performance is generally expressed in terms of permeation flux (J_i) and separation factor (α) or enrichment factor (β). The permeation flux, J_i, which is the permeation rate per unit membrane area, can be calculated by:

$$J_i = \frac{m_i}{t.A_m} \tag{2-10}$$

where m_i is the mass of permeate collected during a period of time t, and A_m is the effective membrane area.

The membrane selectivity, defined as the ratio of permeability coefficients of different permeating species, is given by:

$$\alpha_{i,j} = \frac{P_i}{P_j} = \frac{D_i S_i}{D_j S_j} \tag{2-11}$$

In practice, the membrane selectivity can be characterized by the separation factor which is expressed as:

$$\alpha = \frac{Y_i/Y_j}{X_i/X_j} \tag{2-12}$$

The enrichment factor is defined as the concentration of permeate to the feed concentration ratio by:

$$\beta = \frac{Y_i}{X_i} \tag{2-13}$$

where X and Y are the molar fractions of the permeant in feed and permeate side and the subscripts i and j denote different permeation components. In dilute feed systems, it can be assumed that X_j

≈ 1, where j represents the solvent (i.e., water) and accordingly the separation factor is close to the enrichment factor unless the permeate is substantially enriched with component i. Moreover, in the context of dilute organic solutions, it is reasonable to assume that the overall molar volume concentration remains nearly constant throughout pervaporation. The organic enrichment factor is defined as follows [87]:

$$\beta = \frac{Y_i}{X_i} = \frac{1}{X_i}\frac{J_i}{J_{tot}} \tag{2-14}$$

When the permeate pressure is low enough that can be neglected, by combining equations (2-9) and (2-12), the separation factor can be expressed as:

$$\alpha = \frac{P_i}{P_j}\frac{\gamma_i}{\gamma_j}\frac{p_i^{sat}}{p_j^{sat}} \tag{2-15}$$

It can be perceived from equation (2.15) that the membrane selectivity is dependent on three factors. First, membrane intrinsic property such as permeability coefficient to the permeating species would affect the membrane selectivity. Second, membrane selectivity is influenced by the activity coefficients of permeating species in the feed, which are determined by the feed composition and temperature. Ultimately, the saturated vapor pressure of the permeating species at the given temperature would impact on the membrane selectivity. All in all, pervaporation performance is affected by all these factors which will be discussed further in the following.

2.7.2 Influence of operating condition

Feed concentration

The efficiency of pervaporation is impacted by the concentration of the feed solution through three main factors: mass transfer driving force, sorption, and diffusion. As per the principles of vapor-liquid equilibrium, the concentration of the feed directly affects both the partial vapor

pressure of the components permeating through the membrane and the driving force for transmembrane transport. Moreover, higher feed concentrations result in increased uptake of permeants by the membrane. Both solubility and diffusivity are influenced by the feed concentration. Additionally, when dealing with multiple volatile organic compounds (VOCs), the coupling effect arising from interactions among these compounds can alter the permeation behavior of individual components.

Operating temperature

Temperature has a considerable influence on the pervaporation performance due to temperature dependencies of both solubility and diffusivity coefficients. The relationship between the temperature and the permeation flux generally follows the Arhenius equation:

$$J_i = J_{oi} exp\left(\frac{E_{Ji}}{RT}\right) \tag{2-16}$$

where E_{Ji} is apparent activation energy for the permeation of the component i (J/mol). J_{oi} is a pre-exponential factor, and R and T are the universal gas constant (8.314 J/mol.K) and the temperature (K), respectively. Needless to say, E_{Ji} characterizes the overall effect of temperature on membrane permeability and driving force. As previously mentioned, because both partition and diffusion of the permeant in the membrane can affect the permeation through the membrane, the permeability coefficient is considered a product of diffusivity coefficient and solubility coefficient, i.e., $P_i = D_i \cdot S_i$, and the dependencies of D_i and S_i on the temperature can be given by:

$$D_i = D_{oi} exp\left(\frac{E_{Di}}{RT}\right) \tag{2-17}$$

$$S_i = S_{oi} exp\left(\frac{\Delta H_i}{RT}\right) \tag{2-18}$$

And hence:

$$P_i = P_{oi} exp\left(\frac{E_{Pi}}{RT}\right) \tag{2-19}$$

where $E_P = E_D + \Delta H$, and E_P is the 'true' activation energy of permeation, which is a combination of the activation energy of diffusion E_D and the enthalpy of dissolution ΔH of the permeant in the membrane. D_{oi}, S_{oi}, and P_{oi} are the pre-exponential factors and $P_{oi} = D_{oi} \cdot S_{oi}$. Merging Equation (2-9) with Equation (2-19) gives:

$$\frac{P_i}{L} = \frac{J_i}{\Delta p} = P_{oi} exp\left(\frac{E_{Pi}}{RT}\right) \tag{2-20}$$

where Δp is the transmembrane partial pressure difference. Thus, the activation energy for permeation E_P can be calculated from the slope of $ln(J_i/\Delta p)$ vs. $1/T$ plot. As a rule of thumb, E_P can be estimated by subtracting the molar heat of vaporization ΔH_V from the 'apparent' activation energy of permeation E_J.

$$E_{Pi} = E_{Ji} - \Delta H_{Vi} \tag{2-21}$$

It is much easier to calculate E_P from corresponding E_J data by plotting ln J vs. 1/T. However, cautions are strongly advised because Equation (2-21) only applies when the permeate pressure is sufficiently low.

The numerical values of E_J are usually between 4 to 92 KJ/mol, which are smaller than the heat of vaporization of many organic compounds, resulting in a negative value of E_P [88]. This is perceptible as $E_P = E_D + \Delta H_V$ because though E_D is positive, ΔH_V is negative, resulting in a negative E_P. This is in accordance with observations as in an exothermic sorption process, the dissolution dominates over diffusion, and this is why permeability decreases with an increase in the temperature.

Permeate pressure

Maintaining low permeate pressure is crucial for maximizing the separation efficiency in pervaporation, as higher transmembrane pressure increases the driving force for permeation. Both theoretical analyses and experimental observations have confirmed that increasing permeate pressure significantly reduces permeation flux [89, 90]. Moreover, permeate pressure also affects selectivity, although the direction of this influence varies based on the relative volatility of the permeating components. Typically, components with higher saturated vapor pressures exhibit lower sensitivity to changes in permeate pressure as far as the permeation flux is concerned.

Feed flowrate

The hydrodynamic conditions of the feed solution can also impact pervaporation performance. One notable phenomenon is concentration polarization, where the less selective component accumulates on the membrane surface on the feed side. However, in the pervaporation of volatile organic compounds (VOCs), given their low concentrations in wine, the water concentration on the membrane surface closely mirrors its bulk concentration, resulting in negligible effects of concentration polarization on aroma permeation. Moreover, it has been demonstrated that concentration polarization can hardly dominate the performance of pervaporative membranes due to their limited permselectivity. [90]. In cases involving membranes with high permselectivity, the impact of concentration polarization cannot be overlooked. Therefore, measures must be taken to address this issue by controlling the hydrodynamic conditions of the feed. Typically, employing a circulating feed pump to generate a highly turbulent feed solution is advisable. However, it's important to ensure that the energy consumption of the pump remains within acceptable limits.

This approach can help mitigate concentration polarization and optimize the performance of pervaporative membranes with high permselectivity.

2.7.3 Pervaporation of low volatile organic compounds from dilute aqueous solutions

Despite recent progress in reverse osmosis technology, certain theoretical constraints have been identified in cases where the goal is to remove low molecular weight solutes from dilute aqueous solutions. Achieving effective separation always necessitates a considerable pressure differential across the membrane, leading to high energy consumption. Thus, pervaporation could be seen as a supplementary technique to reverse osmosis for extracting light solutes, given their ability to preferentially adsorb and diffuse to the membrane. In this scenario, only a small portion of the feed needs to pass through the membrane, unlike reverse osmosis where all solvents must traverse. However, these notions are purely theoretical and rely on the availability of appropriate membrane materials and optimal operating conditions [91].

According to some studies on the pervaporability of low volatility organics from water, it was stated that high boiling (low volatility) organic compounds can be separated from water via pervaporation if the following criteria are fulfilled [92, 93]:

(a) The organic compounds exhibit non-ideal behavior when mixed with water, deviating from Raoult's law in a positive manner, indicating activity coefficients greater than 1.

(b) The pure organic species possess a low or negligible vapor pressure.

(c) The membrane is preferentially permeable to the organic components in the solution.

Under these conditions, pervaporation produces an aqueous retentate and an organic contaminated permeate, both of which could serve as the desired output of the process, depending

on target the applications. Implications relevant to pervaporation of a "positive" non-ideal solution behavior, indicative of minimal molecular interaction, include:

(a) Restricted solubility of the organic compound in water, leading to phase separation upon enrichment beyond their respective solubility limits.

(b) Evaporation along with water vapor, meaning that in the vapor phase, the partial pressures sum up to the total of the individual pure component vapor pressures. Consequently, the mole fraction of the low volatility organic compound in the equilibrium vapor phase is:

$$\left.\begin{array}{c} p \approx p^0_{H_2O} + p^0_{org} \\ p^0_{org} \ll p^0_{H_2O} \end{array}\right\} \rightarrow x_{org} = \frac{p^0_{org}}{p^0_{H_2O}} \qquad (2\text{-}22)$$

(c) Another consequence of "positive" non-ideality is the presence of positive azeotropes, which are compositions with constant boiling points and higher vapor pressures than either of the pure components in the solution.

2.8 Membrane material

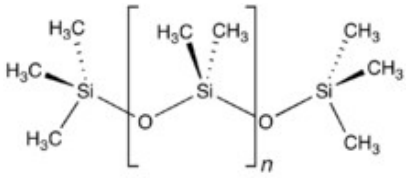
To effectively separate organic compounds from aqueous streams via pervaporation, it's essential that the membrane materials exhibit a preference for organic compounds, necessitating their organophilic or hydrophobic nature to enhance affinity towards these compounds. Common organophilic membrane materials include polydimethylsiloxane (PDMS), PEBA 2533, polyvinylidene fluoride (PVDF), and poly(1-trimethylsilyl-1-propyne) (PTMSP). The membrane's role is pivotal in regulating the pervaporation process, particularly in organic-water mixtures, where the objective is typically either to separate water from organic substances or to extract organic substances from water. Polymer membranes used in pervaporation can be classified into two types: glassy or rubbery (elastomers). These membrane types offer distinct properties and are

selected based on specific application requirements and the nature of the organic-water mixture being processed. [94].

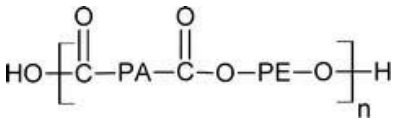
Glassy polymers are defined by having a glass transition temperature higher than room temperature or the operational temperature, falling into three categories: crystalline, semi-crystalline, and amorphous polymers. Typically, glassy polymers demonstrate a tendency to permeate water. Conversely, elastomers have a glass transition temperature below room temperature or the operating temperature. Elastomer polymer chains contain relatively small non-polar side groups, leading to a flexible structure that promotes the permeation of organic substances. Consequently, elastomers serve as suitable membrane materials for selectively extracting organics from water [95].

Figure 2-4 depicts the structures of common polymeric materials utilized in the fabrication of pervaporative membranes. Among these, membranes fabricated from PDMS, also known as silicone rubber, are extensively employed for separating organic compounds from water streams. PDMS is considered a versatile membrane material due to its alternating -O-Si-O- structure, which imparts high flexibility. Its chemical and mechanical stability render it suitable for easy processing into dense tubes or as the selective layer of composite membranes. PDMS exhibits excellent permselectivity, facilitating the separation of various VOCs such as benzene, toluene, methanol, and others, as well as some organics with high boiling points in practical applications [96-102]. Silicone rubber membranes have demonstrated successful implementation in industrial applications, achieving separation factors of up to 1000 for the removal of VOCs from water. Despite the development of other rubbery materials with potentially higher selectivity, PDMS remains prevalent for VOCs separation. This is primarily due to such factors as ease of membrane fabrication and membrane stability. These practical considerations outweigh the potential

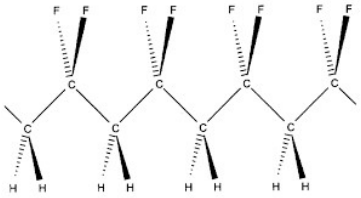
advantages offered by materials with higher selectivity in many cases [103]. In addition to PDMS, other rubbery polymers such as polybutadiene [66], nitrile butadiene rubber, styrene butadiene rubber [67, 68], and polyurethane [69, 70] have also been shown to be excellent materials for the separation of organic compounds from water.



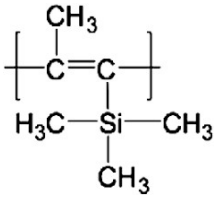
PDMS



PEBA 2533



PVDF



PTMSP

Figure 2-4 Structures of common polymers utilized in fabricating organophilic membranes.

To enhance the permeation flux of rubbery polymers, which typically exhibit low flux, alternative materials with high free volume (e.g., PTMSP, poly-4-methyl-2-pentyne (PMP), and other polymers of intrinsic microporosity are being investigated to achieve higher flux permeation [39, 71]. Among these, PTMSP stands out for its very rigid backbone and exceptionally high fractional free volume (0.34), making it the most permeable glassy polymer known to date. It has garnered significant attention in numerous studies for gas separation and separating organics from water due to its remarkably high permeabilities and separation factors [39, 72]. However, polymers of intrinsic microporosity membranes have not yet found industrial applications due to the

substantial reduction in permeability over time. The performance of these membranes is unstable due to film densification and reduction of free volume resulting from polymer chain relaxation over time [39, 73]. Although maintaining the initial high free volume state is challenging, their separation characteristics and stability can be enhanced through chemical modification (crosslinking, functionalization, graft-polymerization, etc.) or physical modification (incorporation of inorganic or organic fillers). These modifications may improve the prospects of this material for practical applications [74-76].

Chapter 3

Separation of off-odor volatile aroma compounds from binary solutions by pervaporation using PEBA membrane

3.1 Introduction

Pervaporation, an emerging technique for the separation/recovery of VOCs has attracted great attention due to its lower energy consumption, high separation efficiency, and no need to use solvents. To achieve high separation performance (e.g., high permeation flux and separation factor) not only the nature of both membrane and organic compounds but also operating conditions should be considered. Though so far PDMS membranes have been employed in pervaporation processes, PEBA membranes are becoming popular because of their high flux and selectivity for the separation of VOCs [86]. PEBA represents a class of copolymers featuring microbiphasic structures comprising soft polyether segments and hard polyamide segments. Modifying the ratio of these segments allows for the creation of membranes with diverse properties [104]. The soft segments of PEBA 2533 offer flexibility and accommodate molecular interactions during pervaporation, aiding in the permeation of hydrophobic, polar compounds by facilitating membrane swelling. These segments also enhance selectivity towards hydrophobic compounds. The hard segments provide structural integrity and stability to the membrane and prevent excessive swelling in water, and higher affinity to hydrophilic compounds. This balance of soft and hard segments makes PEBA 2533 a suitable choice for the study.

Volatile phenolic compounds in wine are molecules that evaporate easily at room temperature, contributing to its aroma and flavor and perceived by the olfactory system when wine is smelled or tasted, enhancing its complexity and character. Generally, they are polar due to the presence of polar hydroxyl (-OH) groups attached to the benzene ring, but the presence of other functional groups and structural molecules can vary their polarity. Furthermore, they are often hydrophobic, particularly those present in beverages and wine. The winemaking industry can use pervaporation process to meet the different needs like alcohol and acidity adjustment [84], concentration of desirable flavors and pigments [105], removal of off-odor compounds [106], or aging and maturation. While pervaporation has more applied for the alcohol adjustment, evaluation of this technique to separate off-odor ethyl phenols is lacking. Pervaporation using organophilic PEBA membrane is expected to have great potential in the separation of off-odor ethyl phenols due to their hydrophobic and polar nature. It is preferred to other techniques like extraction and distillation because of their high boiling point and lack of compatible solvents. Additionally, since the concentration of ethyl phenols is usually less than 150 ppm, it is pervaporation which can effectively perform the separation using the selective membrane [70].

Accordingly, the separation and recovery of ethyl phenols from red wine is the main purpose of this work. However, separation efficiency of volatile compounds is conducted in this study using the model solutions due to coupling effects of the volatile components. Binary solutions involving only two components (water + aroma) simplify the permeation analysis and allows for a better understanding of the separation behavior. Moreover, studying binary solutions provides baseline data for comparing and evaluating the separation efficiency and selectivity of membranes, and this will serve as a reference point for assessing the performance of membranes in more complex multicomponent mixtures. Finally, analyzing binary solutions helps understand the

interactions between membrane materials and individual components, such as solubility, diffusivity, and permeability behaviors. These all emphasize the importance of investigating pervaporative separation of ethyl phenols in binary solution, particularly in view that little work has been conducted for the separation using PEBA membranes.

Investigation of interactions between permeating components and membranes is commonly performed at different operating conditions (e.g., feed concentration and temperature) [107]. Feed concentration significantly influences the performance of pervaporation of volatile organic compounds in binary solutions as higher feed concentrations typically result in increased driving forces for mass transfer, leading to higher permeation fluxes. Feed concentration is also a significant parameter because activity coefficients vary with the concentration. Moreover, interactions between the membrane and organic solute can change the degree of swelling, which affects permeation flux and selectivity. Operating temperature also influences the properties of the membrane including solubility and diffusivity coefficients, activity coefficient, degree of swelling, and saturated vapor pressure. As a result, permeation flux and selectivity are affected by feed concentration and temperature significantly.

3.2 Experimental

3.2.1 Material

PEBA pellets (grade 2533) (comprised of 80 wt.% poly (tetramethylene oxide) as the ether segment and 20 wt.% nylon 12 as the amide segment) were provided by Arkema Inc. N, N dimethylacetamide (DMAc), which was used to dissolve PEBA polymer during membrane preparation was supplied by Sigma Aldrich. 4-EG and 4-EP were purchased from Sigma Aldrich, and their basic properties are listed in Table 3-1. The feed solutions used in all experiments were

freshly prepared by dissolving a certain amount of aroma compounds in de-ionized water. All the chemical reagents used in this work were of analytical grade and used without any further purification.

Table 3-1. Properties of 4-EG and 4-EP.

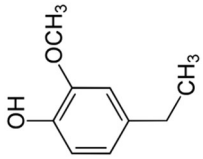
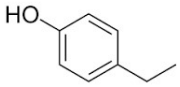
IUPAC name	**4-ethyl-2-mthoxyphenol**	**4-ethylphenol**
Molecular formula	$C_9H_{12}O_2$	$C_8H_{10}O$
Molecular Structure		
CAS No.	2785-89-9	123-07-9
Physical description	Oily liquid	Colourless/white needle like crystal
Odor type	Smoke, clove, spice	Phenolic, barnyard
Odor threshold (ppb)	33	440
Molecular weight (g/mol)	152.19	122.16
Topological Polar Surface Area ($Å^2$)	29.5	20.2
Melting Point (°C)	-7	46
Boiling Point (°C)	235-236 (@ 760 mmHg) 82-85 (@1.3 mmHg)	218 (@ 760 mmHg)

Table 3-1. Continued.

IUPAC name	4-ethyl-2-mthoxyphenol	4-ethylphenol
Solubility in water (g/l)	0.693	2.4
Density (gr/cm^3) (@ 20 °C)	1.064	1.011
Vapor pressure (mmHg)	0.0173 @ 25 °C	0.0372 @ 25 °C
λ_{max} (nm)	285	230
Molar Volume (cm^3/mol)	144.7	124.7
pK_a	10.3	10.38
γ^{∞}	8383	23742

3.2.2 Membrane preparation

Membrane was prepared was by solution-casting, and the procedure was similar to what described in previous studies [108]. The predetermined amount of PEBA 2533 was dissolved in DMAc to reach a 15 wt.% solution. The mixture of PEBA polymer and DMAc was placed in water bath at 80 ℃ with vigorous stirring for 6 h to form a homogenous solution, and the solution was kept in the oven at 70 ℃ overnight to release the gas bubbles generated during stirring. Then the polymer solution was cast onto a hot glass plate (70 ℃) using a preheated casting knife. Thereafter, the glass plate with the cast film was placed in an oven at 70 ℃ for at least 48 h to evaporate the solvent. Finally, the glass plate was removed from the oven and the thin film of the membrane was detached from the glass plate by immersing in de-ionized water for a few seconds. The thickness of the dray PEBA membrane was measured around 50 μm using a Starrett micrometer.

3.2.3 Pervaporation

Pervaporation experiments were conducted using a lab-scale setup, as shown in **Figure 3-1**. The operating temperature of the feed tank was controlled by a Dyna-Sense® Thermoregulator Control System. The feed solution (1.0 L) was continuously circulated through the permeation cell, which had an effective membrane area of 22.1 cm^2. This membrane cell consisted of two detachable stainless-steel parts with an inlet/outlet for feed flow and an outlet for permeate vapor withdrawal (**Figure 3-2**). A porous stainless-steel plate supported the membrane within the cell, and the two parts were tightly sealed with a rubber O-ring. Vacuum was applied using a vacuum pump on the permeate side to induce permeation, maintaining a permeate pressure of approximately 4 kPa absolute. The permeate vapor was condensed and collected in a cold trap immersed in liquid nitrogen, and the permeation rate was measured gravimetrically.

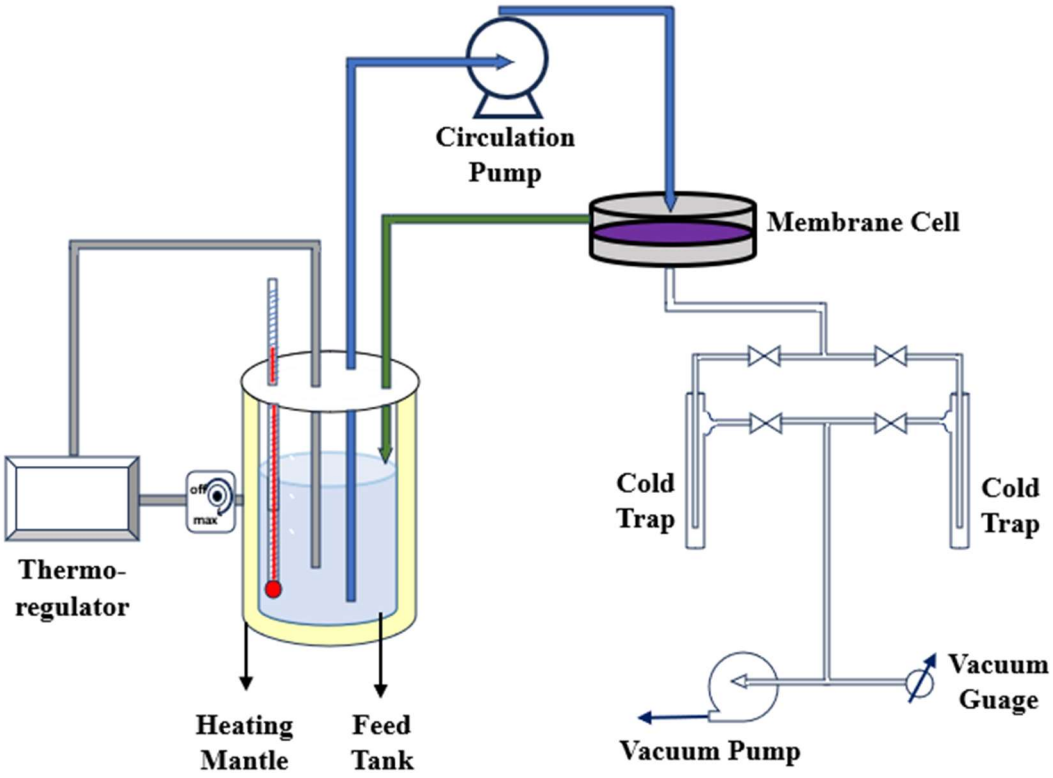


Figure 3-1 Schematic diagram of pervaporation set-up.

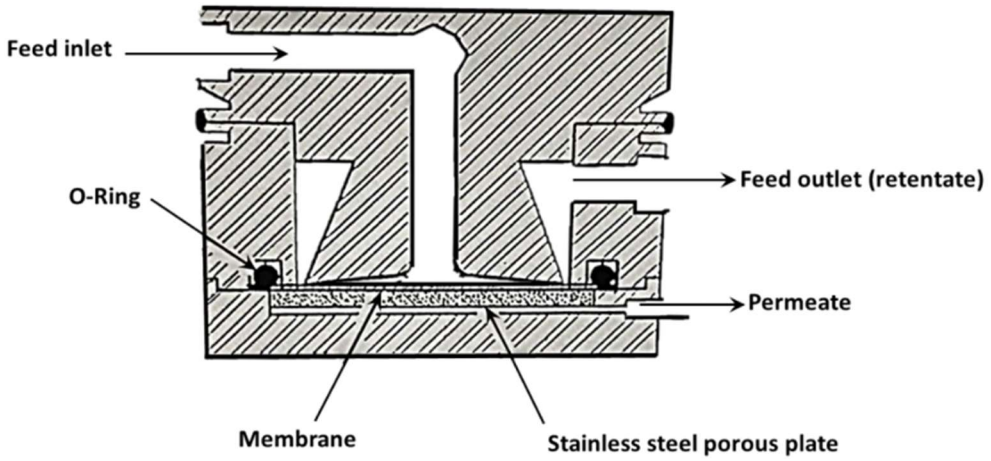


Figure 3-2 Schematic diagram of the membrane cell [86].

Concentrations of feed and permeate mixtures were determined using a Shimadzu UV-vis spectrophotometer for binary aroma/water mixtures. If necessary, samples were diluted with deionized water before analysis. Conditioning the system involved circulating the feed solution through the membrane cell at predetermined operating conditions for at least 2 hours to achieve steady state. Permeation flux was periodically measured until steady state flux was reached, indicating steady-state permeation. Approximately 2 hours were required for the system temperature to stabilize due to continuous circulation of the feed from the feed tank to the membrane cell. When testing the membrane with each aroma compound solutions, the system was flushed with deionized water until none of its trace from previous runs was detected in the flushing solution before introducing the binary solution of another aroma. The membrane performance was characterized in terms of permeation flux (J) and enrichment factor (β).

3.3 Results and discussion

3.3.1 Effect of feed concentration on the membrane performance

The effects of feed ethyl phenols concentrations on the total permeation flux at different temperatures (30 to 60 °C) are shown in **Figure 3-3**.

The impact of varying 4-EG and 4-EP concentrations in feed solutions on total permeation flux during pervaporation processes across a range of temperatures is explored. The total permeation fluxes for 4-EG and 4-EP solutions exhibit only a slight increase with an increase in feed solute concentrations at a given temperature. To better interpret the results, the partial fluxes of ethyl phenol (Figure 3-4) and water (Figure 3-5) were plotted against the VOC concentrations in the dilute binary solutions. It is obvious that both total flux and water flux were similar. On the other hand, it is noticed that the aroma permeation flux increases linearly with an increase in its concentration in the feed. However, the flux of ethyl phenols did not exceed more than about 1.0 $g/m^2.h$ under all testing conditions in this work. This flux is considerably low in comparison to the water flux which is around 86.1 $g/m^2.h$. So, it can be seen that the total flux remains nearly constant and is close to the water flux. This behavior is commonly observed for the pervaporation of dilute solutions [87, 109].

A comparison between the water flux of this membrane in the presence of ethyl phenols with data from other studies shows a significant difference. Though the membrane thickness would be a key parameter affecting the pervaporation permeation flux [110], the low water permeation flux in this work could also be attributed to the nature of VOCs as well as their concentrations in the feed solution. When a membrane is in contact with the organic solutes, the organic molecules are sorbed into the membrane. The sorbate molecules loosen the polymer matrix, which results in membrane swelling. The membrane swelling will facilitate the permeating molecules diffusing

within the membranes. Thus, membrane swelling has a magnificent effect on the flux of the species in the pervaporation process. Apparently, the higher the concentration of the organic compound is in the solution, the greater the degree of membrane swelling. However, in dilute solutions where the solute content in the solution is so low that it does not cause significant swelling, the degree of swelling is too low to lead to considerable changes in the flux in this case. The mole fraction of water is supposed to be near unity and the molar volume of the feed solution is almost equal to the molar volume of water (18.7 cm^3/mol). Hence, it can be concluded that the total flux is almost equal to water flux.

Figure 3-4 illustrates the impact of feed concentration on ethyl phenols permeation flux at different temperatures. At a given temperature, the permeation fluxes of both ethyl phenols increased with an increase in the feed ethyl phenols concentration. This can be easily explained by the increased transmembrane driving force for permeation resulting from higher feed concentrations. Generally, at a given ethyl phenols concentration in the feed, the aroma permeation flux followed the order of 4-EP > 4-EG, which seemed to be inversely correlated to their molecular sizes. This pattern indicated the solute with smaller molecule sizes within the polymer matrix is more permeated through the membrane more easily than solute compounds with larger molecule sizes [87].

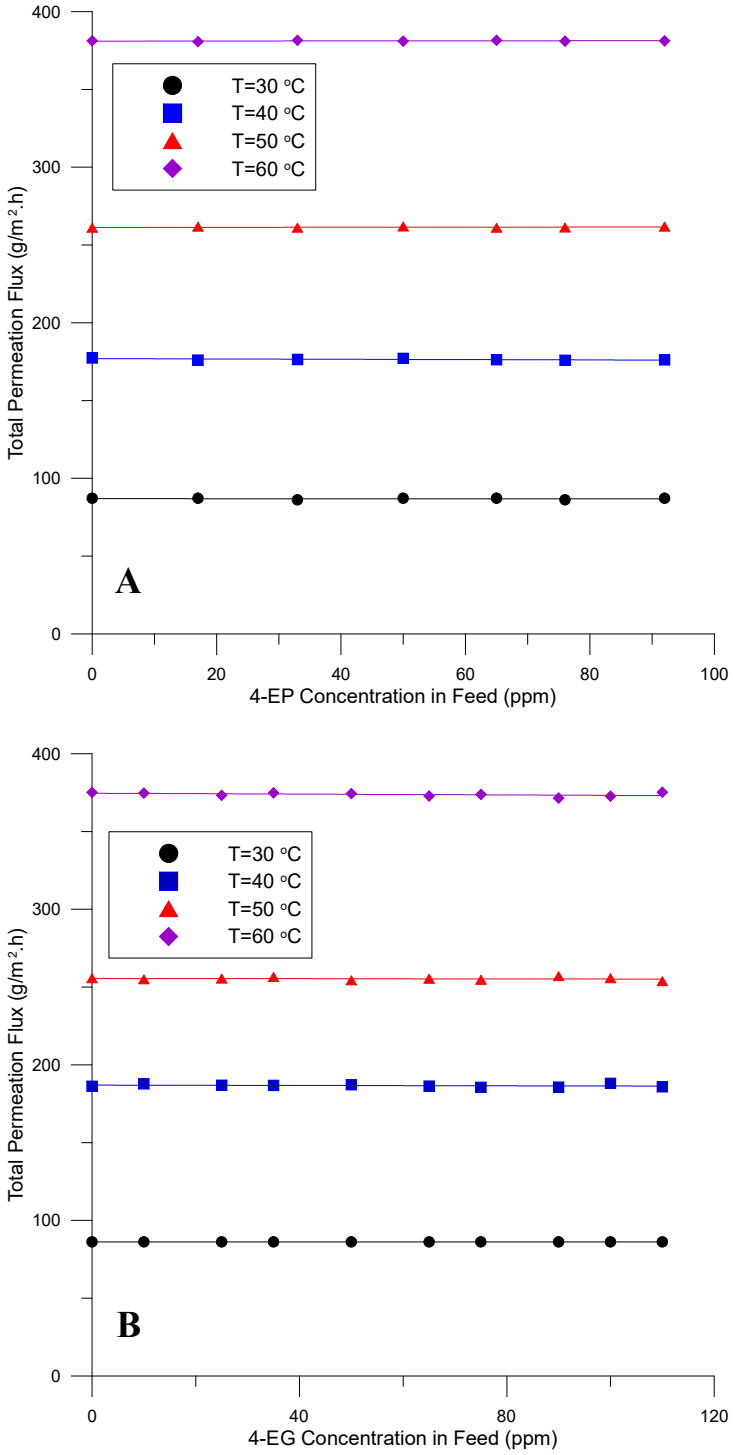


Figure 3-3 Effects of feed aroma concentration on total permeation flux at different temperatures, A: 4-EP, B: 4-EG.

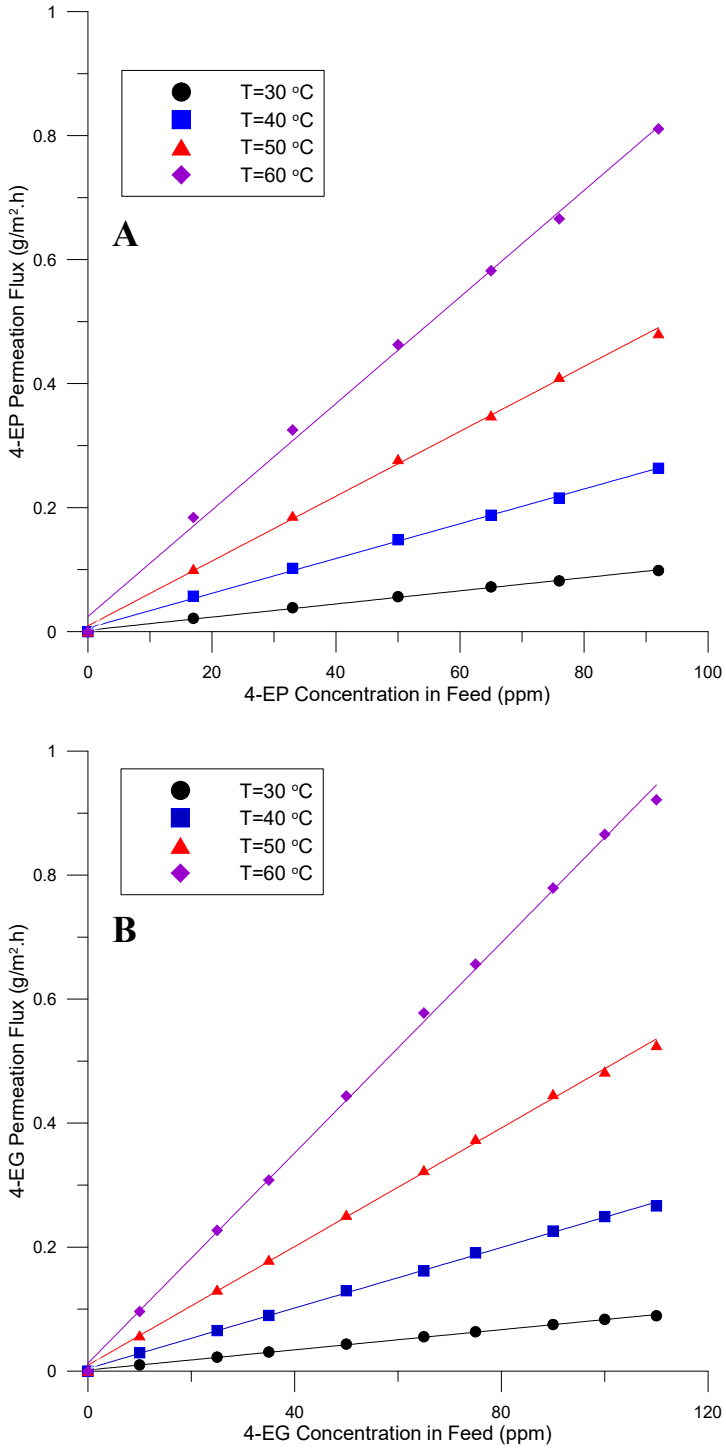


Figure 3-4 Effects of feed aroma concentration on aroma permeation flux at different temperatures, A: 4-EP, B: 4-EG.

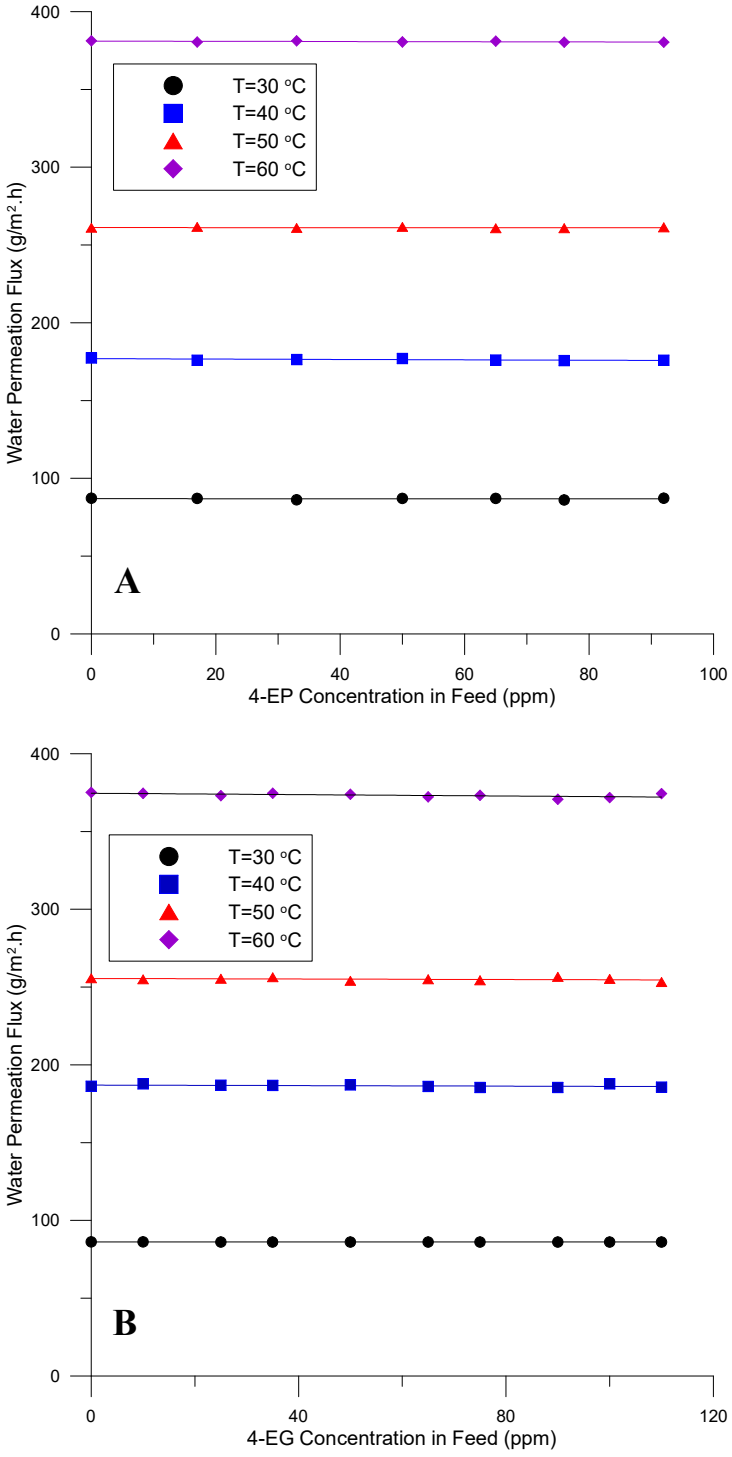


Figure 3-5 Effects of feed aroma concentration on water permeation flux at different temperatures, A: 4-EP, B: 4-EG.

The concentration of 4-EG and 4-EP in the permeate at different feed concentrations and temperatures are depicted in Figure 3-6. It is observed that the concentration of both organic compounds linearly changed with the feed concentration. Moreover, it can be noticed that concentration of 4-EG in the permeate at all feed concentrations exceeded its solubility limit. However, the 4-EP permeate concentration was lower than its solubility limit.

Figure 3-7 depicts the enrichment factor of the volatile organic solutes, 4-EG and 4-EP, based on their concentration in the permeate and their corresponding concentration in the feed solution at various temperatures. At a given temperature, the enrichment factor of both aromas decreased with an increase in feed VOC concentration and then reached a constant level when the feed VOC concentration was high enough. However, when the feed aroma concentration approaches very low values, it shows a little increment. Ignoring this small increase, it can be said that enrichment factor does not significantly vary with the solute concentration. It can be seen from Figure 3-4, that there is a linear correlation between organic permeation flux and feed VOC concentration. Moreover, the water permeation flux remained unchanged regardless of the feed concentration. Thus, referring to the Equation (3-14) , it can be inferred that the enrichment factor would not change significantly with a change in the 4-EG or 4-EP concentration in the feed solution [111].

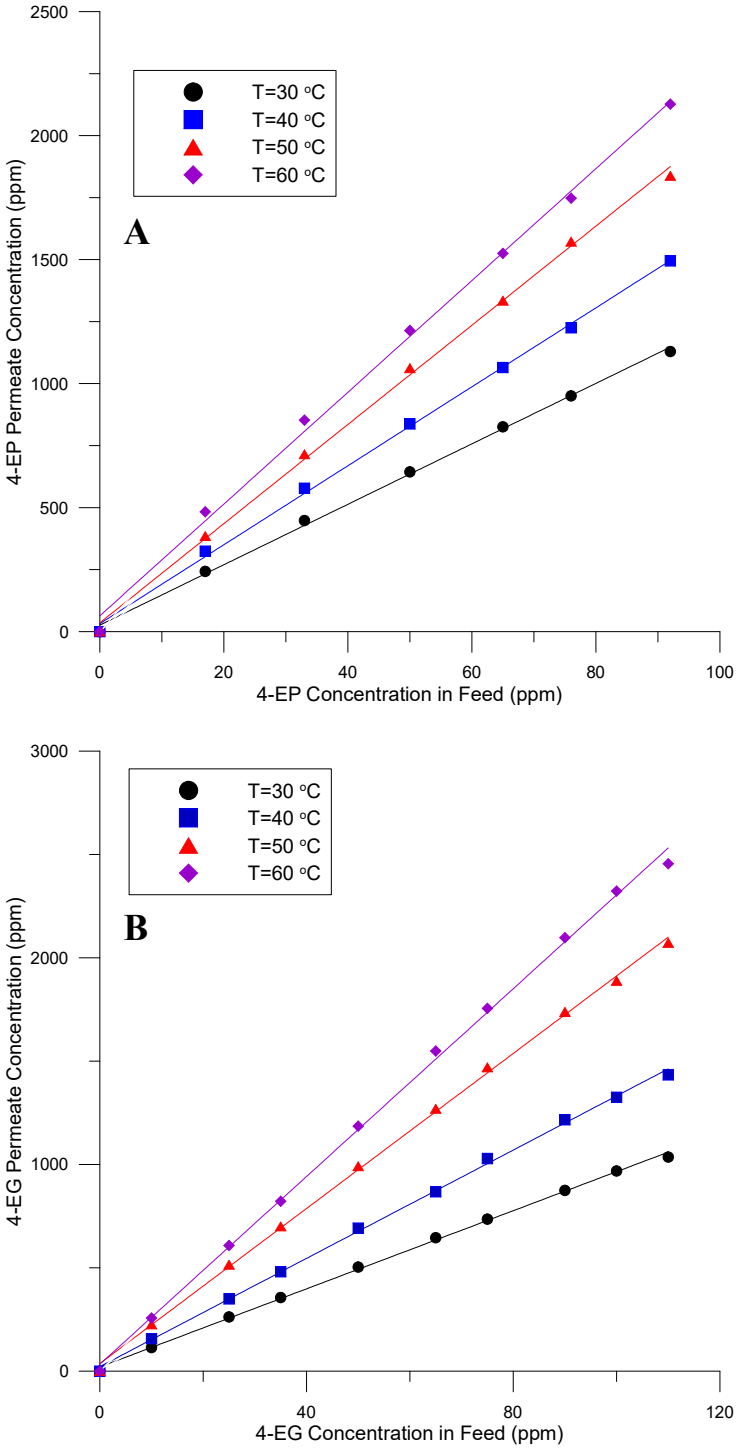


Figure 3-6 Effects of feed aroma concentration on aroma permeate concentration at different temperatures, A: 4-EP, B: 4-EG.

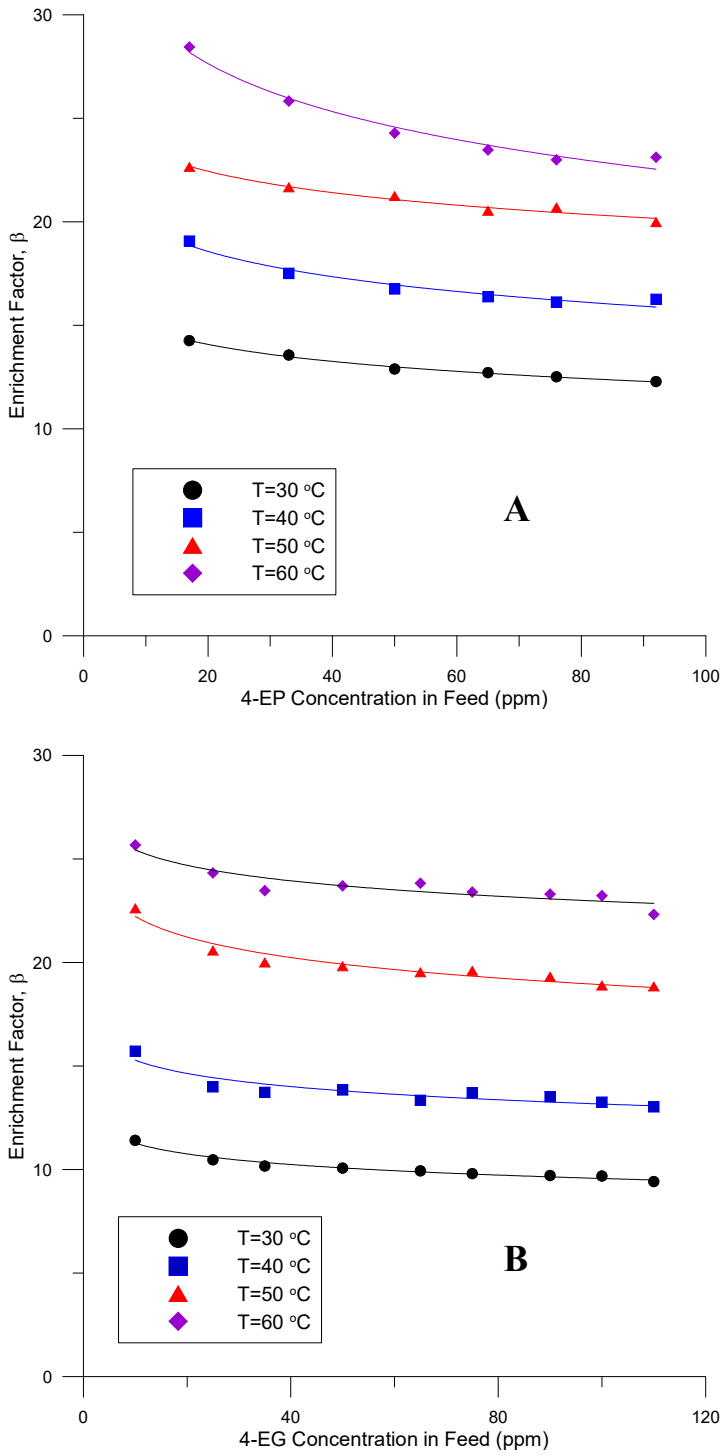


Figure 3-7 Effects of feed aroma concentration on aroma enrichment factor, β, at different temperatures, A: 4-EP, B: 4-EG.

Non-coupling effects also were observed in the pervaporation of these VOCs. The coupling effect pertains to the situation where the permeation rate of one permeant is influenced by that of others. When conducting pervaporation for the separation of a dilute aqueous mixture of VOC, the water flux remains relatively unaffected by changes in feed VOC concentration. However, the flux of the volatile aroma compound exhibits a significant increase with the feed concentration. Additionally, the water permeation flux showed only a little difference in the case of the separation of 4-EG or 4-EP [11]. This behavior was also observed by NGUYEN et al, [109] when they evaluated the pervaporation of chloroform, bromoethane or dichloromethane. They noted that water and organic constituents transported independently within the membrane. This conclusion was reached because the membrane experienced only minimal swelling due to the low concentrations of organics in the feed, which could have prevented plasticization and maintained constant diffusion coefficients for the substances to permeate through. Based on their assumptions, the consistency of the water flux can be attributed to a consistent driving force (the mole fraction of water remains practically equal to 1) and a constant diffusion coefficient within the membrane. The latter can be elucidated by the notion that small water molecules can permeate through the hydrophobic PEBA with minimal interaction with either the polymer or the organic solute. It is worth mentioning that these assumptions are not applicable to highly concentrated organic solutions.

3.3.2 Effect of temperature on permeation performance

The temperature dependency of the permeation flux follows to Arrhenius-type relation. Figure 3-8 illustrates the partial permeation fluxes of aromas and water plotted against reciprocal temperature on a semi-log scale. There was an eight-fold increase in the aroma flux when the operating temperature increased from 30 to 60 °C. This can be attributed to two main factors:

firstly, an elevation in temperature augments the saturated vapor pressure of the penetrant in the liquid feed, thereby enhancing the transmembrane driving force for permeation; secondly, at higher temperatures, the permeating molecules are more energetic, while the thermal motion of the polymer chains is intensified, facilitating penetrant diffusion in the membrane. The permeation flux was positively affected by temperature. The apparent activation energy for permeation (Ea), derived from the slope of the straight lines in Figure 3-8, followed the order of 4-EG > 4-EP > H_2O, the same as their respective molecular sizes (Table 3-2). This observation also corroborates the data presented in Figure 3-7, indicating that the aroma enrichment factor increases with rising temperature. The apparent activation energy for permeation, E_J, obtained from Figure 3-8, characterizes the overall temperature dependency of permeation flux that has accounted for both the driving force and membrane permeability.

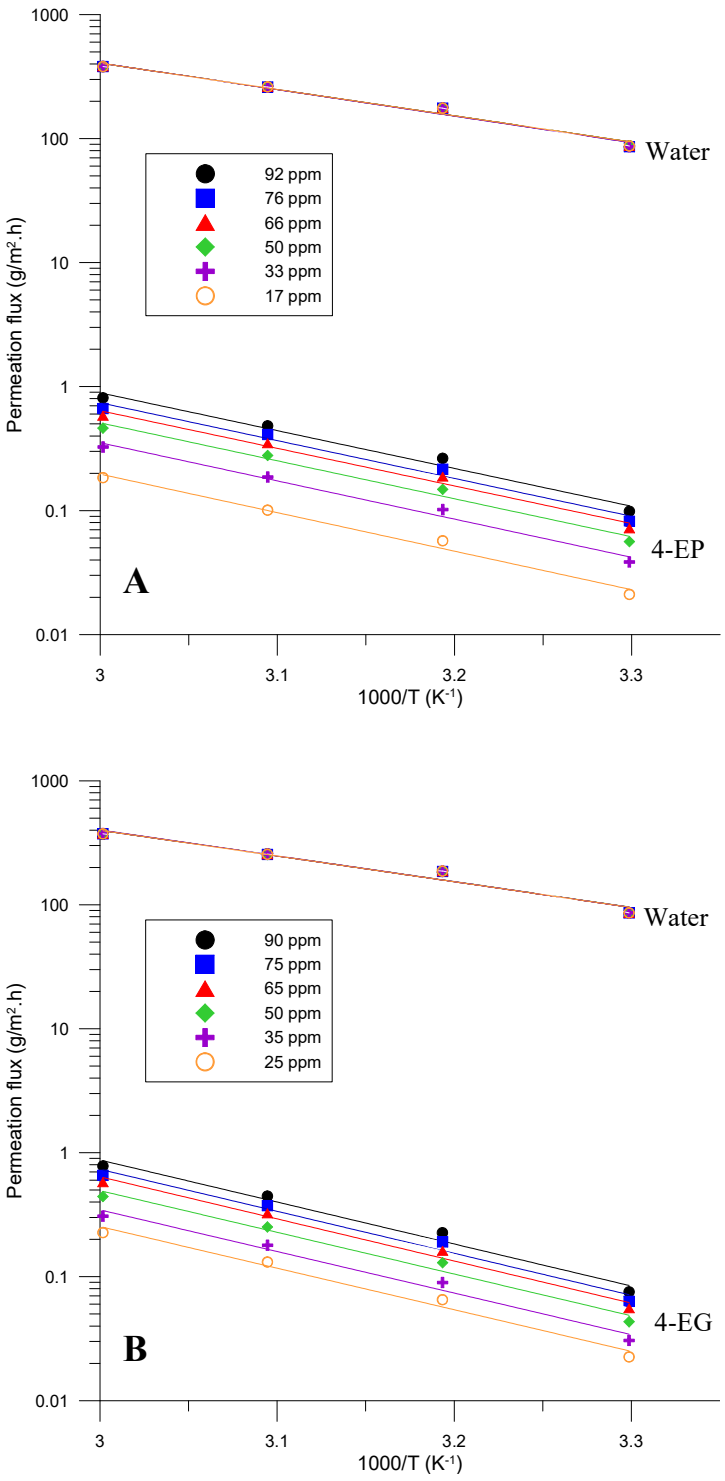


Figure 3-8 Effects of temperature on the partial permeation fluxes at different feed concentrations, A: 4-EP, B: 4-EG.

Table 3-2 Apparent activation energy for the permeation of ethyl phenols (E_{Jp}) and water (E_{Jw}) at various feed concentrations.

Feed conc. of 4-EP, ppm	E_{Jp} KJ/mol	E_{Jw} KJ/mol	Feed conc. of 4-EG, ppm	E_{Jp} KJ/mol	E_{Jw} KJ/mol
92	7.02	4.89	**90**	7.80	4.78
76	7.03	4.92	**75**	7.80	4.79
66	6.98	4.89	**65**	7.82	4.78
50	7.05	4.88	**50**	7.75	4.78
33	7.10	4.92	**35**	7.72	4.80
17	7.16	4.89	**25**	7.73	4.78

3.4 Possible sources of errors in experiments

Though experiments were conducted just one time, there could be some possible sources of errors that could have affected the experiments and caused errors in the range of 3% to 8%:

1. Membrane variability: Although all experiments were conducted using one membrane, there can be slight variations in the pore size or surface properties, which could impact the separation performance. Additionally, during each experiment, the feed solution can impact elasticity and swelling which subsequently affect the separation performance.
2. Sample preparation: Inconsistent sample preparation methods, such as variations in concentration or pH of the 4-ethyl phenols solution, could introduce errors in the results.

3. Operating conditions: Fluctuations in temperature, pressure, or humidity during the experiments could influence the pervaporation process and lead to inconsistent results.
4. Analytical techniques: The accuracy and precision of the analytical techniques used to measure the concentration of 4-ethyl phenols in the permeate and feed solutions could contribute to errors.
5. Data interpretation: Errors in data collection or interpretation, such as inaccuracies in recording measurements or calculations, could lead to incorrect conclusions.

Addressing these potential sources of errors in the experiments can help ensure the reliability and validity of the results and strengthen the overall quality of the interpretation of data.

3.5 Summary

In this phase of the investigation, pervaporation utilizing PEBA 2533 membranes was employed to remove two model aroma compounds from dilute binary solutions. The following findings were obtained:

1. PEBA 2533 exhibited selectivity in removing the aroma compounds (4-EG and 4-EP) from their aqueous solutions.

2. Increasing feed aroma concentration resulted in higher aroma flux, while the membrane permselectivity towards aroma compounds was affected, mainly due to augmented driving forces for permeation. Water flux was largely unaffected over the feed concentration ranges studies because of the low VOC content in the feed.

3. Elevated temperatures significantly increased both aroma and water permeation fluxes, a relationship well-described by Arrhenius-type correlations.

4. The apparent activation energy for aroma and permeation (E_J) followed the order: 4-EG > 4-EP >> H_2O, which was the same as the order of their molecular size.

5. Possible sources of errors in experiments could be membrane variability, sample preparation, operating conditions, analytical techniques, and data interpretation. It would be estimated that these sources could lead to an error in the range of 3% to 8% in the experiments.

Chapter 4

Effects of non-volatile solutes and ethanol on pervaporative separation of 4-EG

4.1 Introduction

Pervaporation results obtained with model feed solutions may differ from those with real wine, fermentation mixture, or during different age of maturation due to the presence of non-volatile components such as sugars (i.e. glucose), yeast extract, and salts (i.e. NaCl). While these components maybe are present in low concentrations compared to water, they are not expected to significantly sorb or diffuse through dense membranes due to their high molecular weights, electric charges, or too low volatilities. However, non-volatile components can still affect the thermodynamic behavior of aroma compounds through interactions, such as hydrogen bonding between sugar and certain aroma compounds, and the change of volatility behavior of aroma compounds through interactions with insoluble yeast extracts [104, 112-114]. The influence of salts on aroma compound recovery in pervaporation is a balance between the "salting out" effect and increased viscosity [115-117].

The presence of ethanol in a solution can impact both the permeation flux and selectivity of volatile aroma compounds during pervaporation. Ethanol is permeable, and thus higher concentrations of ethanol in the solution may increase the overall permeation flux due to changes in solution properties such as viscosity and surface tension. However, excessively high ethanol concentrations could also lead to membrane swelling or fouling, reducing permeation flux. Ethanol

may also influence the selectivity of the pervaporation process, affecting the relative permeation rates of different aroma compounds. Depending on their chemical properties and affinity for ethanol, aroma compounds exhibit higher or lower selectivity. Additionally, ethanol molecules may compete with aroma compounds for sorption onto the membrane surface, impacting their relative permeation rates [84, 107, 113].

Despite research on these interactions, no work has been published on their specific effects on pervaporation of 4-EG. Therefore, this study aimed to investigate how the interactions between non-volatile components and 4-EG impact its separation performance in pervaporation.

4.2 Experimental

4.2.1 Feed solution

The pervaporation experiments were conducted with ternary feed solutions comprising 4-EG, a non-volatile compound (or ethanol), and water. A constant 4-EG concentration of 100 ppm in the feed solutions was used in the study. Concentrations of on-volatile ingredients are different for different winemaking processes. In this study, the concentrations were chosen close to values reported in an article published by Barzinha, et. al. [10], including:

1. Glucose (Sigma-Aldrich concentrations: 0 to 5 wt.%. It is worth mentioning that in fermentation, glucose concentration can be more than 5.0 g/L at the beginning. However, it decreases over time, reaching less than 0.5 g/L at the end of fermentation and about 200 ppm after maturation and aging [3] .
2. Agar (Merck Inc.) was used as a model yeast to evaluate its interactions with 4-EG. Note that agar is not a typical yeast in the winemaking, and it is used sometimes in laboratory studies [118]. The concentration of agar changed between 0 to 0.25 g/L.

3. Sodium chloride, NaCl, (Sigma-Aldrich) concentration: 0 to 2.0 g/L. NaCl in wine mostly originates from salts in soils, which are absorbed in grapes through their roots [5].
4. Ethanol was used as a model alcohol model compound in this work. The concentrations of ethanol were in the range of 0 to 14.0% v/v. This selection was based on the fact that ethyl phenols are less likely to exist when the content of ethanol exceeds 14.5% v/v [113].

The solutions containing glucose and yeast were left for 24 hours before use in pervaporation tests in order to ensure that 4-EG and non-volatile components reach equilibrium.

4.2.2 Membrane fabrication and pervaporation

The experimental setup for pervaporation in this chapter is identical to that of Chapters 3. The PEBA membrane, 50 μm thick, was affixed to the permeation cell with an effective area of 22.1 cm^2. The feed solution circulated continuously at 1.14 L/min through the membrane cell and back into the 1200 mL feed tank via a circulation pump. Permeate pressure was maintained at 40 kPa using a vacuum pump. The feed solution temperature was about 30 °C ± 1 °C with a heating mantle and a Dyna-Sense® Thermoregulator Control System. Permeate samples, condensed in a cold trap with liquid nitrogen, were collected and weighed, then diluted with deionized water and analyzed using a Shimadzu TOC-500 total organic carbon analyzer. TOC detection limit was 1 ppm, with a standard deviation of ± 3%. Post-run, the feed side of the pervaporation unit, including the membrane cell, was rinsed with water for 30 min. Pervaporation performance was assessed based on flux and enrichment factor. In the evaluation of ethanol impact on the pervaporative performance of 4-EG, ethanol permeation flux/concentration could not be measured using UV

analyzer and was not reported in this work. Also, λ_{max} of 4-EG in the ternary mixture of 4-EG/ethanol/water was the same with that in the binary solution of 4-EG/water. Moreover, no absorbance peak in the range of 0-4000 was detected for different compositions of ethanol/water solution.

4.3 Experimental

4.3.1 Effect of glucose on separation of 4-EG

Figure 4-1 shows the effects of glucose on total flux, 4-EG flux and 4-EG enrichment factors. It was shown that there was little change in pervaporation characteristic parameters. It can be rationalized by the following. First, this could occur if the glucose concentration is relatively low. Robinson et. al. [119] investigated the matrix effects of ethanol, glucose, glycerol, catechin, and proline on the volatile partitioning of 20 volatile compounds expected to contribute in wine aroma. Although their assessments revealed that the presence of glucose increased the concentration of volatiles in the headspace, it is worth noting that minimum concentration of glucose in their study was 160 g/L, which was too far from the even highest glucose concentration in this work.

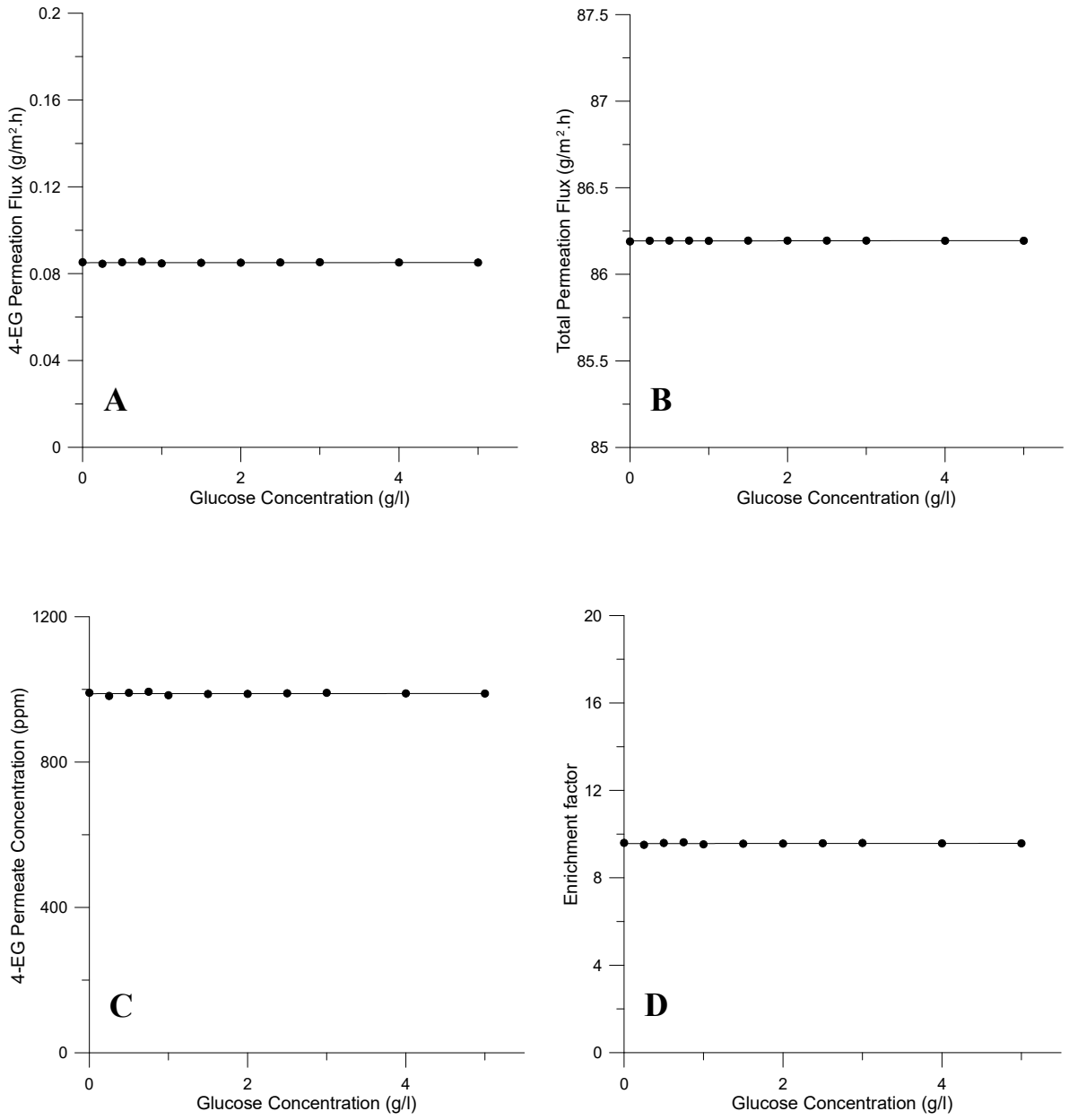


Figure 4-1 Effect of different glucose concentrations on separation performance of 4-EG; A: 4-EG permeation flux, B: total permeation flux, C: 4-EG permeate concentration, D: enrichment factor.

Furthermore, in some cases, glucose may have minimal interaction with volatile aroma compounds or the membrane material, resulting in negligible effects on the permeation flux and

selectivity. Variation of glucose from 0-50 g/L to analyze (headspace and sorption) the interactions between diacetyl and glucose in presence of water proved no interactions and no change in activity coefficient of water [120]. Another proof was found in the study of the effect of addition of glucose (1 wt.% and 20 wt.%) on the rheological properties, release of aroma compounds, and color of the red wine and it was found that both concentrations significantly influenced wine characteristic properties [114]. It means that though minimum dose of glucose (10 g/L) in their work was close to the highest value in this work, glucose and 4-EG did not interact with each another significantly. Additionally, if the membrane material is highly selective for volatile aroma compounds and minimally affected by glucose, the pervaporation performance may remain largely unchanged.

4.3.2 Effect of agar in separation performance of 4-EG

The influence of agar on separation performance of 4-EG in terms of aroma permeation flux, water flux, and 4-EG permeate concentration was shown in **Figure 4-2**. Adding different doses of agar to the feed mixture permeation did not affect the water flux. However, 4-EG permeate concentration first experienced an increase with the addition of agar from 0 to 0.25 g/L, followed by a decrease with a further increase in content. Agar is hardly soluble in water. Prepared solutions of agar showed that agar "particles" tend to swell, producing a cloudy environment, and partially participating in the filtration tank, particularly when the agar concentrations increased from 0.25 to 0.35, 0.5 and 1.0 g/L. That 4-EG permeate concentration first increased with an increase in agar concentration from 0 to 0.25 g/L and then decreased with the further increment of agar dose shows that there were two opposing affects. Addition of agar to the aroma/water solution causes many water molecules to absorb on agar cell walls. This means that the intrinsic concentration of 4-EG in the solution may go up, followed by an increase in driving force for the permeation which results

in higher 4-EG amount in the permeate. However, when the agar dose in the feed solution reached 0.35-1.0 g/L, a rather thick layer of swollen watery agar settled down at the bottom of the tank. This thick layer could trap 4-EG molecules and hence, some part of 4-EG molecules were not circulated through the system, having no contact with the membrane surface. This would lead to a decrease in effective 4-EG concentration from the feed solution, and as a result, its impact dominates the previous one and 4-EG permeate concentration starts to decrease. However, water permeation flux did not undergo a notable change. This can be attributed to the fact that the concentration of 4-EG in the feed solution is still so low in the dilute feed solutions and the mechanism governing water permeation did not change. Thus, as shown in Chapter 3, water permeation flux is not expected to vary with 4-EG concentration in feed.

It is worth mentioning that this observation contrasted with the results obtained by Petrozziello et. al. [113], which was aimed at investigating the influence of ethanol, wine polyphenols and yeast extract on the volatility of 4-EG and 4-EP in red wines. Their evaluations indicated that yeast extract has little effects on volatility of ethyl phenols. This can be explained for two reasons. First, the concentration of yeast was 0.99 mg/L which was quite low because their evaluation was based on the filtered wine in which yeast concentration is dramatically lower than fermentation broth. Second, the yeast extract used in their study was soluble in wine, which means its behavior and interaction with the aroma/water mixture would be different from insoluble agar.

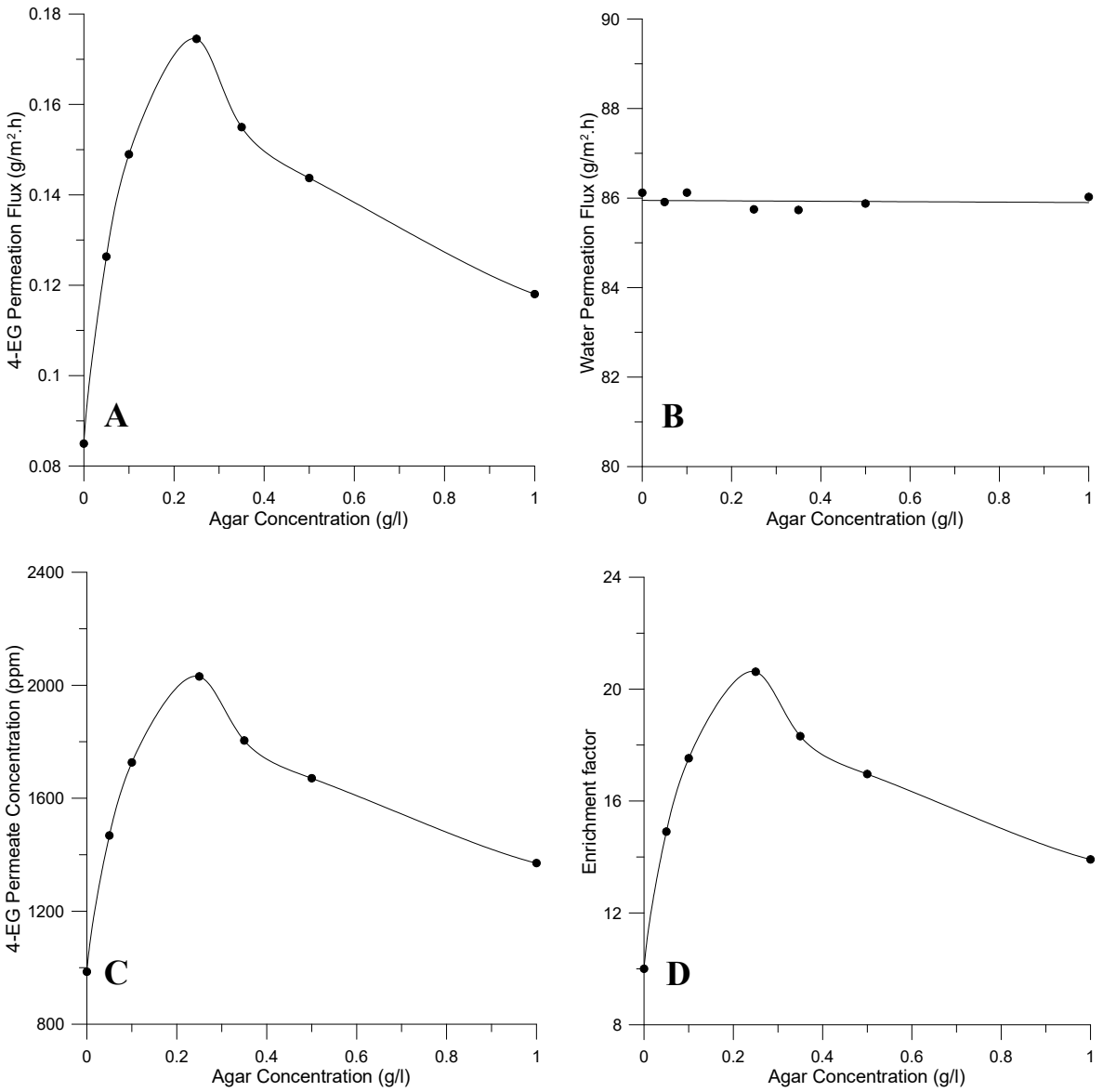


Figure 4-2 Effect of different agar concentrations on separation performance of 4-EG; A: 4-EG permeation flux, B: total permeation flux, C: 4-EG permeate concentration, D: enrichment factor.

4.3.3 Effect of sodium chloride on separation of 4-EG

Figure 4-3 shows the separation performance for extracting 4-EG (water permeation flux, 4-EG permeate concentration, and selectivity) at different concentrations of NaCl in the feed solution. There was a slight decrease in 4-EG permeate concentration or selectivity and no

remarkable variation in water permeation flux, signifying no salting-out or salting-in effects. This is different form some previous reports where salting-out effects were observed in pervaporation of certain organic compounds from aqueous solutions [104, 116]. However, similar to glucose which showed little effects on the separation efficiency, both nature of organic compound and NaCl concentration in the ternary mixture could affect the pervaporative mass transfer. For example, in pervaporative separation of dichloromethane using a commercial tubular membrane made of polydimethylsiloxane, the pervaporation performance of dichloromethane was unaffected by the presence of electrolytes, indicating the absence of any promotion or inhibition. This observation further confirms the absence of a salting-out effect in that system. Additionally, there was no indication of a salting-in effect, as the water flux remained consistent across the studied range of salt feed concentrations (0-10 g/L). That sodium chloride has a minor impact on water activity would support these findings [121]. Nguyen and Nobe [109] also observed no significant alteration in the separation performance during pervaporation of dichloromethane/sodium chloride/water using a silicone tubular membrane.

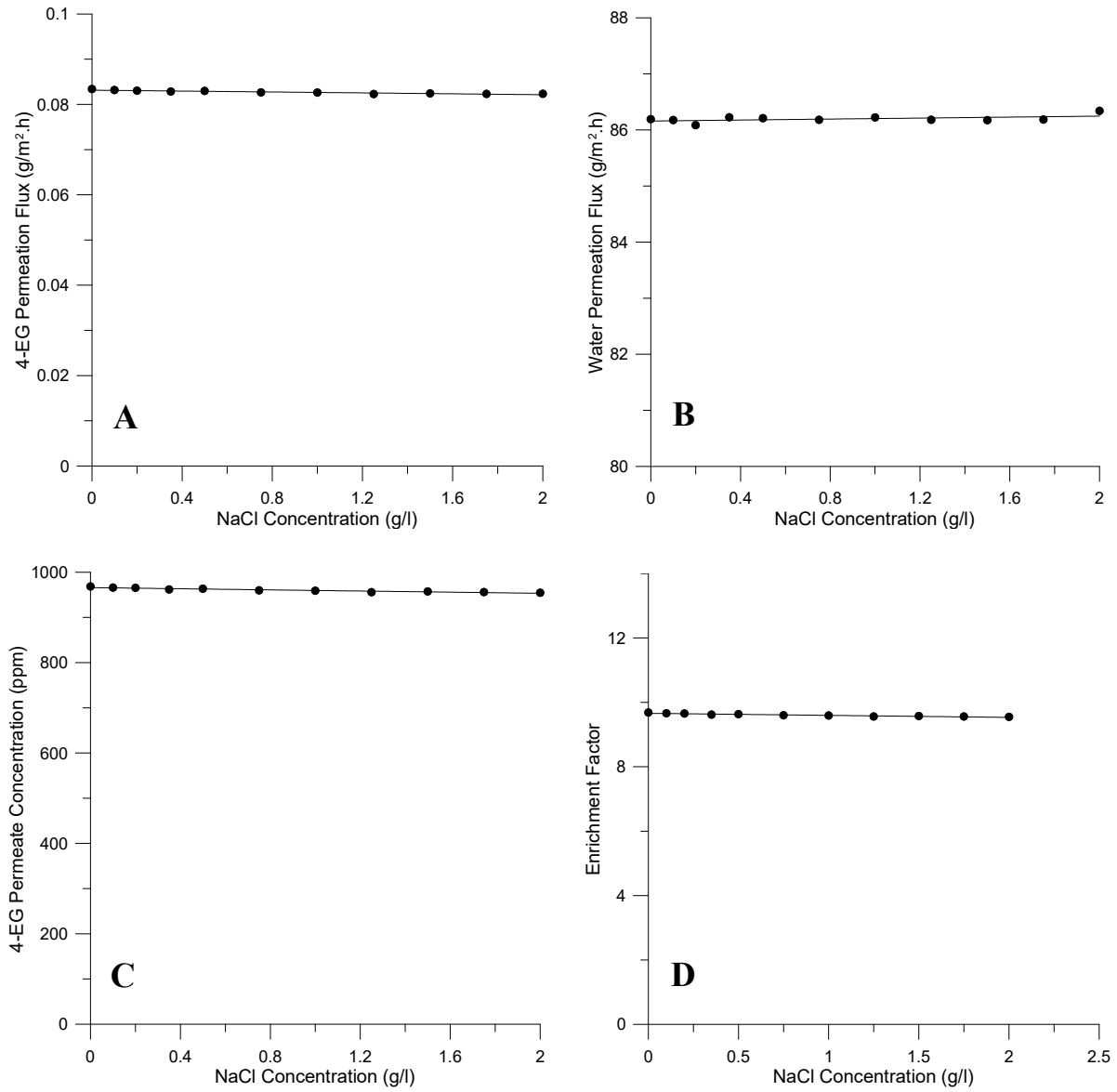


Figure 4-3 Effect of different NaCl concentrations on separation performance of 4-EG; A: 4-EG permeation flux, B: total permeation flux, C: 4-EG permeate concentration, D: enrichment factor.

4.3.4 Effects of ethanol on separation performance of 4-EG

Figure 4-4 shows the effects of ethanol on the performance of 4-EG separation from aqueous solutions including 4-EG permeate concentration, total permeation flux, and selectivity. Consistent with earlier research [113, 119, 122], the presence of ethanol in the feed of 4-EG/water

demonstrated that 4-EG permeate concentration and flux negatively influenced by ethanol, while the total permeation flux and the flux of ethanol + water were greatly enhanced.

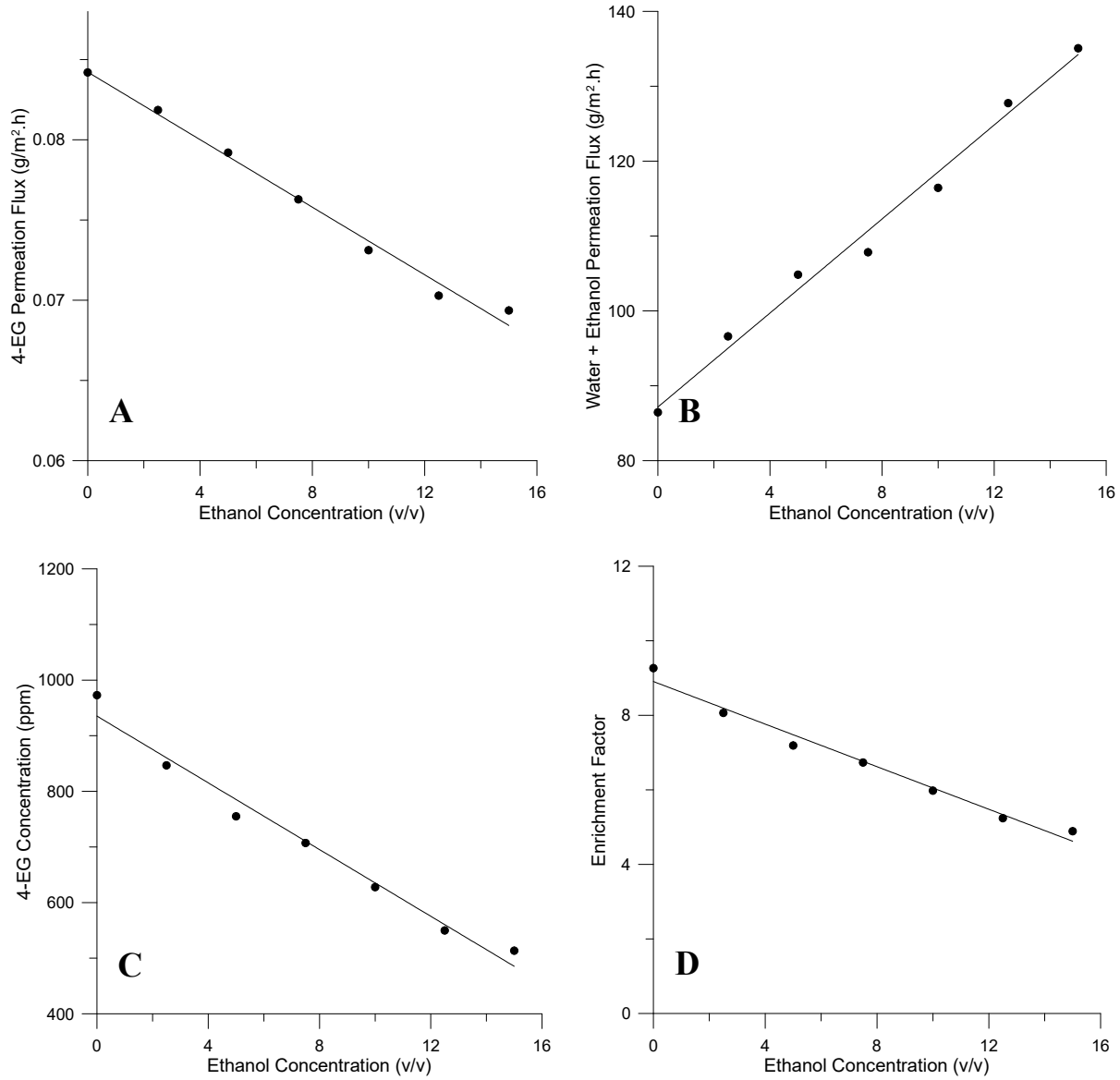


Figure 4-4 Effect of different ethanol concentrations on separation performance of 4-EG; A: 4-EG permeation flux, B: total permeation flux, C: 4-EG permeate concentration, D: enrichment factor.

Ethanol affected the separation of 4-EG from the ternary mixture of 4-EG/ethanol/water due to both interactions with aroma, water and the membrane polymer matrix. In one study, an analysis of the effects of ethanol on the release of 4-EG and 4-EP to the headspace showed that volatility of wine aromas decreases as the ethanol content percentage goes up [113]. This was in accordance with the observations in this study. During preparation of 4-EG/water solution, the smokey, spicy odor was clearly perceived via olfactory system regardless of the fraction of 4-EG in the mixture. However, when ethanol was added to the mixture, the odor perception was hindered noticeably, which confirms the coupling effects between 4-EG and ethanol.

The presence of ethanol in the pervaporation process of aroma/ethanol/water mixtures can result in a decrease in both the permeation flux and the concentration of aroma compounds in the permeate. Indeed, the permeation flux is influenced by the concentration of ethanol in the feed. High ethanol concentrations tend to cause membrane swelling and alter the permeation characteristics. Also, a decreased separation factor suggests that the hydrophobic membrane is partially plasticized by ethanol [123]. Furthermore, as the ethanol concentration in the feed increased, there was a comparatively greater degree of membrane swelling observed in the membrane [122]. Additionally, the concentration of aroma compounds in the permeate may vary depending on the interactions between ethanol and the aroma compounds, potentially leading to changes in their partitioning behavior during pervaporation.

4.4 Summary

Effects of non-volatile wine compounds (glucose, agar, and sodium chloride) as well as ethanol was assessed on separation of 4-EG from aqueous solutions, and the following conclusions may be derived:

1. Non-volatile compounds, that is, glucose, agar, and NaCl had minimal impact on water permeation.

2. The presence of glucose in the feed solutions had limited influence on the permeation flux and permeate concentration of 4-EG due to its low concentration and interaction with 4-EG.

3. Addition of agar to the feed initially increased 4-EG permeation flux due to enhanced 4-EG concentration, but a threshold was reached where adding more agar led to reduced permeation flux of 4-EG due to trapping 4-EG molecules.

4. NaCl had negligible effects on 4-EG permeate concentration and flux, indicating no salting-in or salting-out effects due to low concentration and/or lack of interactions.

5. Higher ethanol content in the ternary mixture negatively affected 4-EG concentration in the permeate and permeation flux, while total permeation flux increased. Ethanol reduced 4-EG volatility through altered partitioning behavior and membrane swelling.

Chapter 5

General conclusions and recommendations

5.1 General conclusions

5.1.1 Separation of ethyl phenols from dilute binary solution using pervaporation

1. PEBA 2533 membrane showed high permselectivity to both 4-EG and 4-EP. The higher the aroma concentration in the feed, the higher the aroma concentration in the permeate. While water permeation flux was largely the same for the separation of both ethyl phenols remained constant, the fluxes of the organic compounds increased with increasing aromas feed concentrations. Nearly constant enrichment factor in the range of aroma feed concentrations proved the non-coupling effects.
2. Increasing the operating temperature caused an increase in water and aroma permeation fluxes, and the permeate aroma concentrations also increased. The dependency of components' permeation flux on temperature is related to their apparent activation energy. The temperature dependencies of on the permeation fluxes of water and aroma compounds showed an Arrhenius type of relation.

5.1.2 Presence of ethanol and non-volatile components on pervaporative separation of 4-ethyl guaiacol from dilute aqueous solutions

1. The presence of on-volatile compounds (including glucose, agar, and NaCl) showed that the permeation of was largely unaffected by the non-volatile compounds.

2. Glucose did not have profound effects on 4-EG separation due to its low concentration and interaction with 4-EG.
3. Addition of agar to the mixture caused 4-EG permeate flux to increase and then decrease if agar content was high enough. On the one hand, agar insolubility and tendency to swell and absorb water molecules resulted in an enhancement in 4-EG concentration in the permeate. On the other hand, a high agar concentration resulted in the agar precipitation in the feed tank, while trapped 4-EG molecules reduced concentration of 4-EG in the feed solution.
4. NaCl exhibited a little influence on the permeate concentration and permeation flux of 4-EG. The insignificant change in both water and 4-EG permeation fluxes demonstrated the absence of salting-in or salting-out effects. The low NaCl concentration and lack of interactions were the main factors for this behavior.
5. The change of concentration of 4-EG in the permeate and its permeation flux were negatively affected by the presence of ethanol in the ternary 4-EG/ethanol/water mixture. Conversely, the total permeation flux experienced a significant enhancement with the ethanol content. A significant reduction in odor perception of 4-EG was noticeable after addition of ethanol to the aroma/water solution. Not only did ethanol decrease volatility of 4-EG through changes in partitioning and activity coefficients, it also affected membrane swelling and plasticization.

5.2 Recommendations for future research

1. This work mainly focused on the separation of off-odor VOCs from their dilute aqueous mixtures by pervaporation using PEBA 2533 membrane, and the effects of operating

conditions and the presence of ethanol and some common non-volatile components on the separation performance of 4-EG were investigated. Use of a wider range of aromas concentration and temperature as well as ternary mixture of 4-EG/4-EP/water is recommended to get a better understanding of the coupling effects. Measuring water uptake and aromas sorption is suggested to obtain the solubility, diffusivity, and permeability coefficients. Prediction of properties of ethyl phenols such as vapor pressure and activity coefficients at different concentrations and temperatures provides a clearer view in the modeling of their separation through pervaporation with fractional condensers. Using a real red wine as feed is another suggestion in order to provide more details on their coupling effects and separation efficiency since their interactions could affect the activity coefficients of the permeants, degree of membrane swelling, solubility of permeant in the membrane. Long term pervaporation is proposed to investigate the role of volatile and non-volatile compounds on the membrane fouling and separation performance.

2. PEBA 2533 membrane used in this study was a dense flat-sheet membrane. To fully harness its potential for practical applications, it is essential to effectively reduce the membrane thickness since thinner membrane will produce a higher permeation flux. Thin films, however, may experience reduced mechanical stability. Therefore, composite membranes, comprising a thin active layer supported on a porous substrate, are recommended to enhance the permeation flux and mechanical strength. It is crucial to guarantee that coating of the active layer forms a defect-free thin film on a porous substrate. The properties of the substrate (e.g., polymeric materials, pore sizes, porosities, and pore size distributions) may significantly impact the formation and performance of composite membranes, necessitating further investigation. Additionally, asymmetric hollow fiber membranes, another widely used

membrane configuration in industries due to their high membrane packing density and self-supporting design, can be fabricated from PEBA 2533 for removing off-flavor VOCs from wine. However, significant permeate pressure build-up along the fiber length may occur when the permeate is drawn from the fiber bores. By evaluating the extent of pressure build-up in the permeate based on experimental data and modeling predictions, membrane performance can be enhanced through optimization of fiber dimensions or modification of permeate withdrawal locations.

3. In fermentation media, both non-condensable gases (e.g., carbon dioxide) and ethanol are frequently generated at significant rates and are present in considerable concentrations. Thus, in the development of a pervaporation-based process for aroma recovery, understanding the effects of carbon dioxide and ethanol on aroma separation and fractionation performance is crucial. Swelling and plasticization of PEBA 2533 in the presence of ethanol and CO_2 are usually accompanied by a change in aroma permeation flux and concentration. Additionally, in bioethanol production process, where ethanol concentrations can be around 15% in the feed solution, it becomes imperative to anticipate the impact of carbon dioxide on the pervaporation process and devise strategies to remove trace amounts of aromas to prevent their presence in the final product. Additionally, the separation performance may be evaluated using headspace vapor which often contains many valuable VOCs in high extent. Capturing and purifying them, instead of purging them into the air, would be a cost-effective technique.

5. PEBA 2533 was used to fabricate the non-porous membrane and it showed good selectivity towards both ethyl phenols. Modification of the membrane using different types of nanoparticles (e.g., zeolites, MOFs, and ZIFs) may change the free volume of the membrane, enhance the diffusivity and solubility, and provide selective separation to specific compounds,

and facilitate the transport of molecules. One of potential modifiers is activated carbon nanoparticles which are frequently used for the extraction of 4-EG and 4-EP from red wine. Incorporating activated carbon nanoparticles into the membrane may improve the membrane performance for recovery of the aroma compounds.

References

1. Berger, R. G., *Flavours and fragrances: chemistry, bioprocessing and sustainability*. Springer Science & Business Media: 2007.

2. Buljeta, I.; Pichler, A.; Šimunović, J.; Kopjar, M., Beneficial Effects of Red Wine Polyphenols on Human Health: Comprehensive Review. *Current Issues in Molecular Biology* **2023,** *45* (2), 782-798.

3. Garde-Cerdán, T.; Ancín-Azpilicueta, C., Review of quality factors on wine ageing in oak barrels. *Trends in Food Science & Technology* **2006,** *17* (8), 438-447.

4. Cerdán, T. G.; Ancín-Azpilicueta, C., Effect of oak barrel type on the volatile composition of wine: Storage time optimization. *LWT-Food Science and Technology* **2006,** *39* (3), 199-205.

5. Morata, A., *Red wine technology*. Academic Press: 2018.

6. Jackson, R. S., *Wine science: principles and applications*. Academic press: 2008.

7. Caboni, P.; Sarais, G.; Cabras, M.; Angioni, A., Determination of 4-ethylphenol and 4-ethylguaiacol in wines by LC-MS-MS and HPLC-DAD-fluorescence. *Journal of agricultural and food chemistry* **2007,** *55* (18), 7288-7293.

8. Cansado, I. P. d. P.; Mourão, P. A. M.; Morais, I. D.; Peniche, V.; Janeirinho, J., Removal of 4-Ethylphenol and 4-Ethylguaiacol, from Wine-like Model Solutions, by Commercial Modified Activated Carbons Produced from Coconut Shell. *Applied Sciences* **2022,** *12* (22), 11754.

9. Carrasco-Sánchez, V.; John, A.; Marican, A.; Santos, L. S.; Laurie, V. F., Removal of 4-ethylphenol and 4-ethylguaiacol with polyaniline-based compounds in wine-like model solutions and red wine. *Molecules* **2015,** *20* (8), 14312-14325.

10. Brazinha, C.; Barbosa, D. S.; Crespo, J. G., Sustainable recovery of pure natural vanillin from fermentation media in a single pervaporation step. *Green Chemistry* **2011,** *13* (8), 2197-2203.

11. Karlsson, H. O.; Trägårdh, G., Pervaporation of dilute organic-waters mixtures. A literature review on modelling studies and applications to aroma compound recovery. *Journal of Membrane Science* **1993,** *76* (2-3), 121-146.

12. Baudot, A.; Marin, M., Pervaporation of aroma compounds: comparison of membrane performances with vapour-liquid equilibria and engineering aspects of process improvement. *Food and Bioproducts Processing* **1997,** *75* (2), 117-142.

13. Valério, R.; Brazinha, C.; Crespo, J. G., Comparative analysis of bio-vanillin recovery from bioconversion media using pervaporation and vacuum distillation. *Membranes* **2022,** *12* (8), 801.

14. Castro-Muñoz, R., Pervaporation: The emerging technique for extracting aroma compounds from food systems. *Journal of Food Engineering* **2019,** *253*, 27-39.

15. Nijhuis, H. H., Removal of trace organics from water by pervaporation: a technical and economic analysis. **1990**.

16. Pereira, M. J.; Ferreira, A.; Brazinha, C.; Crespo, J., Modelling of Fractionated Condensation for Off-Flavours Reduction from Red Wine Fermentation Headspace. *Membranes* **2022,** *12* (9), 875.

17. Schieber, A.; Wüst, M., Volatile phenols—Important contributors to the aroma of plant-derived foods. *Molecules* **2020,** *25* (19), 4529.

18. Maarse, H.; Visscher, C.; Willemsens, L., Volatile compounds in food. *Qualitative and quantitative data* **1989,** *1* (111), 21-29.

19. Dunkel, A.; Steinhaus, M.; Kotthoff, M.; Nowak, B.; Krautwurst, D.; Schieberle, P.; Hofmann, T., Nature's chemical signatures in human olfaction: a foodborne perspective for future biotechnology. *Angewandte Chemie International Edition* **2014,** *53* (28), 7124-7143.

20. Waterhouse, A. L.; Sacks, G. L.; Jeffery, D. W., *Understanding wine chemistry*. John Wiley & Sons: 2016.

21. Veithen, A.; Philippeau, M.; Chatelain, P., High Throughput Receptor Screening Assays. *Springer Handbook of Odor* **2017**, 57-58.

22. Carregosa, D.; Carecho, R.; Figueira, I. s.; N Santos, C. u., Low-molecular weight metabolites from polyphenols as effectors for attenuating neuroinflammation. *Journal of agricultural and food chemistry* **2019,** *68* (7), 1790-1807.

23. Márquez Campos, E.; Stehle, P.; Simon, M.-C., Microbial metabolites of flavan-3-ols and their biological activity. *Nutrients* **2019,** *11* (10), 2260.

24. Atkinson, R. G., Phenylpropenes: Occurrence, distribution, and biosynthesis in fruit. *Journal of agricultural and food chemistry* **2016,** *66* (10), 2259-2272.

25. Vogt, T., Phenylpropanoid biosynthesis. *Molecular plant* **2010,** *3* (1), 2-20.

26. Widhalm, J. R.; Dudareva, N., A familiar ring to it: biosynthesis of plant benzoic acids. *Molecular plant* **2015,** *8* (1), 83-97.

27. Lentz, M., The impact of simple phenolic compounds on beer aroma and flavor. *Fermentation* **2018,** *4* (1), 20.

28. Jiang, D.; Peterson, D. G., Role of hydroxycinnamic acids in food flavor: a brief overview. *Phytochemistry Reviews* **2010,** *9*, 187-193.

29. Czerny, M.; Grosch, W., Potent odorants of raw Arabica coffee. Their changes during roasting. *Journal of Agricultural and Food Chemistry* **2000,** *48* (3), 868-872.

30. Maga, J. A., The flavor chemistry of wood smoke. *Food Reviews International* **1987,** *3* (1-2), 139-183.

31. Zhang, B.; Cai, J.; Duan, C.-Q.; Reeves, M. J.; He, F., A review of polyphenolics in oak woods. *International journal of molecular sciences* **2015,** *16* (4), 6978-7014.

32. Lonvaud-Funel, A. In *Lactic acid bacteria in the quality improvement and depreciation of wine*, Lactic Acid Bacteria: Genetics, Metabolism and Applications: Proceedings of the Sixth Symposium on Lactic Acid Bacteria: Genetics, Metabolism and Applications, 19–23 September 1999, Veldhoven, The Netherlands, Springer: 1999; pp 317-331.

33. Cerdán, T. G.; Mozaz, S. R. g.; Azpilicueta, C. A. n., Volatile composition of aged wine in used barrels of French oak and of American oak. *Food research international* **2002,** *35* (7), 603-610.

34. Chatonnet, P.; Dubourdieu, D.; Boidron, J., The influence of Brettanomyces/Dekkera sp. yeasts and lactic acid bacteria on the ethylphenol content of red wines. *American Journal of Enology and Viticulture* **1995,** *46* (4), 463-468.

35. Coulon, J.; Perello, M.-C.; Lonvaud-Funel, A.; De Revel, G.; Renouf, V., Brettanomyces bruxellensis evolution and volatile phenols production in red wines during storage in bottles. *Journal of applied microbiology* **2010,** *108* (4), 1450-1458.

36. Chatonnet, P.; Dubourdieu, D.; Boidron, J., Effects of fermentation and maturation in oak barrels on the composition and quality of white wines. *Aust. NZ Wine Ind. J* **1991,** *6* (1), 73-84.

37. Spillman, P. J.; Pollnitz, A. P.; Liacopoulos, D.; Pardon, K. H.; Sefton, M. A., Formation and degradation of furfuryl alcohol, 5-methylfurfuryl alcohol, vanillyl alcohol, and their ethyl ethers in barrel-aged wines. *Journal of Agricultural and Food Chemistry* **1998,** *46* (2), 657-663.

38. Boidron, J.-N.; Chatonnet, P.; Pons, M., Influence du bois sur certaines substances odorantes des vins. *OENO One* **1988,** *22* (4), 275-294.

39. Chatonnet, P.; Dubourdie, D.; Boidron, J. n.; Pons, M., The origin of ethylphenols in wines. *Journal of the Science of Food and Agriculture* **1992,** *60* (2), 165-178.

40. Pérez-Prieto, L. J.; López-Roca, J. M.; Martínez-Cutillas, A.; Pardo-Mínguez, F.; Gómez-Plaza, E., Extraction and formation dynamic of oak-related volatile compounds from different volume barrels to wine and their behavior during bottle storage. *Journal of Agricultural and Food Chemistry* **2003,** *51* (18), 5444-5449.

41. Heresztyn, T., Metabolism of volatile phenolic compounds from hydroxycinnamic acids by Brettanomyces yeast. *Archives of Microbiology* **1986,** *146*, 96-98.

42. Macheix, J.; Fleuriet, A.; Billot, J., Fruit phenolics: CRC press. *Boca Raton, FL* **1990**.

43. Hixson, J. L.; Sleep, N. R.; Capone, D. L.; Elsey, G. M.; Curtin, C. D.; Sefton, M. A.; Taylor, D. K., Hydroxycinnamic acid ethyl esters as precursors to ethylphenols in wine. *Journal of agricultural and food chemistry* **2012,** *60* (9), 2293-2298.

44. Filipe-Ribeiro, L.; Cosme, F.; Nunes, F. M., Reducing the negative sensory impact of volatile phenols in red wine with different chitosans: Effect of structure on efficiency. *Food Chemistry* **2018,** *242*, 591-600.

45. Farina, L.; Boido, E.; Carrau, F.; Dellacassa, E., Determination of volatile phenols in red wines by dispersive liquid–liquid microextraction and gas chromatography–mass spectrometry detection. *Journal of Chromatography A* **2007,** *1157* (1-2), 46-50.

46. Lima, A.; Oliveira, C.; Santos, C.; Campos, F. M.; Couto, J. A., Phenolic composition of monovarietal red wines regarding volatile phenols and its precursors. *European Food Research and Technology* **2018,** *244*, 1985-1994.

47. Lyu, G.; Wu, S.; Zhang, H., Estimation and comparison of bio-oil components from different pyrolysis conditions. *Frontiers in Energy Research* **2015,** *3*, 28.

48. Suárez, R.; Suárez-Lepe, J.; Morata, A.; Calderón, F., The production of ethylphenols in wine by yeasts of the genera Brettanomyces and Dekkera: A review. *Food Chemistry* **2007,** *102* (1), 10-21.

49. Couto, J. A.; Neves, F.; Campos, F.; Hogg, T., Thermal inactivation of the wine spoilage yeasts Dekkera/Brettanomyces. *International journal of food microbiology* **2005,** *104* (3), 337-344.

50. Millet, V.; Lonvaud-Funel, A., The viable but non-culturable state of wine micro-organisms during storage. *Letters in applied microbiology* **2000,** *30* (2), 136-141.

51. Ubeda, J.; Briones, A., Microbiological quality control of filtered and non-filtered wines. *Food Control* **1999,** *10* (1), 41-45.

52. Murat, M.-L.; Dumeau, F., Impact of fining on population levels of certain spoilage micro-organisms in red wines. *Australian and New Zealand grapegrower and winemaker* **2003,** (478), 92-94.

53. Renouf, V.; Lonvaud-Funel, A., Racking are key stages for the microbial stabilization of wines. *OENO One* **2004,** *38* (4), 219-224.

54. Du Toit, W. d.; Pretorius, I.; Lonvaud-Funel, A., The effect of sulphur dioxide and oxygen on the viability and culturability of a strain of Acetobacter pasteurianus and a strain of Brettanomyces bruxellensis isolated from wine. *Journal of applied microbiology* **2005,** *98* (4), 862-871.

55. Barata, A.; Caldeira, J.; Botelheiro, R.; Pagliara, D.; Malfeito-Ferreira, M.; Loureiro, V., Survival patterns of Dekkera bruxellensis in wines and inhibitory effect of sulphur dioxide. *International journal of food microbiology* **2008,** *121* (2), 201-207.

56. Pour Nikfardjam, M.; May, B.; Tschiersch, C., 4-Ethylphenol and 4-ethylguaiacol contents in bottled wines from the German 'Württemberg'region. *European Food Research and Technology* **2009,** *230* (2), 333-341.

57. Rubio-Bretón, P.; Lorenzo, C.; Salinas, M. R.; Martínez, J.; Garde-Cerdán, T., Influence of oak barrel aging on the quality of red wines. *Oak: Ecology, Types and Management; Chuteira, CA, Grão, AB, Eds* **2012**, 59-86.

58. Malfeito-Ferreira, M.; Laureano, P.; Barata, A.; D'antuono, I.; Stender, H.; Loureiro, V., Effect of different barrique sanitation procedures on yeasts isolated from the inner layers of wood. *Am J Enol Vitic* **2004,** *55* (3).

59. Fernández de Simón, B.; Cadahía, E.; Jalocha, J., Volatile compounds in a Spanish red wine aged in barrels made of Spanish, French, and American oak wood. *Journal of agricultural and food chemistry* **2003,** *51* (26), 7671-7678.

60. Pollnitz, A. P.; Pardon, K. H.; Sefton, M. A., Quantitative analysis of 4-ethylphenol and 4-ethylguaiacol in red wine. *Journal of Chromatography A* **2000,** *874* (1), 101-109.

61. De Rosso, M.; Panighel, A.; Dalla Vedova, A.; Stella, L.; Flamini, R., Changes in chemical composition of a red wine aged in acacia, cherry, chestnut, mulberry, and oak wood barrels. *Journal of agricultural and food chemistry* **2009,** *57* (5), 1915-1920.

62. Gallardo-Chacón, J.-J.; Karbowiak, T., Sorption of 4-ethylphenol and 4-ethylguaiacol by suberin from cork. *Food chemistry* **2015,** *181*, 222-226.

63. Ivić, I.; Kopjar, M.; Jukić, V.; Bošnjak, M.; Maglica, M.; Mesić, J.; Pichler, A., Aroma profile and chemical composition of reverse osmosis and nanofiltration concentrates of red wine Cabernet Sauvignon. *Molecules* **2021,** *26* (4), 874.

64. Ugarte, P.; Agosin, E.; Bordeu, E.; Villalobos, J. I., Reduction of 4-ethylphenol and 4-ethylguaiacol concentration in red wines using reverse osmosis and adsorption. *American Journal of Enology and Viticulture* **2005,** *56* (1), 30-36.

65. Chassagne, D.; Guilloux-Benatier, M.; Alexandre, H.; Voilley, A., Sorption of wine volatile phenols by yeast lees. *Food Chemistry* **2005,** *91* (1), 39-44.

66. Pradelles, R.; Vichi, S.; Alexandre, H.; Chassagne, D., Influence of the drying processes of yeasts on their volatile phenol sorption capacity in model wine. *International journal of food microbiology* **2009,** *135* (2), 152-157.

67. Garde-Cerdán, T.; Zalacain, A.; Lorenzo, C.; Alonso, J. L.; Salinas, M. R., Molecularly imprinted polymer-assisted simple clean-up of 2, 4, 6-trichloroanisole and ethylphenols from aged red wines. *American journal of enology and viticulture* **2008,** *59* (4), 396-400.

68. Dang, C.; Jiranek, V.; Taylor, D. K.; Wilkinson, K. L., Removal of volatile phenols from wine using crosslinked cyclodextrin polymers. *Molecules* **2020,** *25* (4), 910.

69. Filipe-Ribeiro, L.; Milheiro, J.; Matos, C. C.; Cosme, F.; Nunes, F. M., Reduction of 4-ethylphenol and 4-ethylguaiacol in red wine by activated carbons with different physicochemical characteristics: Impact on wine quality. *Food Chemistry* **2017,** *229*, 242-251.

70. Castro-Muñoz, R.; Ahmad, M. Z.; Cassano, A., Pervaporation-aided processes for the selective separation of aromas, fragrances and essential (AFE) solutes from agro-food products and wastes. *Food Reviews International* **2023,** *39* (3), 1499-1525.

71. Böddeker, K.; Gatfield, I.; Jähnig, J.; Schorm, C., Pervaporation at the vapor pressure limit: Vanillin. *Journal of membrane science* **1997,** *137* (1-2), 155-158.

72. Camera-Roda, G.; Augugliaro, V.; Cardillo, A.; Loddo, V.; Palmisano, G.; Palmisano, L., A pervaporation photocatalytic reactor for the green synthesis of vanillin. *Chemical engineering journal* **2013,** *224*, 136-143.

73. Guichard, E., Interaction of aroma compounds with food matrices. In *Flavour development, analysis and perception in food and beverages*, Elsevier: 2015; pp 273-295.

74. Dufour, C.; Bayonove, C. L., Interactions between wine polyphenols and aroma substances. An insight at the molecular level. *Journal of agricultural and food chemistry* **1999,** *47* (2), 678-684.

75. Jung, D.-M.; De Ropp, J. S.; Ebeler, S. E., Study of interactions between food phenolics and aromatic flavors using one-and two-dimensional 1H NMR spectroscopy. *Journal of Agricultural and Food Chemistry* **2000,** *48* (2), 407-412.

76. Shani, U.; Ben-Gal, A., Long-term response of grapevines to salinity: osmotic effects and ion toxicity. *American journal of enology and viticulture* **2005,** *56* (2), 148-154.

77. Cabello-Pasini, A.; Macías-Carranza, V.; Siqueiros-Valencia, A.; Huerta-Díaz, M. Á., Concentrations of calcium, magnesium, potassium, and sodium in wines from Mexico. *American journal of enology and viticulture* **2013,** *64* (2), 280-284.

78. Lubbers, S.; Charpentier, C.; Feuillat, M.; Voilley, A., Influence of yeast walls on the behavior of aroma compounds in a model wine. *American Journal of Enology and Viticulture* **1994,** *45* (1), 29-33.

79. Sala, C.; Mestres, M.; Martı, M.; Busto, O.; Guasch, J., Headspace solid-phase microextraction analysis of 3-alkyl-2-methoxypyrazines in wines. *Journal of Chromatography A* **2002,** *953* (1-2), 1-6.

80. Martorell, N.; Martı, M.; Mestres, M.; Busto, O.; Guasch, J., Determination of 4-ethylguaiacol and 4-ethylphenol in red wines using headspace-solid-phase microextraction-gas chromatography. *Journal of Chromatography A* **2002,** *975* (2), 349-354.

81. Delgado, P.; Sanz, M. T.; Beltrán, S.; Núñez, L. A., Ethyl lactate production via esterification of lactic acid with ethanol combined with pervaporation. *Chemical Engineering Journal* **2010,** *165* (2), 693-700.

82. Delgado, P.; Sanz, M. T.; Beltrán, S., Pervaporation of the quaternary mixture present during the esterification of lactic acid with ethanol. *Journal of Membrane Science* **2009,** *332* (1-2), 113-120.

83. BELL, S. J.; Henschke, P. A., Implications of nitrogen nutrition for grapes, fermentation and wine. *Australian journal of grape and wine research* **2005,** *11* (3), 242-295.

84. Sun, X.; Dang, G.; Ding, X.; Shen, C.; Liu, G.; Zuo, C.; Chen, X.; Xing, W.; Jin, W., Production of alcohol-free wine and grape spirit by pervaporation membrane technology. *Food and Bioproducts Processing* **2020,** *123*, 262-273.

85. Baker, R. W., *Membrane Technology and Applications*. 3rd ed.; August 2012; p 592.

86. Cao, X. Separation of Phenols and Aniline from Water Streams using Poly(ether-block-amide) Membranes. Chemical Engineering, University of Waterloo, Waterloo, 2021.

87. She, M.; Hwang, S.-T., Effects of concentration, temperature, and coupling on pervaporation of dilute flavor organics. *Journal of membrane science* **2006,** *271* (1-2), 16-28.

88. Feng, X.; Huang, R. Y., Estimation of activation energy for permeation in pervaporation processes. *Journal of Membrane Science* **1996,** *118* (1), 127-131.

89. Neel, J.; Nguyen, Q.; Clement, R.; Lin, D., Influence of downstream pressure on the pervaporation of water—tetrahydrofuran mixtures through a regenerated cellulose membrane (Cuprophan). *Journal of Membrane Science* **1986,** *27* (2), 217-232.

90. Feng, X.; Huang, R. Y., Organic Vapor/Gas Mixture Separation by Membrane–-A Parametric Study. *Separation science and technology* **1992,** *27* (15), 2109-2119.

91. Brun, J.; Larchet, C.; Bulvestre, G.; Auclair, B., Sorption and pervaporation of dilute aqueous solutions of organic compounds through polymer membranes. *Journal of membrane science* **1985,** *25* (1), 55-100.

92. Böddeker, K. W.; Bengtson, G.; Pingel, H., Pervaporation of isomeric butanols. *Journal of Membrane Science* **1990,** *54* (1-2), 1-12.

93. Böddeker, K. W.; Bengtson, G.; Bode, E., Pervaporation of low volatility aromatics from water. *Journal of membrane science* **1990,** *53* (1-2), 143-158.

94. Koops, G.; Smolders, C., Estimation and evaluation of polymeric materials for pervaporation membranes. In *Pervaporation membrane separation processes*, Elsevier Amsterdam: 1991; pp 253-278.

95. Böddeker, K. W.; Bengtson, G., Selective pervaporation of organics from water. **1989**.

96. Kujawski, W.; Warszawski, A.; Ratajczak, W.; Porębski, T.; Capała, W.; Ostrowska, I., Removal of phenol from wastewater by different separation techniques. *Desalination* **2004,** *163* (1-3), 287-296.

97. Jin, M.-Y.; Liao, Y.; Tan, C.-H.; Wang, R., Development of high performance nanofibrous composite membranes by optimizing polydimethylsiloxane architectures for phenol transport. *Journal of Membrane Science* **2018,** *549*, 638-648.

98. Blume, I.; Wijmans, J.; Baker, R., The separation of dissolved organics from water by pervaporation. *Journal of Membrane Science* **1990,** *49* (3), 253-286.

99. Wijmans, J.; Athayde, A.; Daniels, R.; Ly, J.; Kamaruddin, H.; Pinnau, I., The role of boundary layers in the removal of volatile organic compounds from water by pervaporation. *Journal of Membrane Science* **1996,** *109* (1), 135-146.

100. Li, L.; Xiao, Z.; Tan, S.; Pu, L.; Zhang, Z., Composite PDMS membrane with high flux for the separation of organics from water by pervaporation. *Journal of Membrane Science* **2004,** *243* (1-2), 177-187.

101. Li, S.; Qin, F.; Qin, P.; Karim, M. N.; Tan, T., Preparation of PDMS membrane using water as solvent for pervaporation separation of butanol–water mixture. *Green chemistry* **2013,** *15* (8), 2180-2190.

102. Mohammadi, T.; Aroujalian, A.; Bakhshi, A., Pervaporation of dilute alcoholic mixtures using PDMS membrane. *Chemical engineering science* **2005,** *60* (7), 1875-1880.

103. Baker, R. W., *Membrane technology and applications*. John Wiley & Sons: 2023.

104. Zhang, B. Recovery of Dairy Aroma Compounds and Concentration of Dairy Solutions by Membranes. University of Waterloo, 2018.

105. Salgado, C. M.; Fernández-Fernández, E.; Palacio, L.; Carmona, F. J.; Hernández, A.; Prádanos, P., Application of pervaporation and nanofiltration membrane processes for the elaboration of full flavored low alcohol white wines. *Food and bioproducts processing* **2017,** *101*, 11-21.

106. Gómez-Ariza, J.; García-Barrera, T.; Lorenzo, F.; Beltrán, R., Use of multiple headspace solid-phase microextraction and pervaporation for the determination of off-flavours in wine. *Journal of Chromatography A* **2006,** *1112* (1-2), 133-140.

107. Sam, F. E.; Ma, T.-Z.; Salifu, R.; Wang, J.; Jiang, Y.-M.; Zhang, B.; Han, S.-Y., Techniques for dealcoholization of wines: Their impact on wine phenolic composition, volatile composition, and sensory characteristics. *Foods* **2021,** *10* (10), 2498.

108. Cao, X.; Wang, K.; Feng, X., Removal of phenolic contaminants from water by pervaporation. *Journal of Membrane Science* **2021,** *623*, 119043.

109. Nguyen, T. Q.; Nobe, K., Extraction of organic contaminants in aqueous solutions by pervaporation. *Journal of membrane science* **1987,** *30* (1), 11-22.

110. Raisi, A.; Aroujalian, A., Aroma compound recovery by hydrophobic pervaporation: the effect of membrane thickness and coupling phenomena. *Separation and purification technology* **2011,** *82*, 53-62.

111. Martínez, R.; Sanz, M. T.; Beltrán, S., Concentration by pervaporation of brown crab volatile compounds from dilute model solutions: Evaluation of PDMS membrane. *Journal of membrane science* **2013,** *428*, 371-379.

112. Comuzzo, P.; Tat, L.; Tonizzo, A.; Battistutta, F., Yeast derivatives (extracts and autolysates) in winemaking: Release of volatile compounds and effects on wine aroma volatility. *Food Chemistry* **2006,** *99* (2), 217-230.

113. Petrozziello, M.; Asproudi, A.; Guaita, M.; Borsa, D.; Motta, S.; Panero, L.; Bosso, A., Influence of the matrix composition on the volatility and sensory perception of 4-ethylphenol and 4-ethylguaiacol in model wine solutions. *Food chemistry* **2014,** *149*, 197-202.

114. Wang, H.; Ni, Z.-J.; Ma, W.-P.; Song, C.-B.; Zhang, J.-G.; Thakur, K.; Wei, Z.-J., Effect of sodium sulfite, tartaric acid, tannin, and glucose on rheological properties, release of aroma compounds, and color characteristics of red wine. *Food science and biotechnology* **2019,** *28*, 395-403.

115. Martínez, R.; Sanz, M. T.; Beltrán, S.; Corcuera, E., Activity coefficients at infinite dilution of volatile compounds in water: effect of temperature and salt concentration. *Journal of Chemical & Engineering Data* **2012,** *57* (5), 1480-1485.

116. Kujawski, W.; Krajewski, S. R., Influence of inorganic salt on the effectiveness of liquid mixtures separation by pervaporation. *Separation and purification technology* **2007,** *57* (3), 495-501.

117. García, V.; Pongrácz, E.; Muurinen, E.; Keiski, R. L., Recovery of n-butanol from salt containing solutions by pervaporation. *Desalination* **2009,** *241* (1-3), 201-211.

118. Takahashi, M.; Ohta, T.; Masaki, K.; Mizuno, A.; Goto-Yamamoto, N., Evaluation of microbial diversity in sulfite-added and sulfite-free wine by culture-dependent and-independent methods. *Journal of bioscience and bioengineering* **2014,** *117* (5), 569-575.

119. Robinson, A. L.; Ebeler, S. E.; Heymann, H.; Boss, P. K.; Solomon, P. S.; Trengove, R. D., Interactions between wine volatile compounds and grape and wine matrix components influence aroma compound headspace partitioning. *Journal of Agricultural and Food Chemistry* **2009,** *57* (21), 10313-10322.

120. Le Thanh, M.; Thibeaudeau, P.; Thibaut, M.; Voilley, A., Interactions between volatile and non-volatile compounds in the presence of water. *Food Chemistry* **1992,** *43* (2), 129-135.

121. Cocchini, U.; Nicolella, C.; Livingston, A. G., Countercurrent transport of organic and water molecules through thin film composite membranes in aqueous–aqueous extractive membrane processes. Part II: theoretical analysis. *Chemical engineering science* **2002,** *57* (21), 4461-4473.

122. Tan, S.; Li, L.; Xiao, Z.; Wu, Y.; Zhang, Z., Pervaporation of alcoholic beverages—the coupling effects between ethanol and aroma compounds. *Journal of Membrane Science* **2005,** *264* (1-2), 129-136.

123. Seok, D. R.; Kang, S. G.; Hwang, S.-t., Use of pervaporation for separating azeotropic mixtures using two different hollow fiber membranes. *Journal of membrane science* **1987,** *33* (1), 71-81.