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PRODUCTION OF NON-ALCOHOLIC BEER WITH REINCORPORATION OF ORIGINAL AROMA COMPOUNDS



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PREFACE

The present work was carried out under the framework of a cooperation protocol between FEUP (Faculty of Engineering at the University of Porto) and Unicer Bebidas S.A. and the PhD grant (Ref. SFRH/BDE/15564/2005) in industrial environment supported by the Portuguese Foundation for Science and Technology (FCT) and Unicer Bebidas S.A..

Unicer Bebidas S.A. has grown over almost a century as a beer company. Nowadays, Unicer is the largest Portuguese drinks company, producing and distributing several beverages such waters, wines, juices, soft drinks and beer, which is still the main beverage produced by the company. Unicer has several production sites all over the country. This work was developed at Unicer industrial centre of Leça do Balio (Matosinhos, Portugal), which integrates the main beer production unit of the company and the division of research and development of new products and processes.

Based on the actual increasing trend of the market of non-alcoholic beverages, Unicer aimed to increase its sales on that market segment, by developing non-alcoholic beers with aroma profiles similar to the original beers, based on innovative separation technologies. Unicer has been collaborating with LEPAE (Laboratory for Process, Environmental and Energy Engineering), from Chemical Engineering Department of FEUP, since 2003. From this date until 2005, a preliminary study was carried out, aiming the selection of the most promising processes for producing a beer with the desired characteristics, regarding the company interests.

The present work was a part of a broader project outlined by the company for the production of non-alcoholic beer, preserving the original aroma profile. Besides, the development on a non-alcoholic beer from completed fermented beer, contributed to the implementation of knowledge in the field of separation processes, at the Unicer company. This thesis comprises different papers, which were published and submitted for publication during the development of the PhD research work.

ABSTRACT

The market supply of non-alcoholic beverages has experienced an increasing trend in the last years. This trend resulted from the new consumption practices that are reducing the alcohol intake, due to several reasons such as the preference of a healthier lifestyle, new restrictive driving/drinking regulations, religion reasons, pregnancy or abstinence. The main objective of this thesis is the study of a new process for producing a non-alcoholic beer (less than 0.5 vol.%) with an equilibrated aroma profile.

The most common method used to produce non-alcoholic beer is by interrupting the beer fermentation for keeping the ethanol content very low. This method is simple and uses the same resources of standard fermentation. However, it has a drawback related to beer quality, mainly because the reduction of wort compounds and the formation of important beer aroma compounds are also interrupted. As a result, non-alcoholic beer presents a typical warty flavour, very different from the alcoholic beers. This work studies the production of non-alcoholic beer from a fermented and clarified beer (with ca. 5.5 vol.% of ethanol).

Two processes were considered for removing the ethanol from beer: diafiltration, based on reverse osmosis membranes, and vacuum distillation, using a spinning cone column (SCC), based on moderate temperature extraction with water vapour in counter-current. In the diafiltration process, ethanol and water are selectively removed from the original beer through a reverse osmosis membrane and water is returned to the retentate batch-wise so that the water feed concentration is kept more or less constant. Reverse osmosis in diafiltration proved to be effective for removing ethanol from beer and membranes showed a good retention of important beer aroma compounds. Besides, beer is processed at lower temperatures, preserving the heat sensitive compounds from thermal damage. However, this process is industrially unfeasible for obtaining ethanol concentrations below 0.45 vol.%, due to the increasing consumption of diafiltration water.

SCC is a distillation unit made by rotating cones, fixed to a central shaft, alternated with fixed cones, attached to the column wall. Alcoholic beer flows down through the fixed cones under gravity and flows up through the spinning cones under centrifugal force. Water vapour, under vacuum, flows counter-currently and strips the ethanol (as well as aroma compounds) from beer. The dealcoholized beer from SCC can reach ethanol contents below 0.5 vol.% or even lower than 0.05 vol.%. The main disadvantage of this process is the loss of aroma compounds.

The present work proposes the preservation of beer sensorial quality by extracting the aroma compounds previously to their loss in the dealcoholization process, and adding them back to the non-alcoholic beer (dealcoholized beer). The aroma extraction is obtained by pervaporation due to its high selectivity for extracting aroma compounds present in the feed at very low concentrations. Pervaporation was first studied at laboratory level and then it was designed and built an industrial unit. Composite membranes of polyoctylmethylsiloxane (POMS) supported in polyetherimide (PEI) were found to be the most effective for aroma extraction from beer. The effect of critical operating conditions on the performance of POMS/PEI membranes was also studied.

The industrial plant was designed and built up in series with the SCC distillation plant. Several industrial tests were performed for optimizing the amount of extracted beer compounds and the aroma profile of the permeate. The coupling of pervaporation for beer aroma extraction with beer dealcoholization proved to be very effective for producing a non-alcoholic beer with a flavour profile very close to the alcoholic original one. This integrated process was the first one to be implemented at industrial scale, which resulted in a best-selling non-alcoholic beer and a world patent.

Since wine is also an alcoholic beverage with high consumption, it was considered the production of a low alcohol wine (with ca. 7 – 8 vol.% of ethanol) based on the previously described strategy.

RESUMO

A oferta de mercado de bebidas sem álcool tem sofrido um aumento durante os últimos anos. Esta tendência resulta dos novos hábitos de consumo que visam a diminuição da ingestão de álcool, devido a inúmeras razões, tais como um estilo de vida mais saudável, a aplicação de leis cada vez mais restritas na condução sob o efeito de álcool, razões religiosas, gravidez ou abstinência. Esta tese tem como objectivo principal estudar um novo processo para produção de cerveja sem álcool (inferior a 0,5 %vol.) com um perfil aromático equilibrado.

O processo mais comum para produzir cerveja sem álcool é a fermentação interrompida, em que o teor alcoólico é mantido em valores baixos. Este método é simples e usa os mesmos recursos da fermentação. Contudo, apresenta desvantagens no que concerne à qualidade da cerveja obtida, principalmente porque durante este processo a redução dos compostos do mosto e a formação dos compostos aromáticos principais da cerveja são também restringidas. Consequentemente, as cervejas sem álcool produzidas por este método apresentam um aroma e sabor característicos do mosto, muito diferente do sabor das homólogas cervejas com álcool. Este trabalho estuda a produção de cerveja sem álcool a partir duma cerveja completamente fermentada e filtrada (com um teor em etanol de cerca de 5,5 %vol.).

Durante este estudo, foram considerados dois processos para remoção do etanol da cerveja: osmose inversa, operando em diafiltração e destilação sob vácuo em coluna de cones rotativos (CCR), operando com vapor de água em contra-corrente e temperatura moderada. Na diafiltração, o etanol e a água são removidos da cerveja original através de uma membrana de osmose inversa, sendo que a água é readicionada ao retido por partidas de forma a manter a sua concentração aproximadamente constante. Verificou-se que o processo de osmose inversa operando em diafiltração é eficaz na remoção do álcool da cerveja e as membranas mostraram uma boa retenção para os compostos aromáticos principais da cerveja. Além disso, a cerveja é processada a baixas temperaturas, preservando os compostos termosensíveis da degradação térmica. Porém, este processo é industrialmente inviável para reduzir o teor alcoólico da cerveja até valores inferiores a 0,45 %vol. devido ao aumento significativo do consumo de água.

A CCR é uma coluna de destilação constituída por cones giratórios, fixos a um veio central, alternados com cones estacionários, fixos à parede da coluna. A cerveja com álcool desce através dos cones estacionários devido à força gravítica e sobe através dos cones

rotativos devido à força centrífuga. O vapor de água, sob vácuo, sobe pela coluna em contra-corrente e remove o etanol (e outros compostos voláteis) da cerveja. A cerveja desalcoolizada pela CCR pode atingir teores em etanol inferiores a 0,5 %vol. ou mesmo inferiores a 0,05 %vol. A principal desvantagem deste processo é a perda significativa de compostos aromáticos.

O presente trabalho propõe a preservação da qualidade sensorial da cerveja através da extracção dos compostos aromáticos antes da sua perda no processo de desalcoolização, e sua adição à cerveja desalcoolizada. A extracção dos compostos aromáticos é conseguida por pervaporação graças à sua elevada selectividade para extracção dos compostos presentes na alimentação em concentrações muito baixas. A pervaporação foi primeiramente estudada a nível laboratorial sendo depois projectada e construída a unidade industrial. Durante o estudo verificou-se que as membranas de polioctilmetilsiloxano (POMS) suportadas em polieterimida (PEI) são as mais eficazes para a extracção de compostos aromáticos da cerveja. O efeito das condições operatórias críticas no desempenho das membranas de POMS/PEI foi também estudado.

A unidade industrial de pervaporação foi projectada e construída em série com a unidade de desalcoolização (CCR). Foram efectuados vários ensaios industriais com o objectivo de otimizar a extracção de compostos aromáticos e o perfil aromático do permeado. O processo de pervaporação, para extrair os compostos aromáticos, acoplado ao processo de desalcoolização por destilação em coluna de cones rotativos, provou ser eficiente para produzir uma cerveja sem álcool com um perfil aromático semelhante ao da cerveja alcoólica original. O processo integrado resultou numa cerveja sem álcool mais vendida do mercado e foi alvo de concessão de uma patente internacional.

Uma vez que o vinho é igualmente uma bebida alcoólica de grande consumo, foi considerada a produção de um vinho com baixo teor alcoólico (com cerca de 7 – 8 %vol. em etanol), tendo como base a estratégia previamente descrita.

RÉSUMÉ

L'offre du marché des boissons au bas teneur alcoolique a augmenté ces dernières années. Cette tendance est une conséquence des nouvelles habitudes de consommation afin de réduire la consommation d'alcool, pour raisons diverses comme la santé, la répression des abus de l'alcool au volant, des raisons religieuses, la gestation ou l'abstinence. Cette thèse a comme objectif principal d'étudier un nouveau procédé pour la production d'une bière sans alcool (moins que 0,5 %vol.) avec un profil aromatique équilibré.

Le procédé le plus utilisé pour produire de la bière sans alcool est la fermentation raccourcie, afin de rester le teneur alcoolique très bas. Cette méthodologie est très simple et utilise les mêmes ressources que la fermentation classique. Toutefois, cette méthode présente certains inconvénients en ce qui concerne la qualité de la bière produite, surtout parce que pendant cette pratique, la réduction des substances du moût et la formation des substances aromatiques de la bière sont aussi écourtées. Par conséquent, les bières sans alcool produites pour cette pratique ont des arômes et goûts particuliers du moût, très différents de celles de son modèle alcoolisé. Ce travail étudie la production de la bière sans alcool à partir d'une bière complètement fermentée et filtrée (avec une teneur en éthanol de l'ordre 5,5 %vol.).

Au cours de ce projet, deux techniques de réduction de l'éthanol de la bière ont été testées: l'osmose inverse au mode de diafiltration et distillation sous vide, avec une colonne à cônes rotatifs (CCR), qui utilise vapeur d'eau à contre-courant et à la température modérée. Dans la diafiltration, l'alcool et l'eau sont éliminés de la bière originale à travers une membrane d'osmose inverse, et l'eau est réintroduite au rétentat en discontinu afin de rester sa concentration dans la bière constante. Il a été vérifié que la méthode d'osmose inverse est efficace pour éliminer l'alcool de la bière et les membranes ont présenté une bonne rétention aux substances aromatiques de la bière. D'autre part, la bière est traitée aux températures basses, afin de préserver les composés thermosensibles de la dégradation thermique. Cependant, cette pratique n'est pas viable industriellement pour réduire le teneur alcoolique de la bière jusqu' à teneurs inférieures à 0,45 %vol. parce que la consommation de l'eau est significativement augmentée.

La CCR s'agit d'une colonne à distillation composée de cônes tournants, attachés à un axe central et parallèles à cônes fixés à l'intérieure du mur de la colonne. La bière avec alcool descend à travers les cônes fixes par effet de la gravité et ensuite, la bière se déplace vers le haut des cônes en rotation par effet de la force centrifuge. Le vapeur d'eau, sous

vide, coule vers le haut de la colonne à contre-courant et il rassemble l'alcool (et autres composés volatils) de la bière. La bière désalcoolisée par la CCR peut atteindre teneurs en éthanol inférieures à 0,5 %vol. ou même inférieures à 0,05 %vol. Le principal inconvénient de ce procédé est la perte significative des substances aromatiques.

Cette thèse propose la préservation de la qualité sensorielle de la bière à travers l'extraction des substances aromatiques avant sa perte lors du procédé de la désalcoolisation, afin de les réintroduire à la bière désalcoolisée. L'extraction des composés aromatiques est réalisée par pervaporation parce que cette technique a une sélectivité élevée pour extraire les composés présents dans la bière aux concentrations très basses. La pervaporation a d'abord été étudiée à l'échelle laboratoire et ensuite l'unité industrielle a été projetée et construite. Dans cette étude on a vérifié que les membranes de polyoctylméthylsiloxane (POMS) sur un support de polyétherimide (PEI) sont les plus efficaces pour l'extraction des substances aromatiques de la bière. L'effet des conditions de fonctionnement essentiels à l'accomplissement des membranes POMS/PEI a été aussi étudié.

L'unité industrielle de pervaporation a été projetée et construite pour opérer en série avec l'unité de désalcoolisation (CCR). On a effectué plusieurs essais industriels afin d'optimiser l'extraction des substances aromatiques et le profil aromatique du perméat. Le procédé de la pervaporation, pour l'extraction des composés aromatiques, couplé au procédé de la désalcoolisation en colonne à cônes rotatifs, a prouvé être efficient pour produire une bière sans alcool avec un profil aromatique similaire à la bière alcoolique originale. Ce procédé a été le premier à être mis en œuvre à l'échelle industrielle, donc il a résulté à une bière sans alcool, la plus vendue au marché et à un brevet international.

Comme le vin est aussi une boisson alcoolique avec une consommation élevée, on a considéré l'élaboration d'un vin au faible degré alcoolique (avec une teneur en éthanol de l'ordre 7 – 8 %vol.), selon la stratégie décrite avant.

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Chapter I

1. Introduction

Abstract

The present thesis aims the study of a process for enriching the aroma profile of a non-alcoholic beer. Beer is an alcoholic beverage obtained by fermentation of wort (composed by water and cereals). The chemical reactions that convert the sugars from the raw materials to ethanol, carbon dioxide and flavour compounds are due to the metabolism of yeasts. The most usual process for producing non-alcoholic beer is by interrupting the fermentation, which avoids the formation of ethanol. However, this process impairs the formation of the characteristic flavour profile. Beers produced by this process present a characteristic warty taste and have lack of aroma compounds. In order to produce a non-alcoholic beer with the typical taste and aroma of an alcoholic beer, it is considered in the framework of this thesis the use of separation processes for removing the ethanol from a completely fermented beer. However, the separation processes also leads to a loss of important beer flavour compounds, due to the extreme conditions applied or to the low selectivity of the processes. In order to recover the beer aroma compounds lost in the dealcoholization, it was considered coupling a preliminary separation process. This thesis studies for the first time ever the pre-recovery by pervaporation of relevant aroma compounds from the original beer, followed by spinning cone distillation for alcohol removal and then the aroma compounds return to the dealcoholized beer. This process proved to produce an aroma equilibrated non-alcoholic beer.

1.1. Beer

Beer is one of the most popular alcoholic beverages and its origin dates far from a very old period, since Sumerians, Egyptians, until nowadays [1,2].

Beer is an alcoholic beverage obtained by fermentation of wort, which is a mixture of malt, hops and water. Breweries can also use some adjuncts or processing aids to improve beer quality. Malt is the main raw material of the beer and results from the malting process of barley (germination). Malt is a source of enzymes that break down its starches and proteins, in order to be available for the yeast. Special malts, such as coloured malts with improved flavour, are used in lower amounts for producing special beers. Hop is an aromatic plant that imparts a bitter aroma to the beer, contributes for the foam stabilization and the preservation of beer against microbiological contamination, and it is added to the wort as extract from the plant. Process water used to produce beer should be suitable for human consumption and its mineral concentration should be corrected. Processing adjuncts are used to complement the malt starch and decrease the wort proteins content. Examples of adjuncts include non-malted cereals such as grits (obtained from maize), rice, wheat or barley and sugars (sucrose) and syrups (hydrolyzed sucrose) [1–3].

The process of beer production includes four main steps:

- Wort preparation
- Fermentation, maturation and stabilization
- Clarification
- Packing and biological stabilization

Wort preparation is the first phase of beer production and consists on several steps of milling, mashing, filtration, boiling, clarification, cooling and aeration. Milling step aims the exposure of malt components for increasing their extraction and conversion. Usually, non-malted cereals are added already milled to the wort. During the mashing step, hot water is added to malt and other cereals, leading to the conversion of proteins to peptides and amino acids and starches to fermentable sugars (maltose, maltotriose and smaller amounts of sucrose, glucose and fructose), which is provided by malt enzymes (formed during malting process). The filtration goal is the separation of the insoluble fraction of wort (spent grains or *drêche*) from the dense wort. After filtration, it follows the boiling of the filtrated wort and its blending with hop extracts. Boiling aims the sterilization of wort, removal of undesirable volatile compounds, inactivation of enzymes,

precipitation of proteins (precursors of beer haze), solubilisation and isomerisation of hop bitter compounds. During clarification, wort flows to a decanter or a centrifuge for separating the protein precipitate and the non-soluble fraction of hop. In order to prepare the wort for the yeast addition, wort is cooled down to the fermentation temperature and aerated [1–3].

Fermentation begins with the addition of a selected yeast strain to the wort cooled and aerated, before that being transferred to the fermentation vessel (yeast pitching). Beer yeast is a unicellular microorganism that belongs to Fungi and *Saccharomyces* genus. Beer yeast obtains energy by two metabolic pathways: respiration (in the presence of oxygen) which origins the yeast growing (usually by budding¹) and fermentation (in absence of oxygen) that causes the formation of ethanol from wort sugars. During the **main fermentation** (primary) beer yeast reproduces and converts the fermentable sugars from wort into ethanol and carbon dioxide, and some aroma compounds, until a desired content of extract (concentration of sugars) and ethanol, originating an immature beer. This process is followed by a **secondary fermentation** (maturation) at lower temperature and in the presence of lower amount of yeast in order to remove some undesirable beer compounds and to improve the aroma profile. Beer maturation is followed by **stabilization**, where the precipitation of proteins and polyphenols occurs, which contributes to the beer haze. During this stage, the remaining yeast is removed from the beer [1–3].

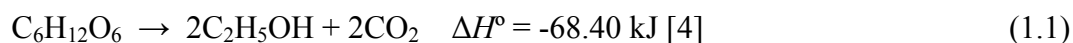
Clarification consists of the elimination, by filtration, of undesirable beer compounds, such as protein-polyphenol colloids, in order to increase the stability of the beer. After being filtered, beer is **packed**, using different pack containers such as bottles, cans or kegs.

Biological stabilization consists of the pasteurization of beer, which aims the reduction of microbial contamination of the beer [1–3].

¹ Budding: a small bubble is formed from the mother cell, receiving part of the cytoplasm and the daughter nucleus, formed by division; resulting into two cells.

1.1.1. Fermentation: ethanol and flavour compounds formation

During fermentation, the most important reaction is the conversion of wort sugars into ethanol and carbon dioxide by yeasts. This conversion is represented by the overall Gay-Lussac exothermic reaction [1]:



This reaction only shows the starting and end compounds of the alcoholic fermentation. Fermentation of wort sugars comprises several steps, which result in intermediate or secondary products. Figure 1.1 shows a simplified sketch of the main groups of fermentation products.

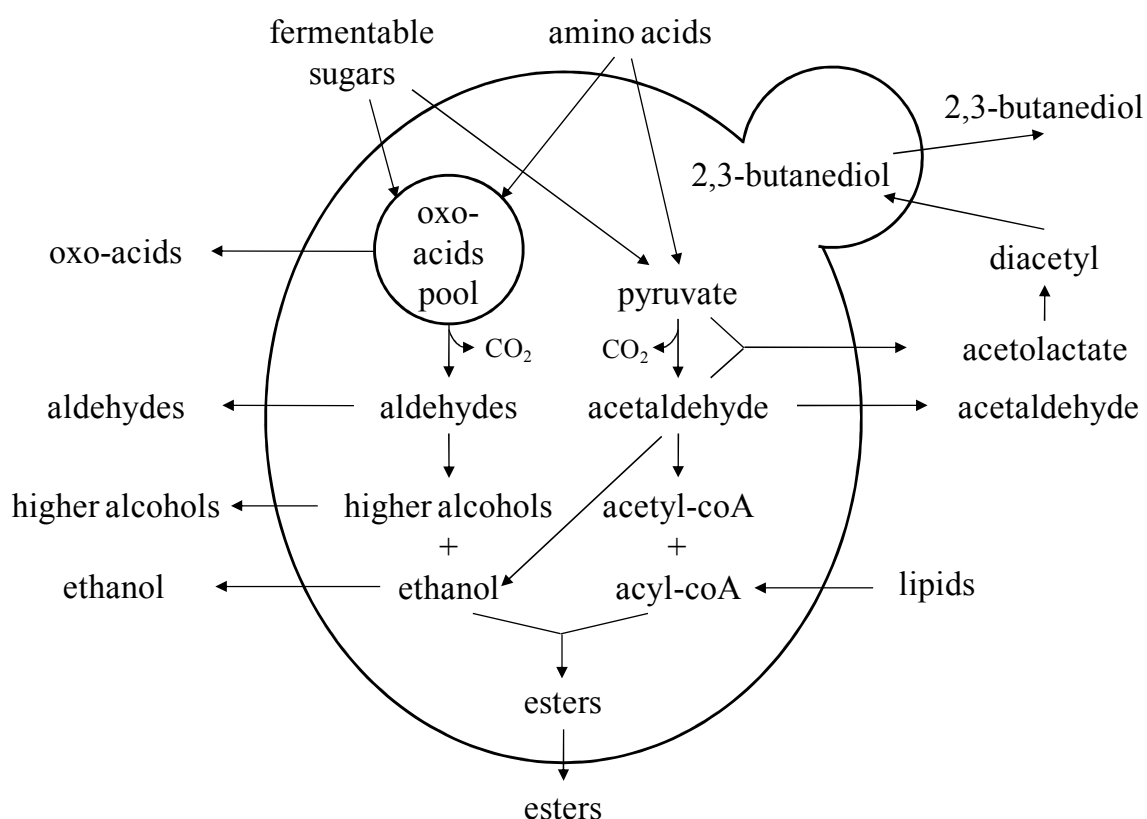


Figure 1.1. Formation of beer compounds by yeast metabolism during fermentation (based on [3,5]).

Fermentable sugars of the wort (maltose, maltotriose and sucrose) are hydrolyzed to glucose. During glycolic pathway, glucose is converted in pyruvate. In the next step, pyruvate suffers decarboxylation, resulting in carbon dioxide (CO₂, responsible for beer carbonation) and acetaldehyde. Afterwards, acetaldehyde is reduced to ethanol [1,3].

Ethanol and carbon dioxide are the main products of the fermentation and as a result, they are the major constituents of the beer besides water. However, during beer fermentation yeast metabolism forms by-products, which are present in the final beer at low concentrations (at ppm level) and have a great contribution on the aroma and flavour profile of beer. Ethanol influences directly the beer flavour, imparting a warming sensation and interacts with other aroma compounds, influencing their contribution to the beer flavour. Carbon dioxide also plays an important role on the beer quality, contributing to the foam formation, to the beer body and to the perception of other aroma compounds [1,6].

Fermentation by-products can be divided in two categories: immature beer compounds and mature beer compounds.

Immature beer flavour compounds

Immature beer flavour compounds include aroma compounds from chemical groups of vicinal diketones, aldehydes and sulphur compounds. These compounds are responsible for an immature flavour of the beer and, at high concentrations they can damage beer aroma and taste. During fermentation or maturation, they can be converted into other compounds [1,2,6].

Diacetyl (2,3-butanedione) and 2,3-pentanedione are two **vicinal diketones** responsible by beer off-flavour. These compounds present a low taste threshold² (0.1 – 0.15 ppm), imparting a buttery flavour to the beer. The removal of vicinal diketones occurs during beer maturation and their amount is used as a criterion to evaluate the level of beer maturation. Yeast forms vicinal diketones precursors (e.g., acetolactate for diacetyl – cf. Figure 1.1) during its metabolism by the amino acids synthesis (pyruvate formation), and expels them to the fermentation broth. These precursors are converted in the respective diketones outside yeast cells. Yeasts absorb vicinal diketones and reduce them to other compounds with higher taste threshold (e.g., 2,3-butanediol for diacetyl – cf. Figure 1.1). As a result, their effect on the final beer flavour is decreased [1–3,6].

² Threshold value: minimum concentration for detecting or identifying a flavour compound.

Carbonyl compounds from wort are highly responsible for beer wort off-flavours due to their low beer threshold. **Aldehydes** are essentially formed during wort production, and during fermentation from oxo-acids decarboxylation. Oxo-acids result from amino acids metabolism – the catabolic pathway, and from sugars metabolism – the anabolic pathway (cf. Figure 1.1) [5,7]. Acetaldehyde is the most representative aldehyde from beer, being an intermediate of ethanol formation during fermentation, as sketched in Figure 1.1. Acetaldehyde is expelled by yeast cell during primary fermentation; it is related to the green beer flavour, giving a “green apples” flavour to the beer. The concentration of acetaldehyde decreases due to its conversion in ethanol [1,6].

Sulphur compounds are present in beer at low concentrations (ppb level), imparting off-flavours to the beer due to their low taste threshold. Hydrogen sulphide is a sulphur compound that results from yeast metabolism, from amino acids containing sulphur and it is released from beer during maturation due to its high volatility. Dimethylsulphide (DMS) is another sulphur compound, which can result from wort preparation, due to the fact of its precursor being present in the malt. DMS is almost completely removed during wort boiling. When the precursors pass to the fermentation, they are converted into DMS, which is removed with beer gases, remaining only at minor levels on the final beer [1,6].

Mature beer flavour compounds

Mature beer flavour compounds are characteristic from finished beer and include higher alcohols and esters. Their concentration increases during beer maturation. The concentration of higher alcohols and esters, within a specified range of values, is essential for a higher beer quality [1,2,6].

Higher alcohols are the compounds in higher concentration in the beer, having a great contribution for the aroma and taste. These compounds are sometimes referred as fusel alcohols or fusel oil and they have higher molecular weight and boiling temperature than ethanol [8]. There are many higher alcohols in beer, of which the most important for its aroma are: propanol, isobutanol, 2-methylbutanol (active amyl alcohol) and 3-methylbutanol (isoamyl alcohol). These alcohols contribute to the beer flavour by an intensification of alcoholic or solvent-like aroma, imparting also a warm tasting sensation. Besides, isoamyl alcohol contributes to a sweet and fruity flavour [5,8]. Propanol (beer threshold – 800 mg·L⁻¹) is present in beer at a concentration range of 7 to 14 mg·L⁻¹ while

isobutanol (beer threshold – $200 \text{ mg}\cdot\text{L}^{-1}$) has a concentration of 8 to $57 \text{ mg}\cdot\text{L}^{-1}$. Amyl alcohols (2-methylbutanol, beer threshold – $70 \text{ mg}\cdot\text{L}^{-1}$ and 3-methylbutanol, beer threshold – $65 \text{ mg}\cdot\text{L}^{-1}$) are the higher alcohols in higher concentration in beer ranging from 27 to $122 \text{ mg}\cdot\text{L}^{-1}$ [9]. Despite the higher flavour threshold of higher alcohols, their effect on the final beer results from the interaction with other flavour compounds, the so-called matrix effect [8].

Higher alcohols result from the assimilation of amino acids – the catabolic route, and from sugars metabolism – the anabolic route (cf. Figure 1.1). In both pathways, the higher alcohols precursors are oxo-acids. During the catabolic route, the amino acids taken by the yeasts from the fermentation broth are transaminated to oxo-acids, which suffer decarboxylation resulting in acetaldehydes that are reduced to the homologue alcohols [3,5,6,8]. Figure 1.2 shows a sketch of the formation of the referred higher alcohols from amino acids metabolism.

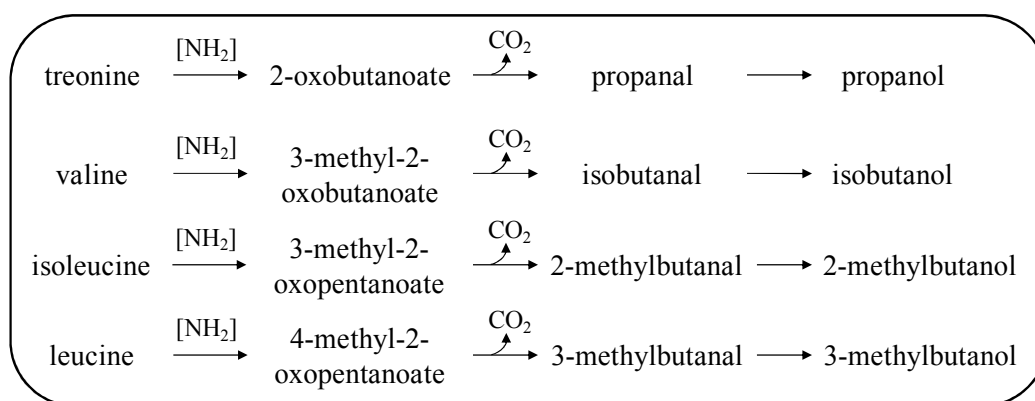


Figure 1.2. Higher alcohols synthesis by catabolic pathway, $[\text{NH}_2]$ represents the group transferred to the transaminase enzyme (based on [3,8]).

Higher alcohols are side products of the synthesis of amino acids (leucine, isoleucine and valine) from pyruvate – anabolic route. The penultimate reaction of amino acids synthesis is the formation of an oxo-acid, which suffers transamination to form the respective amino acid. In such conditions, these oxo-acids are decarboxylated and then reduced to produce the homologue higher alcohols. The difference between the catabolic and anabolic pathways is the source of the oxo-acids; in the first case they result from the wort amino acids assimilated by yeast, and in the second case, they are synthesized from pyruvate [6,8]. Besides, higher alcohols can result from the reduction of some aldehydes present in the wort.

Higher alcohols are also important aroma compounds because they are precursors of another group of flavour compounds, the esters.

Esters are the most important group of aroma flavour compounds. Esters flavour thresholds are very low resulting in a high contribution to the beer aroma and taste [1]. Esters are responsible for the sweet, fruity and perfume-like aroma of the beer. The major group of aroma esters are the acetate esters such as ethyl acetate and isoamyl acetate [5,8]. Ethyl acetate (beer threshold – $30 \text{ mg}\cdot\text{L}^{-1}$) imparts a fruity and solvent-like aroma to the beer and its concentration ranges from 8 to $48 \text{ mg}\cdot\text{L}^{-1}$. Isoamyl acetate (beer threshold – $1.2 \text{ mg}\cdot\text{L}^{-1}$) confers to the beer a banana flavour and it is present in the beer at a concentration ranging from 0.8 to $6.6 \text{ mg}\cdot\text{L}^{-1}$ [5,9]. As esters are present in beer at concentrations around their threshold values, this means that their presence is pronounced and minor changes on their concentration can result in dramatic changes on the beer flavour profile.

Esters are formed during fermentation by the reaction between higher alcohols or ethanol and acetyl-coA (which results in acetate esters) or acyl-coA, both resulting from pyruvate. Ethyl acetate is the most common ester in beer because it results from ethanol [3,5,8]. Figure 1.3 shows the formation of the referred acetate esters from the homologue alcohols and acetyl-coA.

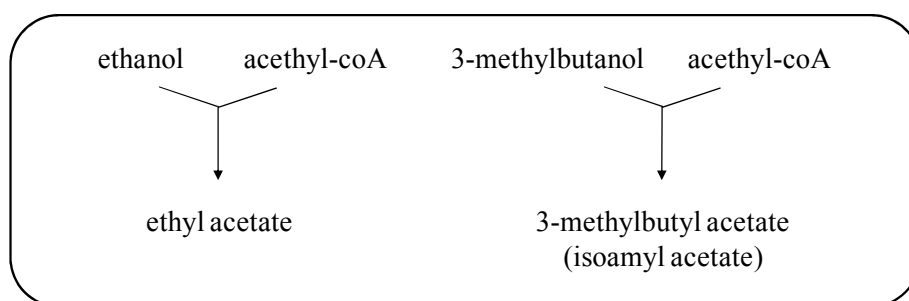


Figure 1.3. Esters synthesis from alcohols reaction with acetyl-coA (based on [3,8]).

It is important to refer that more important than the aroma compounds concentration, beer aroma and taste are influenced by the relationship between the amount of compounds and the respective taste threshold and by the relationship between the concentrations of some group of aroma compounds, such as the higher alcohols to esters ratio (A/E). On the other hand, interactions between compounds can occur and influence the perception of the aroma compounds [8].

1.2. Production of non-alcoholic beers

According to the Portuguese legislation, a non-alcoholic beer should have an ethanol content lower than 0.5 vol.% [10]. Nowadays it has been observed an increasing trend on the consumption of non-alcoholic drinks due to several reasons. People become more aware with the problems that alcohol brings to the society, and choose to have a healthier lifestyle, by decreasing alcohol intake. On the other hand, the increasing restrictive drinking/driving rules lead to consumers being more conscious. Finally, there are other reasons such as religion, abstinence or pregnancy that explain that trend. As a result, brewers are increasing their offer on non-alcoholic or low alcohol drinks, resulting in a demand of improved technological solutions for producing these beverages.

Usually, the processes for producing non-alcoholic beer are divided in two major categories: processes of ethanol formation restriction and processes of ethanol removal [1,3].

Figure 1.4 sketches the most popular methods for producing non-alcoholic or low alcohol beer and Tables 1.1 to 1.4 summarize the main advantages and disadvantages of the same processes.

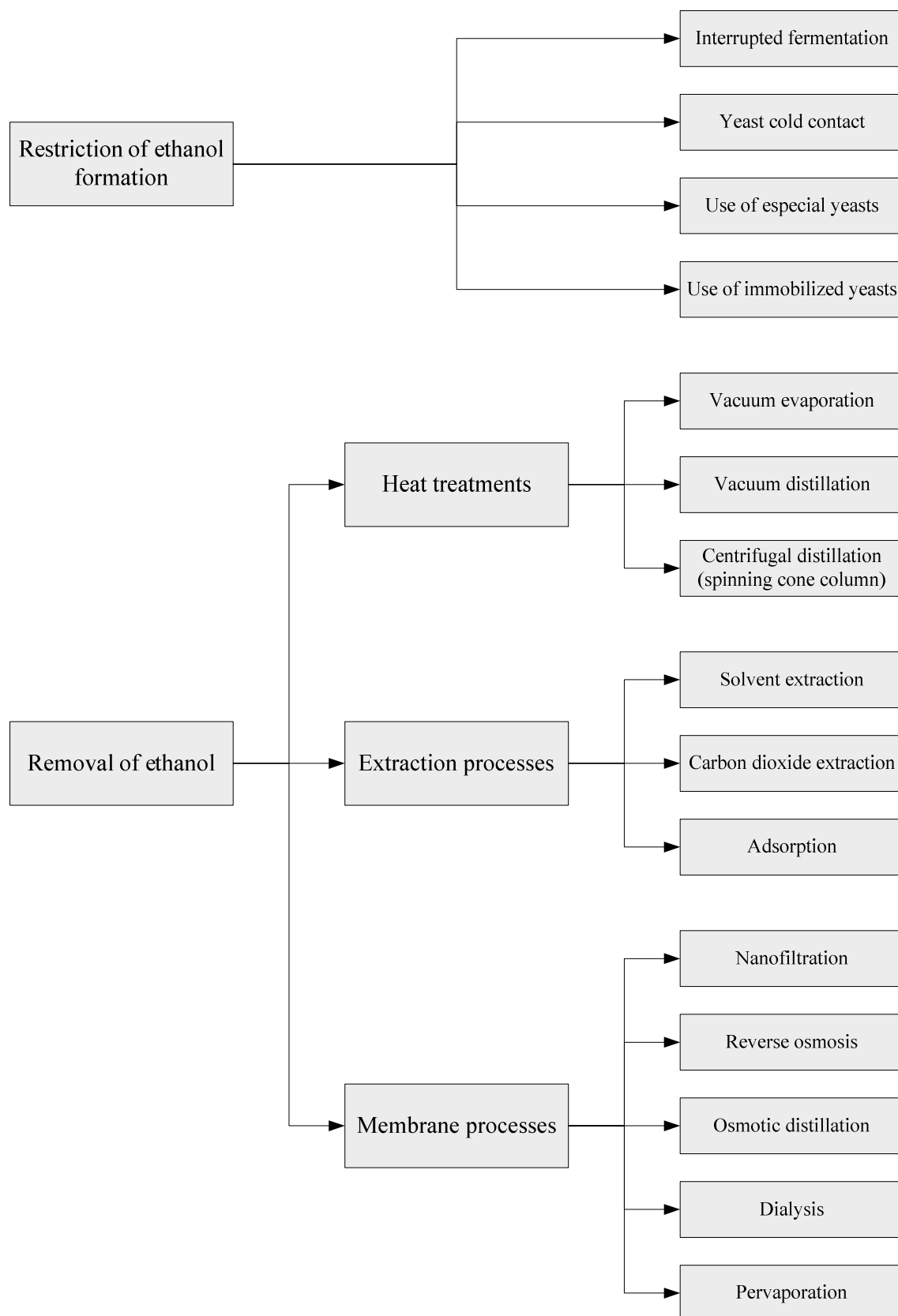


Figure 1.4. Processes for producing non-alcoholic or low alcohol beer.

Table 1.1. Processes for producing non-alcoholic beer by restricting ethanol formation.

Process	Advantages	Disadvantages	Ref.
Interrupted fermentation	• Uses the same equipment of standard fermentation	• The formation of aroma compounds is restricted • Final beer with warty aroma	[1,2]
Yeast cold contact	• Uses the same equipment of standard fermentation • Yeast reduces carbonyl compounds from wort and produces aroma compounds	• Yeasts can convert amino acids into aldehydes, which contribute to off-flavours	[1,11–13]
Use of especial yeasts	• Uses the same equipment of standard fermentation	• High content of sugars on the final beer – sweet taste	[1,2]
Use of immobilized yeasts (continuous fermentation)	• Yeast reduces aldehydes from wort • Yeast forms beer aroma compounds • Good utilization of raw materials	• Difficult to control the process • High price of the carriers • Risk of contamination • Need of continuous bioreactor	[1,7,14,15]

Table 1.2. Processes for producing non-alcoholic beer by removing ethanol from a finished beer – heat treatment processes.

Process	Advantages	Disadvantages	Ref.
Vacuum evaporation	• Allows ethanol content of 0.05 vol. % • Moderate temperatures, resulted from the vacuum	• Need of additional evaporator • High energy costs • Thermal impact of sensitive compounds • Volatile aroma compounds are removed with ethanol	[3]
Vacuum distillation	• Allows ethanol content of 0.05 vol. % • Moderate temperatures, resulted from the vacuum	• Need of additional distillation column • High energy costs • Thermal impact of sensitive compounds • Volatile aroma compounds are removed with ethanol	[1]
Centrifugal distillation (spinning cone column)	• Allows ethanol content of 0.05 vol. % • Thermal impact is minimized • Low residence time and moderate temperatures • High turbulent flows and high contact area between two phases	• Need of additional spinning cone column • High energy costs • Stripping medium also removes volatile aroma compounds	[16–19]

Table 1.3. Processes for producing non-alcoholic beer by removing ethanol from a finished beer – extraction processes.

Process	Advantages	Disadvantages	Ref.
Solvent extraction	Solvents are immiscible with water and present high solubility to ethanol	- Additional liquid-liquid extraction unit is needed - Aroma compounds that are soluble in the solvent are removed - Product can show traces of the solvent - Solvents must be food approved	[17]
Carbon dioxide extraction	- Carbon dioxide extracts ethanol, without extracting water and other larger molecules of beer - Can be performed at room temperature, avoiding thermal impact of beer	- Additional extraction unit is required - Carbon dioxide strips other volatile compounds - High operation costs	[17,20,21]
Adsorption	Hydrophobic adsorbents such zeolites have good affinity with ethanol	- Additional separation unit is needed - Adsorbents must be regenerated - Aroma compounds co-adsorb with ethanol - High operation costs	[22,23]

Table 1.4. Processes for producing non-alcoholic beer by removing ethanol from a finished beer – membrane processes.

Process	Advantages	Disadvantages	Ref.
Nanofiltration	• Beer is treated at low temperature and pressure • Membranes show high retention to aroma compounds	• Need of additional nanofiltration plant • Need of diafiltration water	[1,24]
Reverse osmosis	• Beer is treated at low temperatures • Some membranes show high retention to aroma compounds	• Additional membrane unit is required • High pressure is unbeneficial to the beer • Some membranes can show low retention to aroma compounds • Need of diafiltration water • Difficult to achieve ethanol below 0.45 vol. %	[1,25–27]
Osmotic distillation	• Dealcoholization is performed at low temperature • The permeation of water is reduced	• Additional separation unit is required • Need to recirculate the strip solution • Loss of beer aroma compounds	[28–31]
Dialysis	• Dealcoholization is performed at low temperature • Water does not permeate the membranes	• Additional dialysis unit is required • Need to recirculate the dialysate • Loss of beer aroma compounds	[1,3]
Pervaporation	• Beer is dealcoholized at low temperatures • Ethanol removal is increased with hydrophilic membranes • Water extraction is reduced by using a sweep gas with steam	• Additional pervaporation unit is required • Aroma compounds removal is higher than ethanol with hydrophobic membranes • Permeation fluxes are low, demanding high membrane areas • High costs of condensation and vacuum	[32–34]

1.2.1. Restriction of ethanol formation processes

The production of non-alcoholic or low alcohol beer by restricting the ethanol formation can be accomplished by interrupting the beer fermentation and by using special or immobilized yeasts in order to keep the ethanol content very low.

Interrupted fermentation is performed at a temperature lower than a regular fermentation, until reaching an ethanol content below 0.5 vol.%. The fermentation is then stopped by removing the yeast (by centrifugation or filtration) or by flash pasteurization. The beer is then matured at very low temperature (0 – 1 °C). This process has the disadvantage of limited aroma compounds formation (cf. Table 1.1). As a result, beer flavour does not change towards the typical alcoholic flavour profile and a warty sensation is present on the alcohol free beer [1,2,7].

In **yeast cold contact** processes, beer yeast contacts with wort at low temperatures, avoiding the ethanol production. At these conditions, yeast is able to produce beer aroma compounds and to reduce the carbonyl compounds (aldehydes) from wort [1,11,12]. Despite the ability of yeast to reduce aldehydes from wort at low temperatures, yeast can also produce aldehydes from wort amino acids during cold contact fermentation [13].

The restriction of ethanol formation can be achieved by substituting typical beer yeasts by **especial yeast** strains, such as *Saccharomyces ludwigii* species, that ferment fructose and glucose and do not convert maltose, resulting in a beer with low alcohol content (less than 0.5 vol.%) and higher content of sugars, which confers however a sweet taste [1,2].

The use of **immobilized yeasts** is another technology for producing alcohol free beer by avoiding the ethanol formation. The immobilization of yeasts consists of their attachment to a carrier/support, in order to allow the formation of yeast colonies on it. Usually, there are used porous glass particles or brewing and agricultural by-products, such as spent grains or corncobs, as carrier materials. Wort flows continuously through the packed bed of the colonized carrier. The control of operating conditions, such as temperature and wort flowrate (residence time) influences the degree of fermentation, and thus, the alcohol content of the beer at the bioreactor outlet. The ethanol formation is restricted but yeasts still produce beer flavour compounds, by reducing the wort aldehydes to the homologue alcohols [1,7,14,15]. Despite the formation of beer flavour compounds,

this process has some disadvantages: it is difficult to control the process, the high price of the carriers and the high risk of contamination beyond the need of a continuous bioreactor [14].

1.2.2. Ethanol removal processes

In order to obtain a non-alcoholic or a low alcohol beer, ethanol can be removed from a completely fermented beer, and then containing the original aroma profile.

1.2.2.1. Heat treatments

In heat treatment processes, ethanol is removed from the original beer by means of heating. At atmospheric pressure, the ethanol boiling point is 78 °C while water boils at 100 °C, so applying a temperature lesser than 100 °C, alcohol evaporates preferentially and its separation from beer is possible – single or multiple stage distillation. However, high temperature is unbeneficial to heat sensitive compounds, which can suffer physical or chemical modifications [21]. These changes lead to a decrease of beer quality during the dealcoholization process. In order to overcome this disadvantage, it can be applied low pressure or vacuum and consequently the separation of ethanol can be achieved at moderate temperatures (lower than 78 °C). Some separation processes are based on this principle [1,2].

In **vacuum evaporation** beer is heated with steam, under vacuum, in plate evaporators. The evaporated beer flows to a separator where the dealcoholized beer is collected from the bottom and the ethanol rich vapour is led to a condenser. In order to reduce even more the ethanol content, alcohol free beer can be made recirculating through the plate evaporator; instead, multistage evaporation plants can be used. Non-alcoholic beer obtained by vacuum evaporation can achieve ethanol contents lower than 0.05 vol.% [3].

Vacuum distillation uses typical distillation columns, working under vacuum, for removing ethanol from beer. The bottom product of the distillation column consists of alcohol free beer while the distillate consists of an ethanol rich stream, which is condensed at the distillation column outlet [1].

Centrifugal distillation is a variation of vacuum distillation, which uses a column with a special design – the **spinning cone column**. Spinning cone column (SCC) distillation is a worldwide popular method for beverages dealcoholization. This technology was invented by Flavourtech Pty. Ltd. (Australia) and consists in a gas-liquid counter-current column, where the stripping medium extracts the ethanol from the beverage [16,17]. The spinning cone column operates as a pure stripping column because the beer is fed on the top of the column and there is no rectification or enrichment as in typical distillation.

This column comprises a rotating central shaft and spinning cones attached to the shaft intercalated with static cones fixed to the column wall. The beer travels down through the stationary cones due to gravity force and flows up through the spinning cones as a thin layer under centrifugal force. The stripping medium (e.g., steam) is fed at the column bottom and collects the alcohol. The vapour with alcohol is carried out of the column for being condensed. The dealcoholized beer flows down the column and is collected from the bottom outlet [16,18].

SCC distillation has advantages such as low residence time and moderate temperatures, resulted from the applied vacuum, which minimizes the thermal impact on the beverage, high turbulent flows and high contact area between the two phases, which increases ethanol removal kinetics [17,18].

Despite SCC advantages, this method has also some disadvantages concerning the alcohol free beer quality, once the stripping medium also removes other volatile compounds, namely beer aroma compounds, together with ethanol [19]. Other advantages and disadvantages are summarized in Table 1.2.

Generally, all heat treatments affect the aroma flavour and taste of the non-alcoholic beer. The applied temperatures (even moderate ones) or the strip streams spoil the beer quality; several important beer compounds are removed and some of beer compounds suffer chemical reactions during heat processing [1,21].

1.2.2.2. Extraction processes

Extraction processes use an extraction medium to remove ethanol from beer.

In **solvent extraction**, feed beer contacts with an immiscible phase (the solvent, e.g., pentane or hexane) that presents a good solubility to ethanol. Ethanol is thereby removed from the beer into the solvent. This technology has a serious drawback since the final product contains solvent traces. On the other hand, aroma compounds that are soluble in the solvent are also removed with the ethanol [17].

Carbon dioxide extraction is based on the same principle of the extraction with solvents. In the present case, the solvent is food compatible and consists of supercritical or liquid carbon dioxide. At some conditions of temperature and pressure, carbon dioxide has properties similar to organic solvents. This process produces a good quality beverage, mainly because water, salts and other larger molecules (proteins and carbohydrates) are not extracted and the process can be performed at room temperatures, minimizing thermal degradation of beer compounds. On the other hand, carbon dioxide also strips some important aroma compounds. In this case, a first stage of carbon dioxide extraction is used for extracting aroma compounds that are added to the dealcoholized beverage from the second stage. Different operating conditions of the two stages influence the selective extraction of aroma compounds and ethanol. The operation costs of this process are usually high [17,20,21].

Adsorption can be used for beer dealcoholization. This separation process is based on the adsorption and molecular sieving of ethanol in hydrophobic adsorbents, such as zeolites. The original beer is thereby separated in an aqueous stream (alcohol free beer) and an alcoholic adsorbed phase. After ethanol removal, a gaseous stream, such as carbon dioxide, thermally regenerates the adsorbent. Usual adsorbents also extract other beer aroma compounds, thus an additional distillation column is required for dealcoholizing the desorbed phase, resulting in an alcoholic distillate and an aroma concentrated stream. The last one is added to the alcohol free beer for balancing the aroma profile [22,23]. This approach is however very expensive and is only feasible for very specific applications.

1.2.2.3. Membrane-based processes

Membrane is a semi-permeable physical barrier, placed between two bulk phases, which allows the transport of one or more species between these phases [35,36]. This transport is controlled, among other factors, by membrane nature. In membrane processes, the product which is intended to be treated (the feed stream) flows tangentially to the membrane surface and is separated in two fractions, the permeate that crosses the membrane and the retentate that remains in the feed side. This type of separation is known as cross-flow filtration and it can be applied to the dealcoholization of beer. Various membrane separation processes can be used differing in the physical effects that allow the ethanol separation [1,35,36].

Nanofiltration (NF) and **reverse osmosis** (RO) are used to purify solvents from low molecular weight solutes, such as sugars and salts. Both processes use the pressure difference between the retentate and permeate sides as the driving force for solvent transport [35]. In beer dealcoholization by NF or RO, beer flows through the membrane module, water and alcohol permeate the membrane against the natural osmotic pressure and are recovered in the permeate stream. On the other hand, larger molecules such as beer flavour compounds remain in the beer (retentate). The process can be performed by recirculating the retentate back to the feed tank or using multi-stage module configuration. In both cases, since water permeates the membrane, deaerated and deionized water must be continuously added to the retentate for balancing the removed one. As a result, the ethanol content on the retentate is continuously reduced. This operation mode is called diafiltration. The diafiltration is carried out until beer reaches the desired content of ethanol [1,25].

Reverse osmosis requires more pressure than nanofiltration, which can be unbeneficial for beer besides consuming more energy [1]. It was also found that some nanofiltration and reverse osmosis membranes present high rejection of aroma compounds [24,25]. Reverse osmosis proved to be economically unfeasible for removing ethanol from beer below 0.45 vol.% [27].

Osmotic distillation (OD) or **evaporative perstraction** (EP) is another membrane process used for removing ethanol from beverages. OD uses hydrophobic porous membrane contactors to provide the ethanol transfer from the alcoholic beverage to the strip solution (usually water) that flows counter-currently at the downstream side of the

module. The mass transport is driven by the difference of the vapour pressure of ethanol between the beer and the strip solution. Once the vapour pressure of water (less volatile than ethanol and other aroma compounds) is basically the same in both sides of the membrane, almost no water permeates to the strip solution [28–31]. Osmotic distillation also has the disadvantage that a significant fraction of beer flavour compounds are lost to the permeate side [30,31].

Dialysis is based on the use of membrane contactors (e.g., hollow-fibres) where beer flows counter-currently to the dialysate (e.g., water). Low molecular weight solutes, such as ethanol, cross the membrane as a result of the concentration gradient between two solutions. Ethanol permeates from beer to the dialysate until the equilibrium between concentrations at both sides of the membrane is reached. The resulted alcoholic stream can be sent to a distillation unit for ethanol removal and the aqueous stream reused in the dialysis unit to minimize the permeation of non-volatile compounds. Dialysis has a minimum impact in beer degradation since the separation process is carried out at atmospheric pressure and low temperature (below room temperature). On the other hand, this process is more expensive than typical membrane processes (NF and RO) due to the small driving force for the ethanol removal. In addition, dialysis also loses a great deal of beer aroma compounds to the dialysate [1,3].

Pervaporation (PV) is a relative new membrane process that can also be applied to beverages dealcoholization. In a pervaporation process, a liquid feed contacts with a dense polymeric membrane and volatile compounds permeate the membrane and suffer evaporation on the downstream side of the membrane, which is kept under high vacuum. The driving force of pervaporation is the chemical potential gradient through the membrane thickness. This chemical potential gradient can be written as a function of the partial pressures and corresponding activity coefficients [35,37]. The partial pressure of compounds in the feed side (liquid phase) is related to their concentration and saturation pressure, while the partial pressure of compounds in the permeate side (gas phase) depends on their concentration and total permeate pressure (vacuum applied). The permeate stream is then collected in a cryogenic condenser before the vacuum system [32,35].

Pervaporation can be used for beer dealcoholization using hydrophobic membranes that favour the permeation of ethanol against the permeation of water. However, most of beer aroma compounds have higher affinity to hydrophobic membranes than ethanol,

resulting in an aroma depleted dealcoholized beer [32,33]. Hydrophilic membranes are then normally used for beer dealcoholization. These membranes are highly permeable to water, permeable to low-hydrophobic compounds such as ethanol, and low permeable to hydrophobic species, such as flavour compounds. In this case, water is more permeable than ethanol. Thus, using a low pressure sweep stream of water vapour on the permeate side for keeping the partial pressure of all other beer compounds very low, the driving force of water is reduced and only ethanol and few aroma compounds permeate the membrane [32,34]. Despite the good quality of the alcohol free beer obtained, this process is very expensive and found no industrial application. The cost is mainly due to the low fluxes of pervaporation membranes, resulting in high membrane areas. On the other hand, the costs associated to the vacuum and condensing system for dealcoholizing are very high [33].

1.3. Recovery of beer flavour compounds

The recovery of beer aroma compounds plays an important role during the production of non-alcoholic beer, since most of the above-mentioned processes for producing alcohol free beers result in a product whose aroma profile is unpleasant or distinct compared to the homologue alcoholic beer. Most popular interrupted fermentation processes avoid the formation of flavour compounds and the corresponding alcohol free beers have a typical worty taste. On other hand, the ethanol removing processes also originate the loss of important beer flavour compounds as a consequence of chemical reactions or physical losses [1,21].

The addition of aroma recovered from the original sources (as compared to synthetic products), is preferable in the beverages industry due to their natural character and thus their higher commercial value [38,39]. The recovery of natural beer compounds can be achieved by:

- i) removing the lost aroma compounds, through side streams of the dealcoholization system;
- ii) extracting the aroma compounds directly from the original beer, before being submitted to dealcoholization.

The second approach is normally preferable since the aroma compounds are very sensitive and should suffer the least possible treatments. In both cases, the recovered beer aroma

compounds are returned to the dealcoholized beer to improve its lack of aroma compounds [21].

The processes shown in Tables 1.2 to 1.4 for removing ethanol from a completed fermented beer can also be used for recovering the aroma compounds lost during beer dealcoholization. Analysing all the advantages and disadvantages of these processes, heat processes (Table 1.2) should be avoided since they are operated at moderate or high temperatures, resulting in the partial degradation of the aroma compounds. The resultant degraded compounds are usually unpleasant and contribute to a decrease in beer quality [21]. On the other hand, the energy consumption of heat treatments, such as vacuum evaporation or distillation and spinning cone column, are high due to the deionized water vapour required and the use of vacuum conditions.

Extraction processes (Table 1.3) can also be effective for recovering beer aroma compounds. However, they need a food approved extraction medium that increases the operating costs. The use of adsorption requires the regeneration of the aroma-saturated adsorbents, which can be accomplished by increasing the temperature, decreasing the pressure, or by flowing a liquid or gas stream that removes the aroma phase [21,40]. When the regeneration is accomplished by temperature increase, it originates the degradation of the aroma compounds.

Membrane processes (Table 1.4) seem to be the best approach to recover beer aroma compounds lost during ethanol removal [41,42]. As described before, these separation processes have additional advantages when compared with traditional separation processes: i) the operation costs of membrane-based processes are usually low; ii) they can be carried out at low temperatures and iii) they do not need chemical additives, such as solvents or adsorbents [43–45].

Comparing the membrane processes previously described (Table 1.4), all of them allow the permeation of aroma compounds together with ethanol. However, nanofiltration, reverse osmosis, osmotic distillation and dialysis, show high permeability to ethanol compared to other aroma compounds, even employing membranes with low aroma compounds rejection. As a result, the permeate consists of an aqueous solution with high ethanol content. To improve the beer flavour of a dealcoholized beer, by returning the aroma extract to the dealcoholized beer, the resulting reconstructed beer will have an ethanol content above the legal limits or will display insufficient concentration of aroma compounds.

Pervaporation is probably the membrane process that can have the highest aroma selectivity and then can originate an extract with the highest aroma-to-ethanol ratio [40,46–49]. As a result, the obtained permeate is highly concentrated in aroma compounds and only a small amount is needed for improving the aroma profile of dealcoholized beers without increasing significantly their ethanol content.

Despite the referred high costs related to the pervaporation process, its use for recovering aroma compounds is feasible since only low quantities of the permeate are required for improving the aroma profile of depleted beers.

1.3.1. Pervaporation as a promising process for beer aroma recovery

As mentioned before, pervaporation (PV) is a membrane separation process based on cross-flow filtration, in which a feed liquid mixture contacts with a non-porous membrane and some of the feed compounds preferentially permeate through it. Vacuum is applied to the permeate side allowing the permeating species to leave the membrane in the vapour phase.

Pervaporation is a membrane process that has observed an increasing importance during the past decade. The nature of the membranes employed in pervaporation is related to the type of the separation and the selectivity of the process. PV is especially suitable for solvent dehydration, though it is also applied in the separation of mixtures with isomers, mixtures that form azeotropes, and mixtures with thermo sensitive compounds [21,50,51]. In summary the applications of pervaporation comprises three main groups [35–37]:

- a) dehydration of organic-aqueous mixtures;
- b) removal of organic compounds from aqueous solutions;
- c) separation of organic-organic mixtures.

The employment of pervaporation for removing organic compounds from aqueous solutions is also carried out at industrial level, but in minor extent [50], since it has been proposed only recently. This application requires the use of hydrophobic membranes. Lately, pervaporation has been used in chemical and petrochemical industries for the separation of organic mixtures [51].

Nowadays, one can observe an increasing trend in the use of pervaporation for recovering aroma compounds in food applications, especially in the recovery and enrichment of aroma compounds from fruit juices. Heat treatment processes, such as pasteurization and conventional processes for juice concentration such as evaporation, lead

to the loss of the original aroma compounds and consequently to a decrease in the quality of the beverages [21,32,43,52,53]. Besides being used in the fruit juice industry, PV is also used in the aroma recovery from fermented beverages, such as beer or wine, due to the loss of aroma compounds that occurs during heat treatments of these beverages and even in dealcoholization processes [54–57].

Introduction to the pervaporation theory

In pervaporation, the transport of chemical species from the liquid feed to the vapour phase, through a dense polymeric membrane comprises three steps [35,36]:

- i) selective sorption of the permeating species into the membrane on the feed side;
- ii) selective diffusion of compounds through the membrane due to concentration gradients;
- iii) desorption into the vapour phase at the permeate side of the membrane.

The transport mechanism can be described based on the sorption-diffusion model, being the selectivity determined by the selective sorption and the selective diffusion [35,36]. The permeability (L) of a component i in a mixture is a function of the diffusivity (D) and solubility (S), according to:

$$L_i = D_i \times S_i \quad (1.2)$$

Diffusivity is a kinetic parameter that indicates the transporting rate of a chemical species through the membrane, being dependent on the geometry of the species; the diffusivity normally increases with the decrease of molecular size. However, in non-ideal systems, diffusivity is affected by concentration, and even large molecules can swell the membrane and as a result, their diffusivity increases. Solubility is a thermodynamic parameter that indicates the sorbed concentration in the membrane at equilibrium conditions. In ideal systems, such as permanent gas mixtures, solubility is very low and can be described by Henry's law. In contrast, in liquid mixtures, the system is normally strongly non-ideal and the Henry's law is not applicable. In this case, the solubility is also dependent on the other components concentration [35].

As referred before, the driving force of pervaporation transport is the chemical potential gradient across the membrane thickness. According to that, the flux (J_i) of component i is given by [35,36]:

$$J_i = -\frac{D_i C_i}{RT} \frac{d\mu_i}{dx} \quad (1.3)$$

where D_i is the diffusivity of component i in the membrane, C_i is the concentration of component i , R is the gas constant, T is the absolute temperature, μ_i is the chemical potential of component i and x is the distance across the membrane thickness. The chemical potential is given by:

$$\mu_i = \mu_i^\circ + RT \ln a_i \quad (1.4)$$

where μ_i° is the standard chemical potential and a_i is the activity of the chemical species, which, for ideal systems, is given by:

$$a_i = \frac{p_i}{p_i^\circ} \quad (1.5)$$

where p_i is the vapour pressure of component i and p_i° is its saturation pressure.

Substituting Eqs. (1.4) and (1.5) into Eq. (1.3) one obtains:

$$J_i = -D_i C_i \frac{d \ln p_i}{dx} = -\frac{D_i C_i}{p_i} \frac{dp_i}{dx} \quad (1.6)$$

where C_i/p_i , assuming Henry's sorption, is equal to the sorption coefficient (S_i) of component i , expressed as a function of the partial pressure of chemical species. As S_i can be considered constant for diluted solutions and D_i can be assumed independent of the distance across the membrane [48], the integration of Eq. (1.6) between boundary conditions:

$$\begin{cases} x=0; & p_i = p_{f,i} \\ x=\ell; & p_i = p_{\ell,i} \end{cases}$$

results in:

$$J_i = \frac{D_i S_i}{\ell} (p_{f,i} - p_{\ell,i}) = \frac{L_i}{\ell} (p_{f,i} - p_{\ell,i}) \quad (1.7)$$

where L_i is the permeability coefficient, ℓ is the membrane thickness, $p_{f,i}$ and $p_{\ell,i}$ are the partial pressure of component i at the feed and permeate side.

The partial pressures of component i at the feed and permeate sides are given by:

$$p_{f,i} = X_i \gamma_i p_i^\circ \quad (1.8)$$

$$p_{\ell,i} = Y_i P \quad (1.9)$$

Eq. (1.8) is the Raoult's law, where X_i is the molar fraction of component i in the liquid feed, γ_i is the activity coefficient of component i , p_i° is the saturation pressure of the pure component at a specific temperature. Eq. (1.9) is the Dalton's law where Y_i is the molar fraction of component i in the vapour phase and P_ℓ is the total pressure of the permeate (downstream side) [42,56,58].

Substituting Eqs. (1.8) and (1.9) into Eq. (1.7) gives:

$$J_i = \frac{L_i}{\ell} (X_i \gamma_i p_i^\circ - Y_i P_\ell) \quad (1.10)$$

This equation represents the global equation of pervaporation transport where the permeation flux of component i is directly proportional to the difference of its partial pressure at the feed and permeate sides of the membrane, and inversely proportional to membrane thickness.

Once most of the times the membrane thickness is unknown, Eq. (1.10) can be expressed as:

$$J_i = k_{ov,i} (X_i \gamma_i p_i^\circ - Y_i P_\ell) \quad (1.11)$$

where $k_{ov,i}$ is the overall mass transfer coefficient or permeance and is given by:
 $k_{ov,i} = L_i / \ell$.

According to the resistance-in-series model for flat-sheet membranes, $k_{ov,i}$ is given by:

$$\frac{1}{k_{ov,i}} = \frac{1}{k_{bl,i}} + \frac{1}{k_{m,i}} + \frac{1}{k_{p,i}} \quad (1.12)$$

where $k_{bl,i}$ is the mass transfer coefficient of the feed boundary layer, $k_{m,i}$ is the mass transfer coefficient of membrane and $k_{p,i}$ is the mass transfer coefficient of the permeate side [42,55].

Taking in account the contribution of these three resistances, some simplifications can be made:

- a) When the permeate side of the membrane is kept at very low pressure (high vacuum) and/or the permeate is continuously removed, the partial pressure of component i in the permeate side is negligible when compared to its partial pressure on the feed side. As a result, Eqs. (1.11) and (1.12) become:

$$J_i = k_{ov,i} (X_i \gamma_i p_i^o) \quad (1.11a)$$

$$\frac{1}{k_{ov,i}} = \frac{1}{k_{bl,i}} + \frac{1}{k_{m,i}} \quad (1.12a)$$

- b) When a good mixing is maintained in the feed side and turbulent regimes are used (high feed flowrates), there is no concentration polarization and the resistance related to the feed boundary layer is negligible, $k_{ov,i} = k_{m,i}$. As a result, Eq. (1.11a) is simplified into:

$$J_i = k_{m,i} (X_i \gamma_i p_i^o) \quad (1.11b)$$

Eq. (1.11b) is normally used for calculating $k_{m,i}$. Using the same feed conditions (temperature and composition), Eq. (1.11b) can be converted into:

$$J_i = k_{m,i}^c C_{f,i} \quad (1.13)$$

where $k_{m,i}^c$ is the mass transfer coefficient of the membrane based on concentration of component i and $C_{f,i}$ is the concentration of the aroma compound in the feed. This equation is used for comparing membranes [59].

The membrane selectivity ($\alpha_{i/j}$) towards a generic aroma compound i compared to a generic compound j (e.g., ethanol) is obtained as follows [35,36]:

$$\alpha_{i/j} = \frac{w_{p,i}^* / w_{p,j}^*}{w_{f,i} / w_{f,j}} \quad (1.14)$$

where $w_{p,i}^*$ and $w_{p,j}^*$ are the mass fractions of both compounds in the condensed permeate and $w_{f,i}$ and $w_{f,j}$ are their mass fractions in the feed.

The enrichment factor (β_i) is also used as a membrane performance indicator and is expressed by [36,59]:

$$\beta_i = \frac{w_{p,i}^*}{w_{f,i}} \quad (1.15a)$$

or by:

$$\beta_i = \frac{C_{p,i}^*}{C_{f,i}} \quad (1.15b)$$

where $C_{p,i}^*$ is the concentration of the component i in the condensed permeate and $C_{f,i}$ is the concentration of component i in the feed.

1.4. Motivation and thesis outline

The present project was born from a visit to Unicer (Leça do Balio, Portugal), where Prof. Adélio Mendes challenged the beer company to produce a high quality non-alcoholic beer based on the reincorporation of extracted aroma compounds obtained from the fresh beer by pervaporation. It was first proposed the beer dealcoholization based on reverse osmosis diafiltration but later, it was elected the spinning cone column (SCC) distillation technology since this one proved to be more versatile. The project resulted a few years later in an international patent, in a best-selling beer and in this thesis work. The idea behind this project benefited from the collaboration of Prof. Adélio Mendes with Dr. Klaus-Viktor Peinemann (GKSS – Geesthacht, Germany), and his knowledge about a similar work performed by Thomas Schäfer, supervised by Prof. João Paulo Crespo (UNL – Lisboa, Portugal) [60].

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In the first part of the project it was studied the beer dealcoholization by reverse osmosis diafiltration. It was concluded that this process was not flexible for the company objectives neither suitable for producing a beer below 0.45 vol.% of ethanol, as requested. After that, the beer company decided to select a distillation process for reducing the ethanol content from beer until almost 0.05 vol.%. During that period, several distillation pilot plants were tested and it was concluded that spinning cone column was the best technology for achieving that target. Also, during the first part of this work some pervaporation membranes were tested to extract aroma compounds from the reverse osmosis permeate, from the distillation alcoholic stream and from the original beer. It was found that the extract from the original beer presented a more balanced beer profile. This result led to consider the recovery of beer aroma compounds previously to the dealcoholization, as initially proposed.

According to this preliminary study, membranes of polydimethylsiloxane (PDMS) supported in PAN (polyacrylonitrile) and polyoctylmethylsiloxane (POMS) supported in polyetherimide (PEI) showed to be the most selective to beer aroma compounds. The

selection of the most promising membrane was based on the flux, selectivity and the profile of aroma compounds in the permeate, since the core of this thesis is the production of an aroma extract which is intended to improve the aroma profile of a depleted dealcoholized beer. This study was performed using a laboratory pervaporation set-up, which results are reported in **Chapter II**. From these results, it was found that the thinnest POMS/PEI membrane (ca. 1 μm thick) was the most feasible for the industrial process of aroma compounds extraction from beer. Based on the selected membranes properties, an industrial pervaporation plant was designed and assembled at Unicer. The pervaporation industrial plant was designed by Prof. Adélio Mendes with Unicer, GKSS (Geesthacht, Germany) and GMT (Rheinfelden, Germany), and built by Arsopi (Vale de Cambra, Portugal). The operation mode of both pervaporation laboratory unit and industrial plant is described in **Chapter II**.

Chapter III describes the use of reverse osmosis diafiltration for removing ethanol from beer. During this study, several membranes were evaluated and the influence of operating conditions on the ethanol removal and beer aroma compounds retention assessed.

The optimization of the pervaporation process is very complex because the operating conditions affect the process responses in different ways. Thus, a trade-off between the parameters must be solved for obtaining a high permeate flux and a balanced aroma profile on the beer extract. In **Chapter IV**, the use of pervaporation POMS/PEI membranes for extracting beer aroma compounds is studied. A response surface methodology (RSM) was used for interpolating the role of operating conditions on the permeation flux, on the membrane selectivity towards beer aroma compounds and on the aroma profile of the permeate. RSM was also used for optimizing the operating conditions considering a compromise among the referred process responses.

The industrial integrated process of beer aroma extraction, beer dealcoholization and aroma reincorporation is presented in **Chapter V**. Beer dealcoholization was accomplished by spinning cone column distillation, which promotes the counter-current contact between beer and water vapour that strips the ethanol and other volatile aroma compounds. The aroma profile of the resulted depleted beer was improved with the aroma extract, previously obtained by pervaporation. The industrial pervaporation runs were performed for maximizing the permeate volume and obtaining a permeate with a balanced aroma profile, to be integrated in the target dealcoholized beer.

Chapter VI reports a new application for the dealcoholization/reincorporation idea. In this scope, the production of a low alcohol wine is described. Several membranes of nanofiltration and reverse osmosis were tested for dealcoholizing red wine while pervaporation was used for extracting aroma compounds from the original wine. Finally, the dealcoholized wine samples were enriched with the extracted wine aroma and its taste assessed.

Finally, **Chapter VII** presents the main conclusions of this research work and gives suggestions for future work.

The use of pervaporation for extracting beer aroma compounds for adding them to a depleted beer (such as a dealcoholized beer) had never being applied before at industrial level, resulting in the application of an international patent. This patent is presented in **Appendix A**.

1.5. List of symbols

a	activity of the chemical species (–)
C	concentration ($\text{kg}\cdot\text{m}^{-3}$)
D	diffusivity ($\text{m}^2\cdot\text{s}^{-1}$)
J	flux ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
k	mass transfer coefficient ($\text{m}\cdot\text{s}^{-1}$)
L	permeability ($\text{kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$)
ℓ	membrane thickness (m)
P	total pressure (Pa)
p	partial pressure (Pa)
p°	saturation pressure (Pa)
R	gas constant ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
S	solubility as a function of partial pressure ($\text{kg}\cdot\text{m}^{-3}\cdot\text{Pa}^{-1}$)
T	absolute temperature (K)
w	mass fraction (–)
X	molar fraction in liquid phase (–)
x	distance across the membrane thickness (m)
Y	molar fraction in vapour phase (–)

Greek letters

α	selectivity (–)
β	enrichment factor (–)
γ	activity coefficient (–)
μ	chemical potential ($\text{J}\cdot\text{mol}^{-1}$)
μ°	standard chemical potential ($\text{J}\cdot\text{mol}^{-1}$)

Subscripts and superscripts

bl	boundary layer
c	concentration
f	feed
i	generic compound
j	generic compound
ℓ	low (permeate side)
m	membrane
ov	overall
p	permeate
$*$	relative to condensed phase

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Chapter II

2. Beer pervaporation – experimental unit and industrial plant designs

Abstract

This chapter concerns the development and characterization of a lab set-up and the corresponding industrial unit designed for extracting beer aroma compounds by pervaporation, used for correcting the aroma profile of depleted dealcoholized beer, produced by spinning cone column. The two units are thoroughly described as well as the operating mode. Several pervaporation membranes were assessed for aroma extraction and the operating variables investigated. It was concluded that the best membrane was a flat-sheet composite POMS (polyoctylmethylosiloxane) supported in PEI (polyetherimide) membrane with an active thickness of ca. 0.7 μm . The relevant operating variables, such as the feed temperature, the feed velocity and the permeate pressure, were studied. Some limitations in the effectiveness of the industrial plant were found. However, it was possible to obtain, with the industrial plant, an aroma extract similar to the one obtained with the laboratory unit.

This thesis describes the use of a laboratory set-up of reverse osmosis and nanofiltration (Chapters III and VI) and an industrial plant of spinning cone column distillation (Chapter V). Though, this chapter only emphasizes the use of pervaporation units, which is the core process of the thesis.

2.1. Introduction

Pervaporation is a very selective process, suitable for extracting aroma compounds from aqueous solutions [1,2]. For removing traces of solutes from a solvent, membranes should have preferential selectivity to these solutes [3]. In the case of extraction of organic aroma compounds from an aqueous solution, hydrophobic membranes, which have higher permeability towards nonpolar compounds, should be chosen [1,2]. Composite membranes are normally preferable because they have a very thin selective layer, which imposes a smaller permeation barrier without compromising the selectivity, supported in a reinforced porous layer that gives to the membrane the necessary mechanical strength [2]. Crosslinked silicone composite membranes, such as PDMS (polydimethylsiloxane) and POMS (polyoctylmethylsiloxane) have been successfully used for extracting aroma compounds from beverages [4–8].

In order to accomplish the extraction of aroma compounds, membranes are enclosed in modules that comprise the feed and retentate side and the permeate side, which is kept under high vacuum. At laboratory level, the most used configuration uses flat-sheet membranes arranged in a plate-and-frame module. However, at industrial level, since larger areas are required, membranes need to be packed for optimizing the area per volume ratio. There are available several separation module configurations, which are based on two types of membranes: flat and tubular. Plate-and-frame, envelope and spiral-wound modules use flat membranes, while tubular, capillary and hollow-fibre modules employ tubular membranes. Plate-and-frame and spiral-wound designs are the most used for pervaporation applications [1–3]. The envelope type module was developed by GKSS (Geesthacht, Germany) and offers advantages over spiral-wound since it shows better flow distribution and lower pressure drop in the permeate side [2].

The present chapter describes a lab set-up and an industrial pervaporation unit developed for implementing an innovative process of enriching an aroma depleted dealcoholized beer [9]. The experimental set-up uses a flat-sheet membrane inserted in a cell with radial geometry. Composite PDMS and POMS membranes were compared concerning permeation and selectivity towards relevant aroma compounds. After selecting the most promising membrane, an industrial plant was designed and built and its performance assessed under real operating conditions. The design of the industrial plant is described and its effectiveness critically compared to the laboratory set-up.

2.2. Materials and methods

2.2.1. Key beer aroma compounds

The most distinguishing aroma compounds are formed during beer maturation and are characteristic of a finished beer. These aroma compounds belong to two main chemical groups, higher alcohols and esters, and their concentration has a great impact on beer organoleptic quality [10]. The selected higher alcohols to characterize the beer were propanol (*Pr*), isobutanol (*iB*) and isoamyl alcohols (*AA*, 2-methylbutanol plus 3-methylbutanol), while the esters considered were ethyl acetate (*EA*) and isoamyl acetate (*iAA*). Besides these two major chemical groups it was followed the concentration of acetaldehyde (*Ac*).

The concentration of these aroma compounds was evaluated using Headspace Capillary Gas Chromatography (HCGC) and Flame Ionization Detection (FID). The analysis was performed in a gas chromatograph (Varian Star 3400) equipped with a capillary column Supelcowax 10 (60 m, 0.53 mm, Sigma-Aldrich/Supelco) and a flame ionization detector (FID). The temperature was raised from 75 to 130 °C at a rate of 25 °C·min⁻¹, with initial and final holds of 11 minutes and 4.5 minutes, respectively. The detector temperature was 250 °C while the injector temperature was 110 °C. The chromatograph used nitrogen as carrier gas with a flowrate of 3 cm³·min⁻¹ and the split ratio was 8:1. The internal standard used was 1,3-dichloropropane.

The ethanol concentration was evaluated with an ethanol analyser – Alcolyzer Plus (Anton Paar – Graz, Austria). This analyser is based on near infrared (NIR) spectroscopy for selective quantification of ethanol. A densitometer (DMA 4500, Anton Paar) was used for determining the density of the samples. Both analytical methods are recommended methods by the European Brewery Convention (EBC) [11].

2.2.2. Membranes

During a preliminary study, different approaches were considered to recover the aroma compounds lost during the dealcoholization process, using pervaporation. It was considered to recover the compounds from the side stream of dealcoholization processes, such as reverse osmosis permeate or the top product (alcoholic stream) from distillation. In the first case, the reverse osmosis permeate is richer in ethanol than in beer aroma compounds, as a result the pervaporation extract presented a very poor aroma profile

compared to the ethanol concentration. In the second case, the side stream of distillation is highly alcoholic and presents a high concentration of aroma compounds. Nonetheless, the aroma profile of the extract obtained pervaporating this stream presented a high concentration of ethanol (e.g., 80 vol.%) and an unbalanced aroma profile. As a result, the addition of this extract to the dealcoholized beer would contribute to an intensification of an alcoholic and solvent-like aroma. It was then decided to extract the aroma compounds directly from the original beer, preserving their natural characteristics, and adding then back to the dealcoholized beer.

Several membranes of PDMS (polydimethylsiloxane) and POMS (polyoctylmethylsiloxane) with different supports were tested in order to select the best one concerning the permeate flux, the selectivity towards aroma compounds and the aroma profile of the permeate.

From this study, it was concluded that PDMS membranes supported in PAN (polyacrylonitrile) and POMS membranes supported in PEI (polyetherimide) were the most promising for beer aroma recovery.

In this chapter, a PDMS/PAN membrane and POMS/PEI with different thicknesses of the selective layer were tested. These membranes were kindly offered by GKSS. The different membrane thicknesses were obtaining using polymer solutions of different concentrations, namely 10, 15 and 25 wt.% of POMS, coated in PEI, referred hereafter as 10% POMS, 15% POMS and 25% POMS, respectively. The thickness of the PDMS and 10% POMS membrane were obtained by SEM – Figure 2.1. The corresponding average thicknesses are 1.8 μm and 0.7 μm , respectively. One can estimate that the thicknesses for 15% POMS and 25% POMS are 1.1 μm and 1.8 μm , respectively.

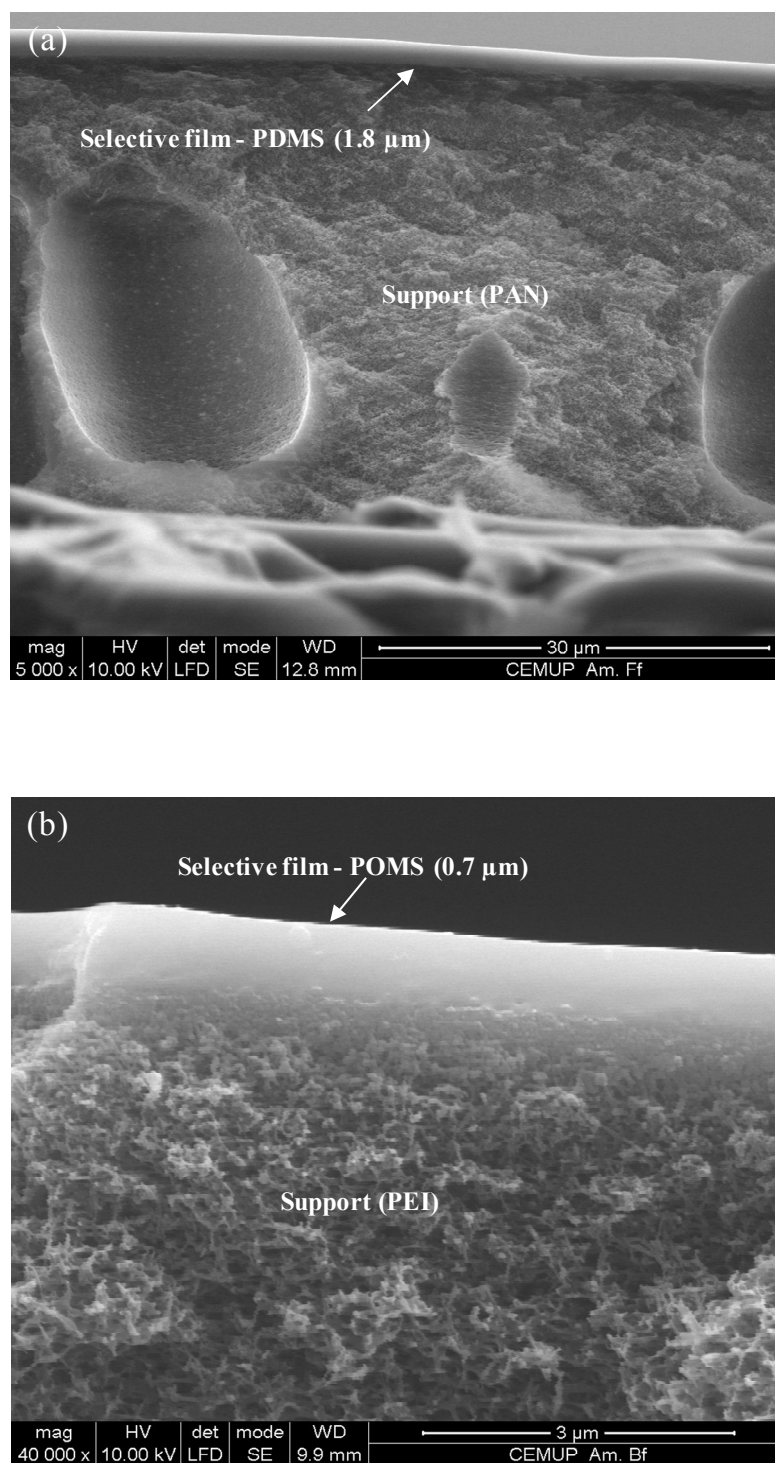


Figure 2.1. SEM micrographs of: (a) PDMS and (b) 10% POMS membranes side views (membranes layers).

2.2.3. Pervaporation laboratory set-up

In the pervaporation process, aroma compounds are recovered from the feed solution by means of an organophilic membrane, which is submitted to vacuum at the permeate side. During the laboratory study, it was used a flat-sheet membrane inserted in a cell. The membrane cell, shown in Figure 2.2, presents a radial geometry, as originally designed by GKSS. Figure 2.3 shows a sketch of the same membrane cell.

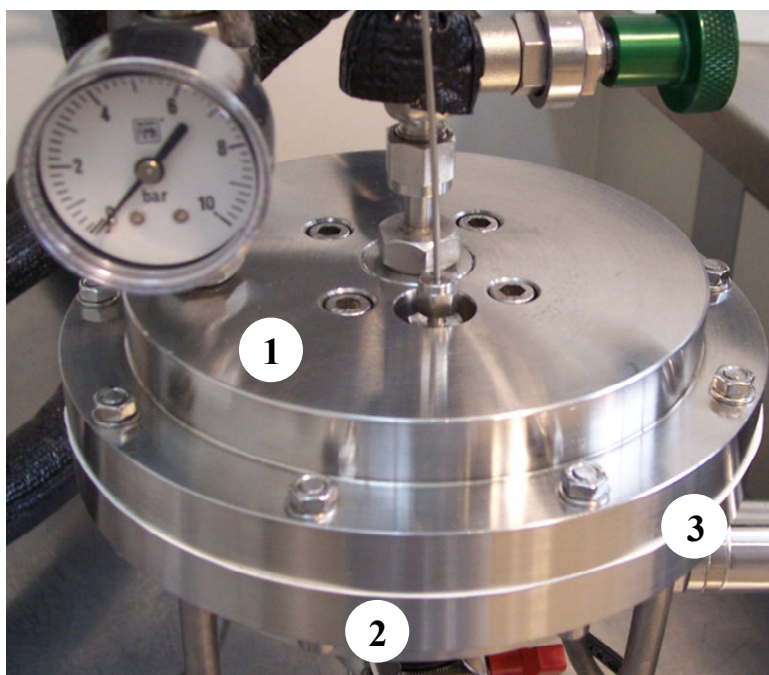


Figure 2.2. Photograph of the membrane cell (1, feed and retentate chamber; 2, permeate chamber; 3, membrane).

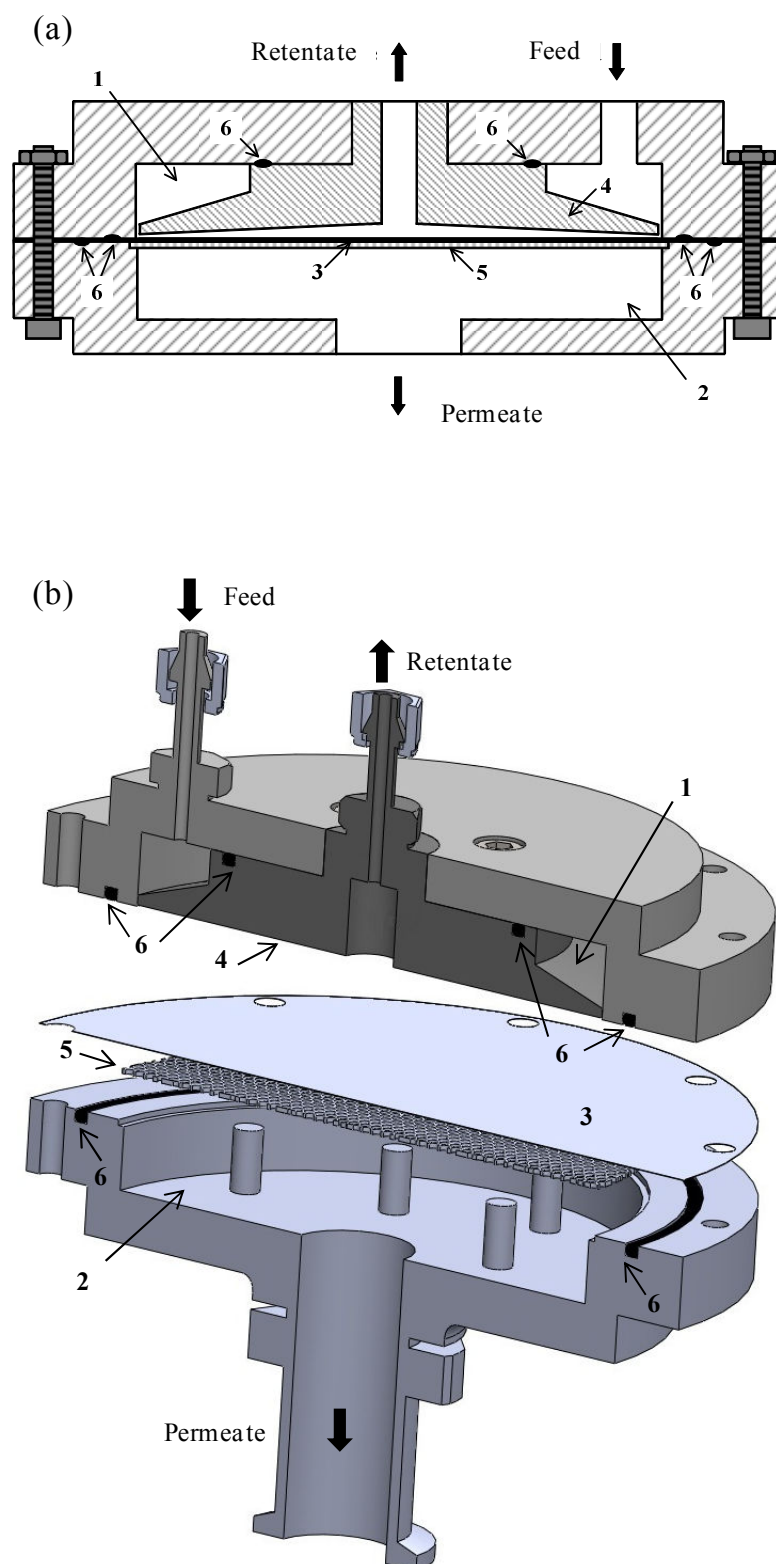


Figure 2.3. Sketch of the laboratory membrane cell: (a) two-dimensional and (b) three-dimensional representations (1, feed and retentate chamber; 2, permeate chamber; 3, membrane; 4, cone central hole; 5, metal grid; 6, o-ring seals).

The membrane cell consists of two compartments: the feed and permeate chambers separated by a membrane with an effective area of 107.5 cm^2 (effective diameter 117 mm). The feed enters through the outer perimeter of the distribution cone (see Figure 2.3), flows tangentially to the membrane and leaves through the cone central hole. The height above the membrane decreases towards the outer perimeter; this geometry assures approximately constant cross flow velocity of the feed stream.

Figure 2.4 shows the cross flow velocity as a function of the radius of the cell (cf. Figure 2.3) where r_i and r_o are the internal and external radius of the distribution cone, respectively.

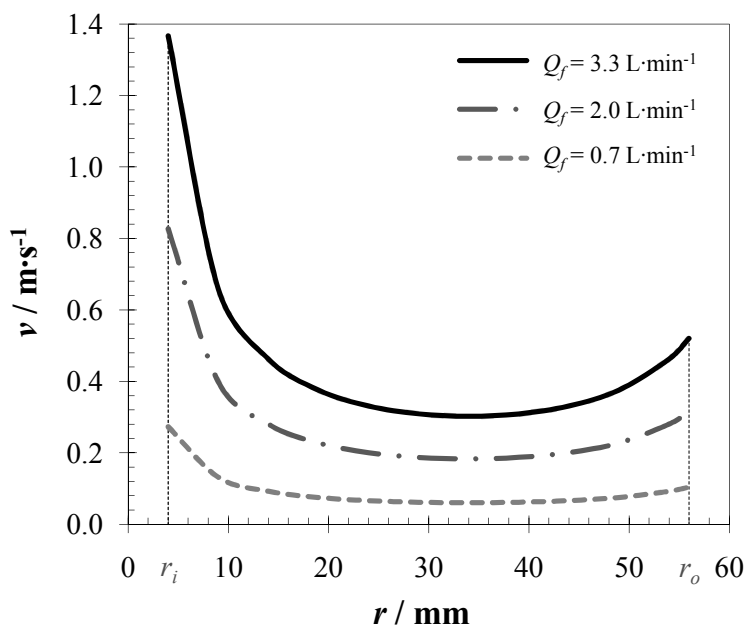


Figure 2.4. Cross flow velocity as a function of cell radius (r_i – inner radius of the distribution cone, r_o – outer radius of the distribution cone).

Figure 2.5 shows a sketch of the pervaporation set-up and Figure 2.6 shows a photograph of the same set-up. Beer stored in the feed tank (1 – cf. Figures 2.5 and 2.6) is fed to the membrane cell (3) by means of a circulation pump (2, Efacec E-JET 100M). Before the inlet of the cell, a fraction of the feed stream was recycled back to the feed tank through a plate heat exchanger (8, Arsopi-Thermal, with 0.20 m^2 of transfer area). The retentate stream leaved the membrane cell and was also returned to the feed tank, through the heat exchanger (8), and its flowrate read using a rotameter (7a). A manometer (9) indicates the feed stream pressure, while three needle valves (12a, 12b and 12c) control the feed pressure and flowrate. A PT100 (11a) and a thermocouple (11b) measure the feed and cell temperatures, respectively. A refrigeration fluid (an aqueous solution of glycol

supplied at $-3\text{ }^{\circ}\text{C}$) is fed to the heat exchanger (8) in counter-current mode for controlling the feed and cell temperatures. The cooling fluid flowrate is controlled by regulating the diaphragm valve (14b) and measured by a rotameter (7b). A vacuum pump (6, Edwards RV5) is used to keep the permeate side of the membrane at a reduced pressure (from 1 to 20 mbar). The permeate stream is condensed before reaching the pump in a stainless steel cold trap (4), immersed in liquid nitrogen at $-196\text{ }^{\circ}\text{C}$ (5), before the vacuum pump (6). A pressure sensor (10a, Druck) measures the permeate pressure while and a diaphragm valve (14a) placed after the cold trap, at vacuum pump admission, regulates the vacuum pressure.

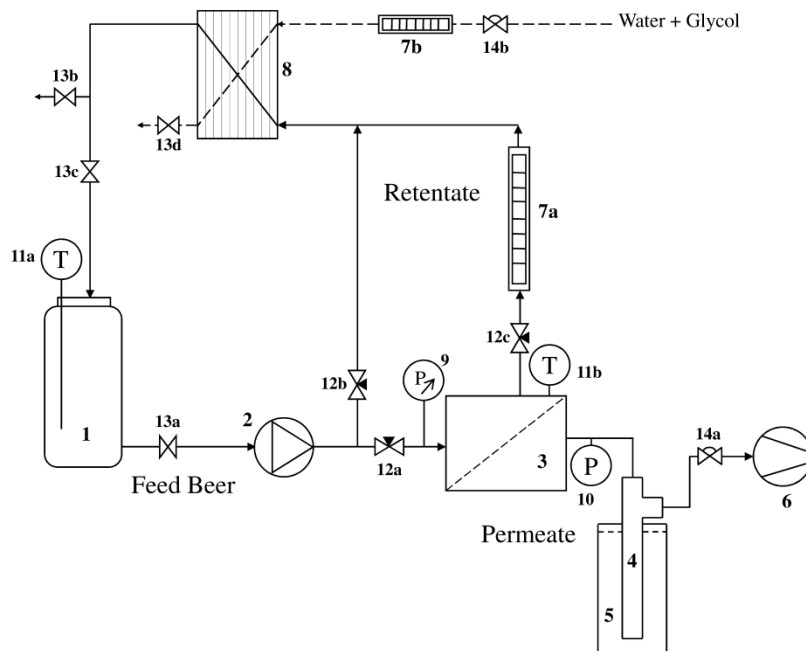


Figure 2.5. Pervaporation experimental set-up (1, feed tank; 2, centrifuge pump; 3, membrane cell; 4, permeate reservoir; 5, liquid nitrogen dewar; 6, vacuum pump; 7, rotameters; 8, plate heat exchanger; 9, manometer; 10, pressure sensor; 11, temperature sensors; 12, needle valves; 13, on/off valves; 14, diaphragm valves).

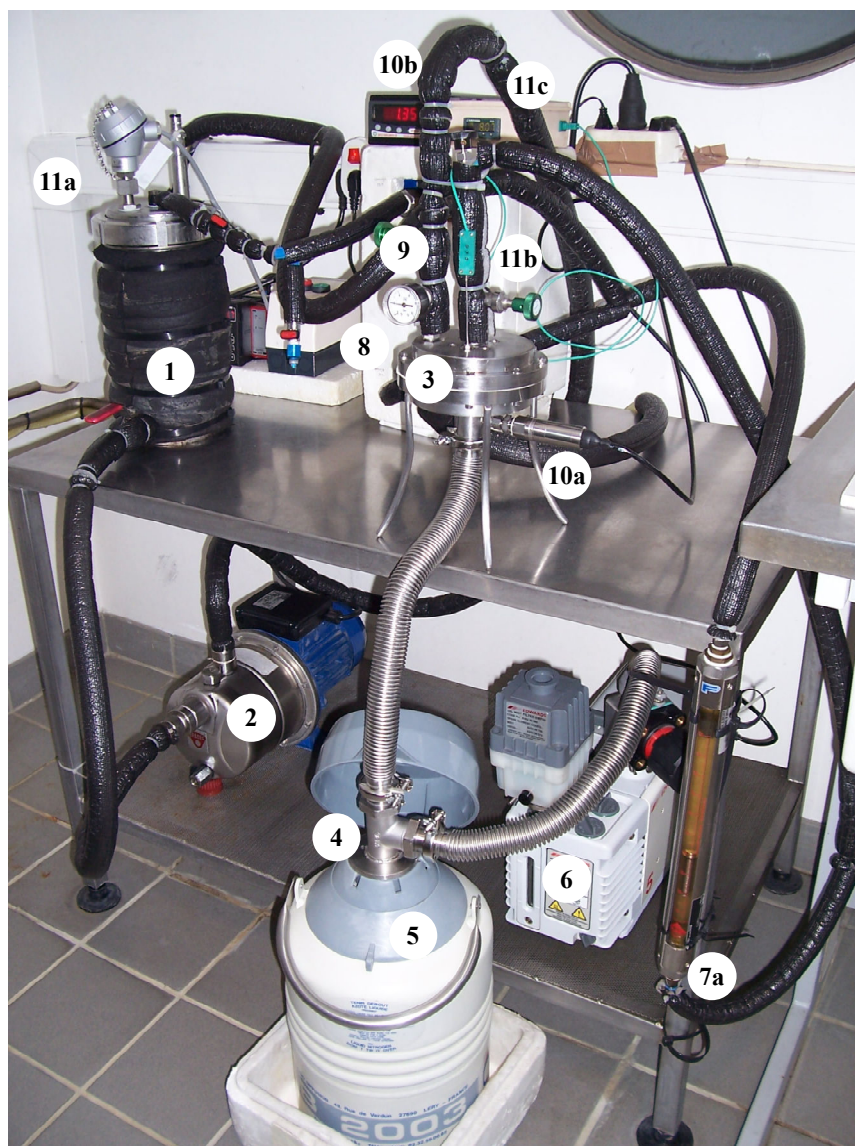


Figure 2.6. Photograph of the pervaporation lab set-up (1, feed reservoir; 2, feed pump; 3, membrane cell; 4, permeate cold trap; 5, dewar with liquid nitrogen; 6, vacuum pump; 7a, retentate rotameter; 8, heat exchanger; 9, feed manometer; 10a, permeate pressure sensor; 10b, permeate pressure indicator; 11a, PT100; 11b, thermocouple; 11c, cell temperature indicator).

Membranes were immersed in the feed solution during ca. 12 hours and dried with an absorbent tissue before the permeation experiments. The feed solution was recirculated until the feed temperature stabilized (without applying vacuum to the permeate side). The feed pressure and the flowrate were regulated independently by tuning the needle valves. Once the feed conditions were achieved, the vacuum pump was turned-on and the permeate pressure adjusted using the diaphragm valve. The aroma compounds collected in the cold trap were defrosted by placing the cold trap in cold water. This procedure allowed

the permeate solution to melt without evaporating the aroma compounds. The permeate solutions of each experiment were weighted and transferred to glass flasks and stored in a freezer at ca. 5 °C. Subsequent experiments under the same conditions resulted in reproducible membrane flux and selectivity.

The experimental set-up was always washed with hot water (ca. 40 °C) and then flushed with ultrapure water and dried with oil free compressed air or carbon dioxide.

2.2.4. Pervaporation industrial plant

The beer dealcoholization was performed using a spinning cone column distillation (SCC) by Flavourtech [12]. SCC is a counter-current device that provides the contact between beer and water vapour, stripping ethanol and other volatile compounds from beer. The operation process of beer dealcoholization by SCC distillation is described in Chapter V.

The dealcoholization plant delivers a continuous production of dealcoholized beer (ethanol ca. 0.0 vol.%) at a typical flowrate of 2200 L·h⁻¹. From the laboratory results, it was found that the amount of aroma extract necessary to improve the flavour profile of the dealcoholized beer, without increasing the ethanol content, was around 0.3 – 0.4 vol.% of the dealcoholized beer. According to these results the permeate flowrate of the pervaporation plant should be around 6.6 – 8.8 L·h⁻¹. The effective membrane area for producing the required aroma extract should be ca. 40 m².

Plant design

It was performed a procurement of a producer of pervaporation plants for food applications. Since it was not found a suitable supplier, it was decided to design and build the industrial pervaporation unit presently operating at Unicer. The design of the pervaporation industrial plant was not easy to achieve since many questions had to be considered. Namely, the feed flowrate, type and number of membrane modules, diameter of the vacuum tubes, condensing temperature and power of the cooling/heating circulator, type and size of the condensers, vacuum pump size and ultimate vacuum, CIP (clean in place), controlling system and finally the expected condensing flowrate. The pervaporation plant is fed continuously, removing a small amount of aroma compounds from the feed stream. The retentate stream is then forwarded to the dealcoholization plant where it meets

a second stream of fresh beer. The pervaporation unit was designed to operate in a semi-continuous mode.

In pervaporation, the transport of aroma compounds is driven by the chemical activity difference between the retentate and the permeate sides. This driving force is obtained by applying vacuum at the permeate side. In the present plant, the permeate flowrate represents a small fraction of the feed flowrate, ca. 0.3 vol.%. On the other hand, it is necessary to consider the exhaustion of non-condensable gases present in the beer feed, such as carbon dioxide, which affects the capacity of the vacuum pump and condensers. The vacuum pump should not return oil to the condensers.

At laboratory level the permeate condensation was accomplished by liquid nitrogen at $-196\text{ }^{\circ}\text{C}$, which is impracticable at industrial level due to the high volume of liquid nitrogen needed. The selection of the condensing temperature should be such that for the total pressure observed at the permeate side (ca. 1 mbar) most of the more volatile aroma compounds are condensed. For instance, the vapour pressure of ethyl acetate at $-85\text{ }^{\circ}\text{C}$ is 7 μbar . Since the permeate stream contains approximately 0.031 mol% of ethyl acetate, the maximum vapour pressure at $-85\text{ }^{\circ}\text{C}$ is ca. 2 nbar, which allows the condensation of most of this aroma compound in the condensers. The lowest temperature that is usually used in industrial plants is ca. $-85\text{ }^{\circ}\text{C}$. For the present application it was implemented a cooling/heating circulator using a thermal fluid suitable for a large temperature range, from $-90\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$. This permits that the same fluid can be used for condensing and defrosting the extracted aroma compounds at the condensers. Besides the operating temperature, also the power capacity of the condensing system was determined according to the condensation enthalpy (the aroma stream has to be condensed from the vapour state to the solid phase) and the best knowledge concerning the heat transfer kinetics.

The condensing system comprises four heat exchangers organized in two sets of two condensers in parallel. The condensers were designed assuming a minimum flowrate of non-condensable gases. The condensers are made of stainless steel with two jackets; in the inner jacket the thermal fluid flows at ca. $-85\text{ }^{\circ}\text{C}$ while the outer jacket was designed for receiving the defrosting thermal fluid (water). The two sets of condensers were designed for operating in semi-continuous mode, while the first set is used for condensing the other is being defrosting and the other way round, allowing a continuous production of aroma. However, it was verified that the desorbed carbon dioxide that permeates the

membrane impairs the efficiency of the condensers. It was then necessary to use simultaneously the two sets of condensers for condensing the permeated stream. The production of aroma extract becomes then batch-wise.

The membrane module type and configuration were also chosen for increasing the permeation rate of the industrial plant. The membrane modules are envelope type from GKSS for gas separation (GKSS-GS module [2]), manufactured by GMT – Rheinfelden, Germany. The membrane envelope consists of two flat-sheet membranes thermally welded at their edges and separated by spacers for allowing easier drain of the permeate, which flows in radial direction towards the central hole [2,13–15]. Figure 2.7 shows a representation of the membrane envelope. The membrane module is assembled with 87 membrane envelopes (useful area of 10 m²) arranged in compartments of three envelopes each, attached to a central permeate tube with two open outlets. This membrane arrangement in compartments allows to keep the feed flow velocity almost constant, in order to avoid the formation of boundary layers and minimizing the concentration polarization phenomenon. The sets of compartments form the membrane stack, which is enclosed by the pressure vessel [2,13–15]. The feed stream flows through the module, contacting both sides of the envelope and the permeate is released on the central tube and drawn from both outlets. Figure 2.8 shows a sketch of the GKSS-GS envelope module.

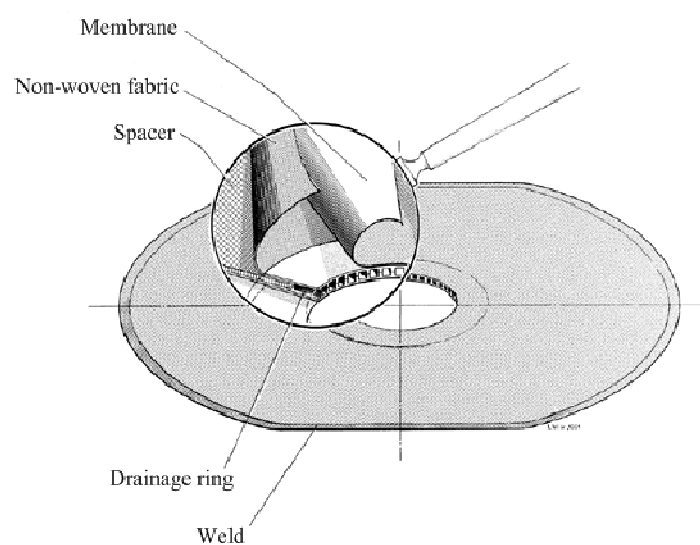


Figure 2.7. Envelope type membrane (adapted from [2]).

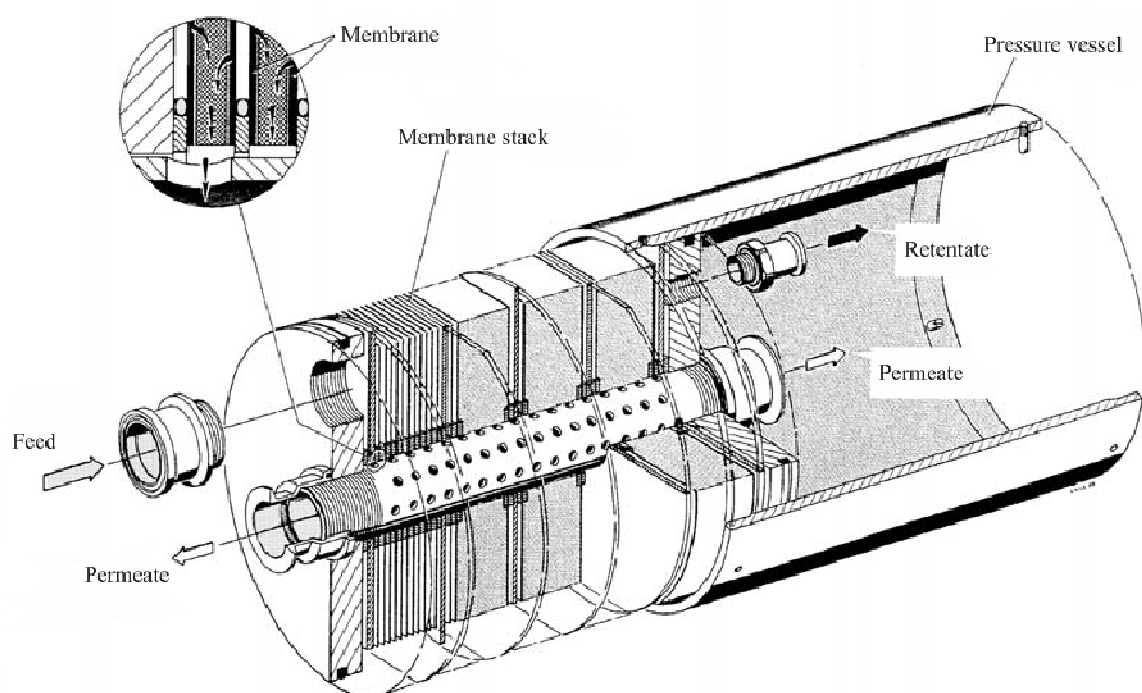


Figure 2.8. Sketch of the GKSS-GS envelope module (adapted from [2]).

Figure 2.9 shows a sketch of the pervaporation plant at Unicer, Figure 2.10 presents a photograph of the same plant and Figure 2.11 shows a photograph of a membrane module of that plant. This plant is made by a feed circulation pump (P1 – cf. Figures 2.9 and 2.10); a plate heat exchanger (PHE1, Arsopi-Thermal) for controlling the temperature of the feed beer; four plate-and-frame membrane modules (MM, GMT), each one with 10 m² of effective area and arranged in two parallel lines with two modules in series at each line; a vacuum pump (P2, Boc Edwards) for keeping the permeate side of the membranes at sub-atmospheric pressure; four permeate condensers (PC, Arsopi-Thermal, each one with 3 m² of condensation area); a cooling/heating circulator (CH, Huber) that supplies the thermal fluid for condensing the permeate; a plate heat exchanger (PHE2, Arsopi-Thermal) that supplies hot water to the condensers jacket for defrosting the permeate; a permeate reservoir (PR) and a permeate discharge pump (P3).

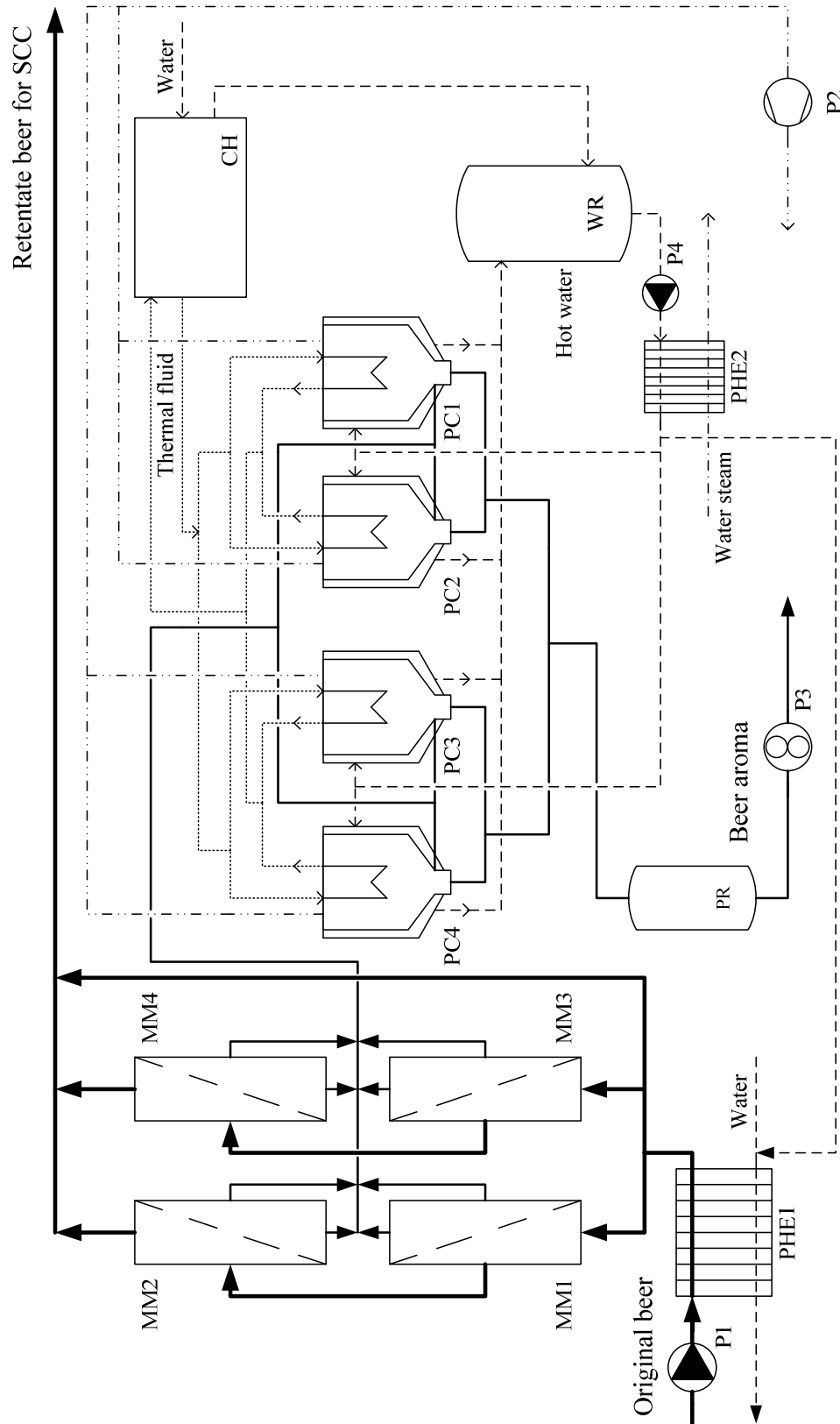


Figure 2.9. Sketch of the industrial plant of pervaporation for beer aroma compounds extraction (P1, feed pump; P2, vacuum pump; P3, permeate discharge pump; P4, hot water pump; PHE, plate heat exchangers; MM, envelope membrane modules; PC, permeate condensers; PR, permeate reservoir; CH, cooling/heating circulator; WR, water reservoir).

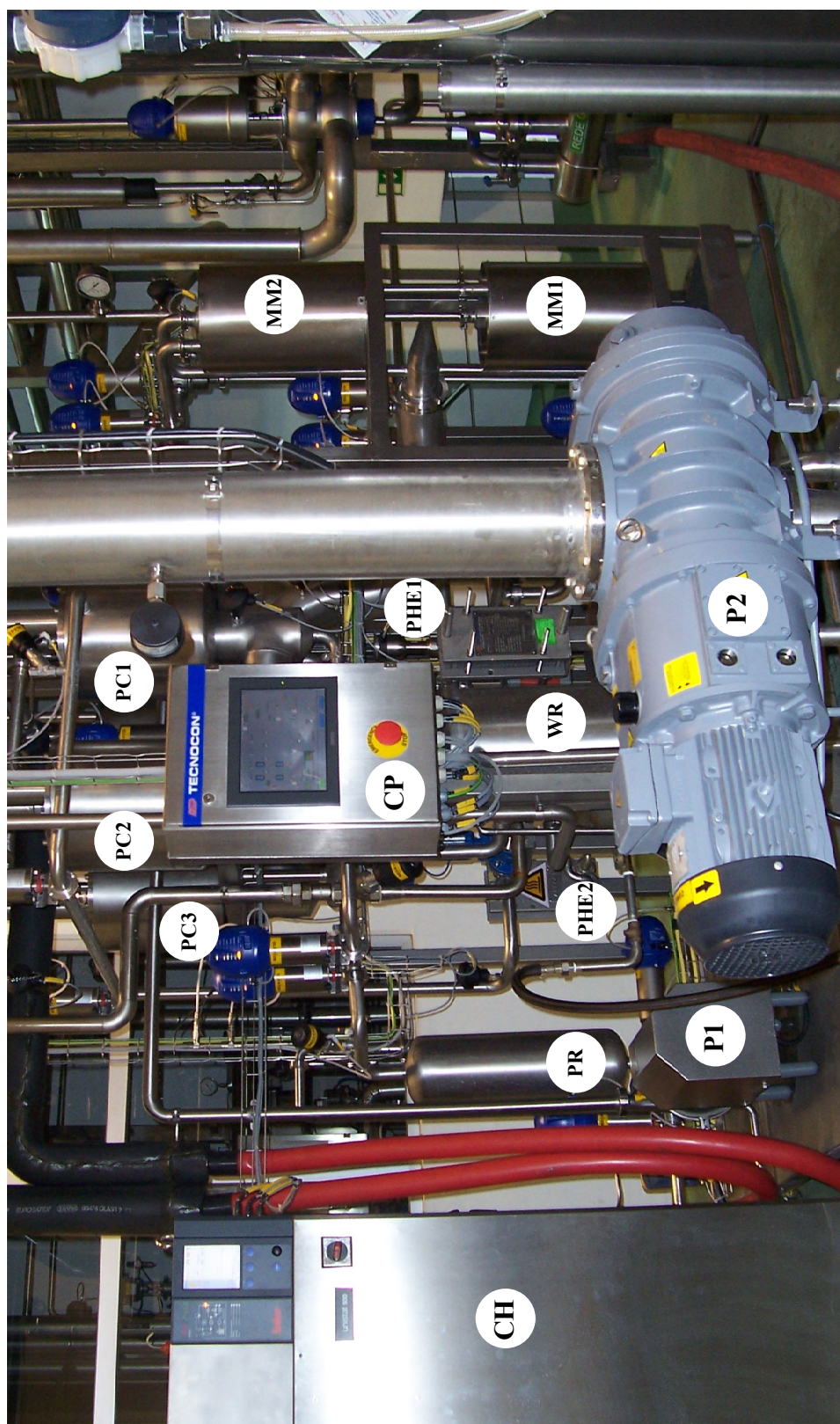


Figure 2.10. Photograph of the pervaporation industrial plant (P1, feed pump; P2, vacuum pump; PHE, plate heat exchanger; MM, envelope membrane modules; PC, permeate condensers; PR, permeate reservoir; CH, cooling/heating circulator; WR, water reservoir; CP, control panel).

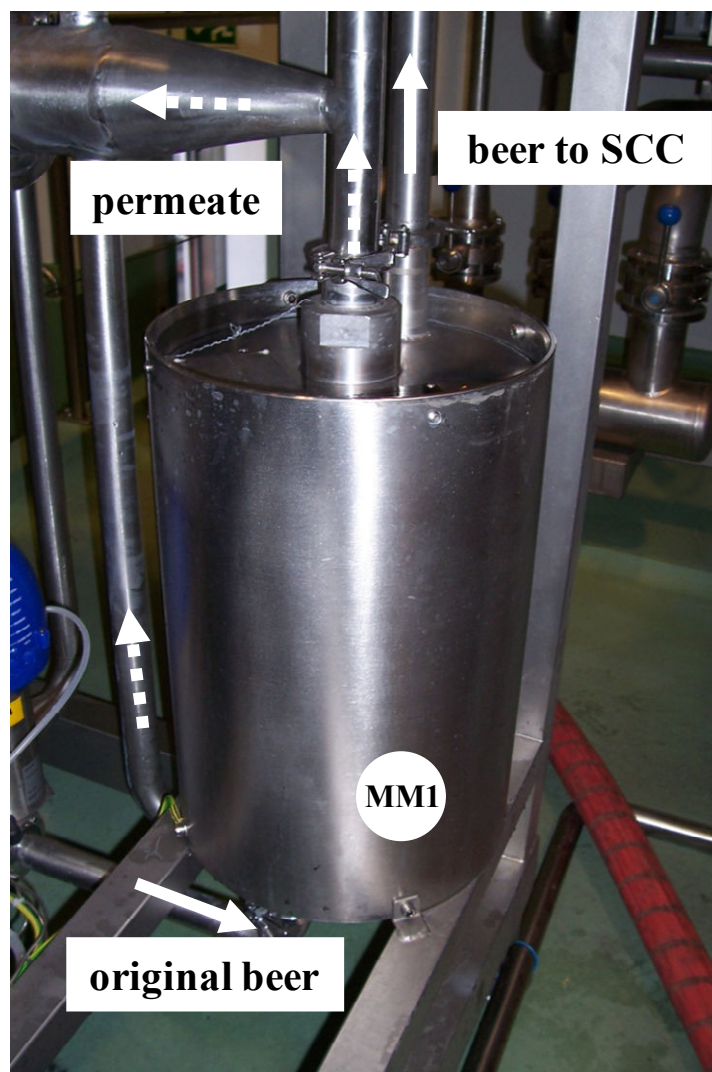


Figure 2.11. Photograph of an envelope membrane module, showing the operation configuration (permeate is drawn through two outlets).

The operation mode of the pervaporation industrial plant comprises several steps that were optimized. The industrial plant can operate semi-continuously or batch-wise. In the semi-continuous mode of aroma production, beer is fed continuously to the membrane modules (MM – cf. Figures 2.9 and 2.10). The vacuum pump (P2) keeps the permeate side of the membrane module at low pressure, allowing the mass transfer of aroma compounds from the feed to the permeate side and the subsequent evaporation on the downstream side of the membranes. The permeate stream flows to the first set of two condensers (PC1 and PC2, with a condensation area of 3 m² each), where it is condensed at around -85 °C using a thermal fluid supplied by the cooling/heating circulator (CH). Then, hot water is made circulating through the jackets of the condensers for defrosting the permeate, which is

collected in the aroma tank (PR) and then discharged and stored in containers. As the first set of condensers defrost, the second set of condensers (PC3 and PC4, with a condensation area of 3 m² each) collect the permeate. The two sets of condensers work out of phase condensing/defrosting the aroma compounds.

In batch-wise operation mode, the two sets of condensers are used simultaneously for condensing the aroma compounds. During the defrosting step, besides the hot water circulating in the condensers, the thermal fluid is heated up to 40 °C, increasing the defrosting rate. The second embodiment was preferred over the first one due to the improved aroma compounds condensation. Figure 2.12 shows the steps for the industrial production of beer aroma, according to the batch-wise approach. The unit operation begins with a *Pre-start* step where the operating conditions are selected and established, then follows the first stage of aroma production, which comprises the *Start*, *Aroma extraction* and *Aroma defrost and storage* steps. The aroma production stages continue until the desired volume of beer aroma is achieved. The characterization of the different steps of beer aroma production is described in Appendix 2.A.

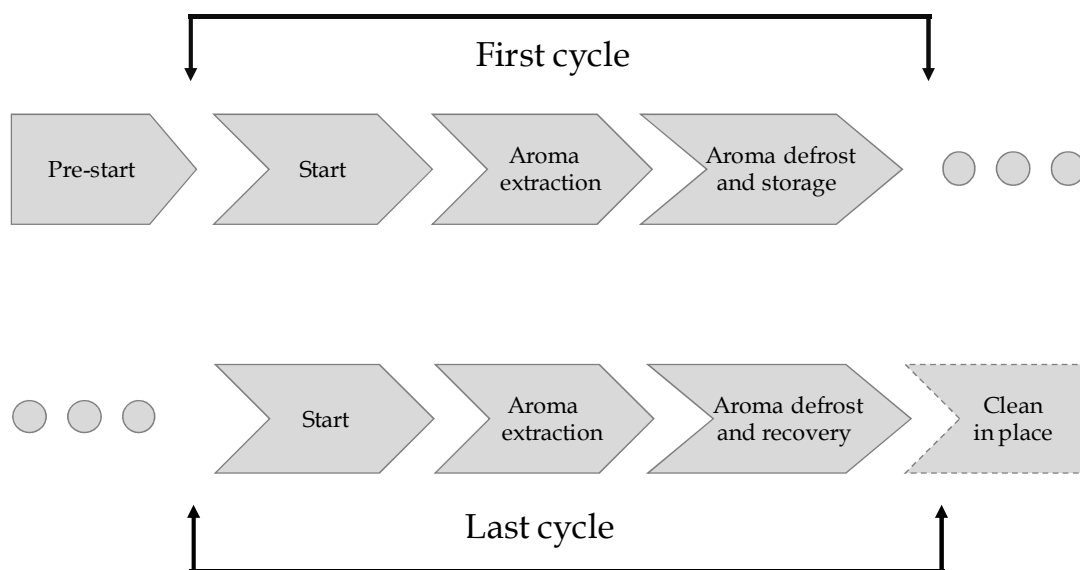


Figure 2.12. Operation mode of pervaporation industrial plant.

As it is common in food industry, the pervaporation plant can require the *Clean in place* (CIP) of the equipments and pipelines, depending on the disinfection needs, for preventing product contaminations. Typical CIP solutions are alkaline aqueous solutions (usually sodium hydroxide), acid aqueous solutions (such as phosphoric acid) and disinfection solutions (usually peracetic acid aqueous solution). To select the appropriate CIP procedure for the pervaporation industrial plant the membranes resistance to the normal chemical solutions used in beverage industry were evaluated. It was found that the membranes could be cleaned with all these solutions if at room temperature.

2.2.4.1. Remarks on the pervaporation industrial plant

The industrial plant was designed based on the lab scale results of the permeate flux and selectivity towards aroma compounds of the selected membrane. However, there are some differences between both units.

In laboratory scale, beer was recirculated batch-wise over the membrane surface, allowing a quick removal of carbon dioxide from beer through the vacuum pump. In industrial scale, beer is fed continuously to the pervaporation plant and fresh carbon dioxide permeates continuously the membrane affecting the permeate pressure and the condensers capacity. The industrial plant operated at a permeate pressure above the recommended 1 mbar and aroma compounds were condensed at ca. -85 °C in the presence of carbon dioxide (reduced residence time). In lab scale, the vacuum pump was oversized allowing permeate pressure as low as 0.5 mbar. Also, the permeate was condensed in a cold trap immersed in liquid nitrogen (-196 °C) with the ability to virtually condense all aroma compounds.

The above-mentioned design differences led that the extracted aroma profile and permeating flux were different. Especially the condensing system of the industrial plant should be redesigned to accommodate the flow of carbon dioxide, otherwise a carbon dioxide removal system should be implemented to treat the pervaporation feeding stream.

2.3. Brief characterization of the pervaporation units

2.3.1. Lab scale results

In order to select the best performing membrane for extracting aroma compounds from beer, a set of pervaporation membranes were obtained and assessed. These membranes were compared in terms of permeate flux, permeance and selectivity towards a selected set of aroma compounds over ethanol. The pervaporation experiments were performed at 5 °C, 4 bar and $0.5 \text{ m}\cdot\text{s}^{-1}$ of feed conditions and 1 mbar of permeate pressure (5 mbar for PDMS membranes), using a Pilsner type beer with a regular alcohol content (ca. 5.5 vol.%). Figure 2.13 shows the permeate flux of the PDMS membrane and of the three POMS membranes. It can be observed that the PDMS membrane shows higher permeate flux than POMS membranes, even for a higher permeate pressure.

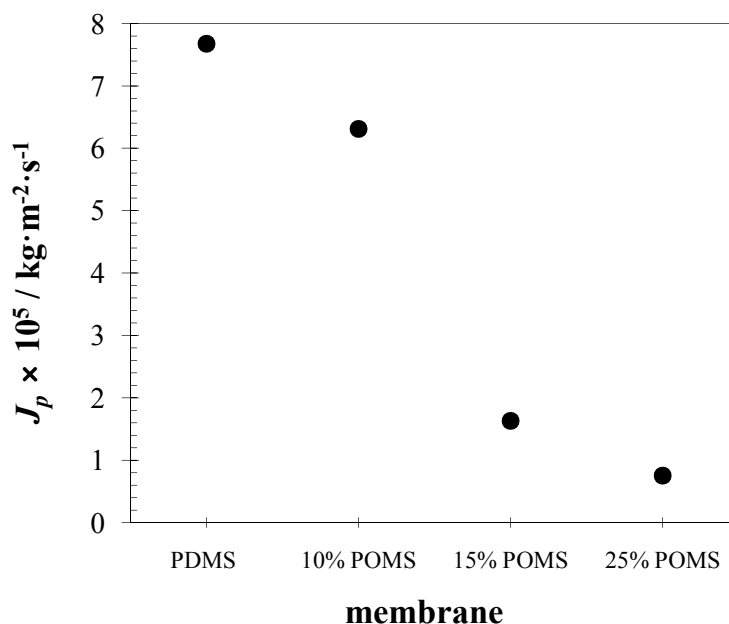


Figure 2.13. Permeate flux (J_p) as a function of the membrane type in the lab set-up.

Figure 2.14 shows the permeance (cf. Eq. (1.13)) of the membranes towards ethanol and the set of selected aroma compounds. One can observe that PDMS membranes show the highest values for ethanol permeance followed by 10% POMS, 15% POMS and 25% POMS. On the other hand, 10% POMS membrane shows the highest permeances towards the aroma compounds, followed by PDMS, 15% POMS and 25% POMS. It is also possible to see that isoamyl acetate is the more permeable compound in all membranes, followed by ethyl acetate, amyl alcohols, isobutanol, propanol and acetaldehyde. Finally, ethanol is the least permeable compound.

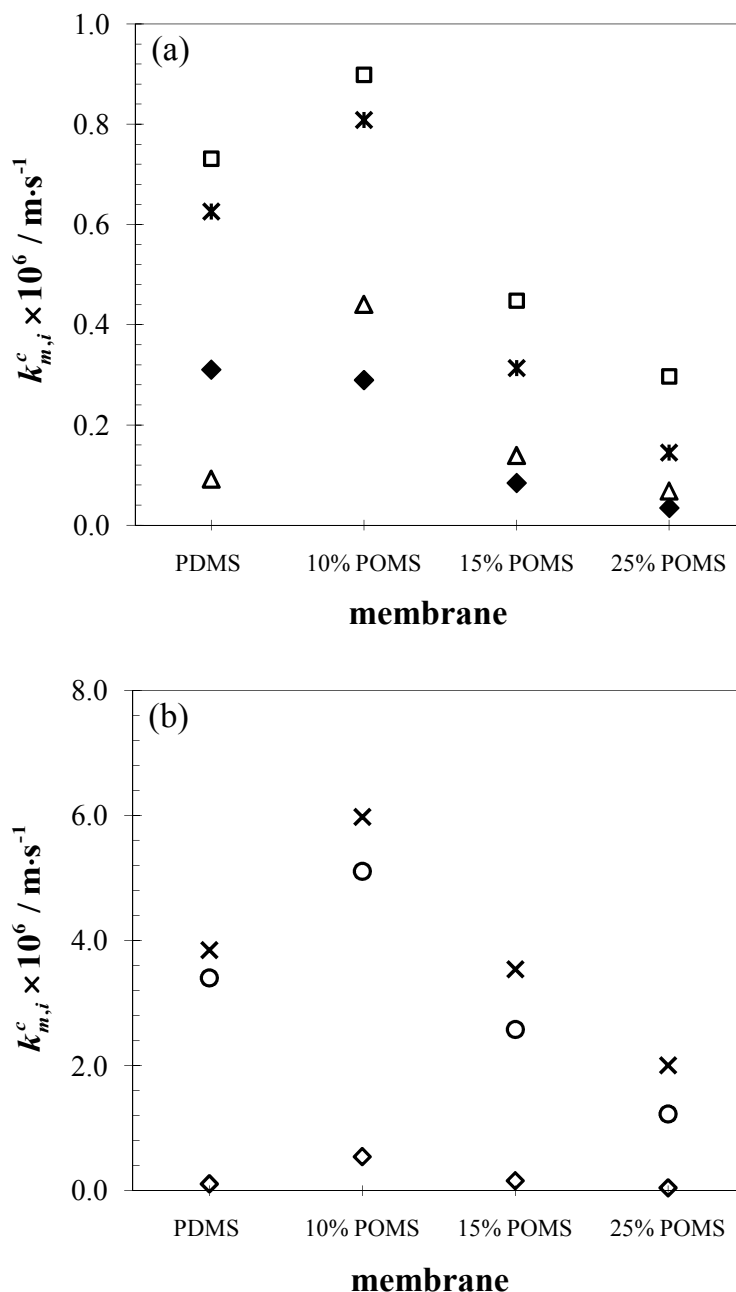


Figure 2.14. Membranes permeance ($k_{m,i}^c$) towards ethanol and beer aroma compounds:

(a) ◆ ethanol and higher alcohols (Δ propanol, × isobutanol and □ amyl alcohols); (b) esters (○ ethyl acetate and × isoamyl acetate) and ◇ acetaldehyde, in lab scale.

Ideal membrane selectivity characterizes the ability of a membrane to concentrate one component compared to another. In the present study it was chosen the ethanol as reference component since the objective is to increase the aroma compounds concentration in the aroma extract compared to the ethanol content. Figure 2.15 shows the membrane selectivity towards beer aroma compounds (higher alcohols, esters and acetaldehyde) over

ethanol. It was found that POMS membranes show higher selectivity towards beer aroma compounds over ethanol than PDMS membranes, due to the higher sorption affinity of POMS to organic aroma compounds [16–18]. On the other hand, it was observed an increase of the POMS membranes selectivity with their thickness. Other authors found similar results for PDMS and POMS membranes [4,7,8,19].

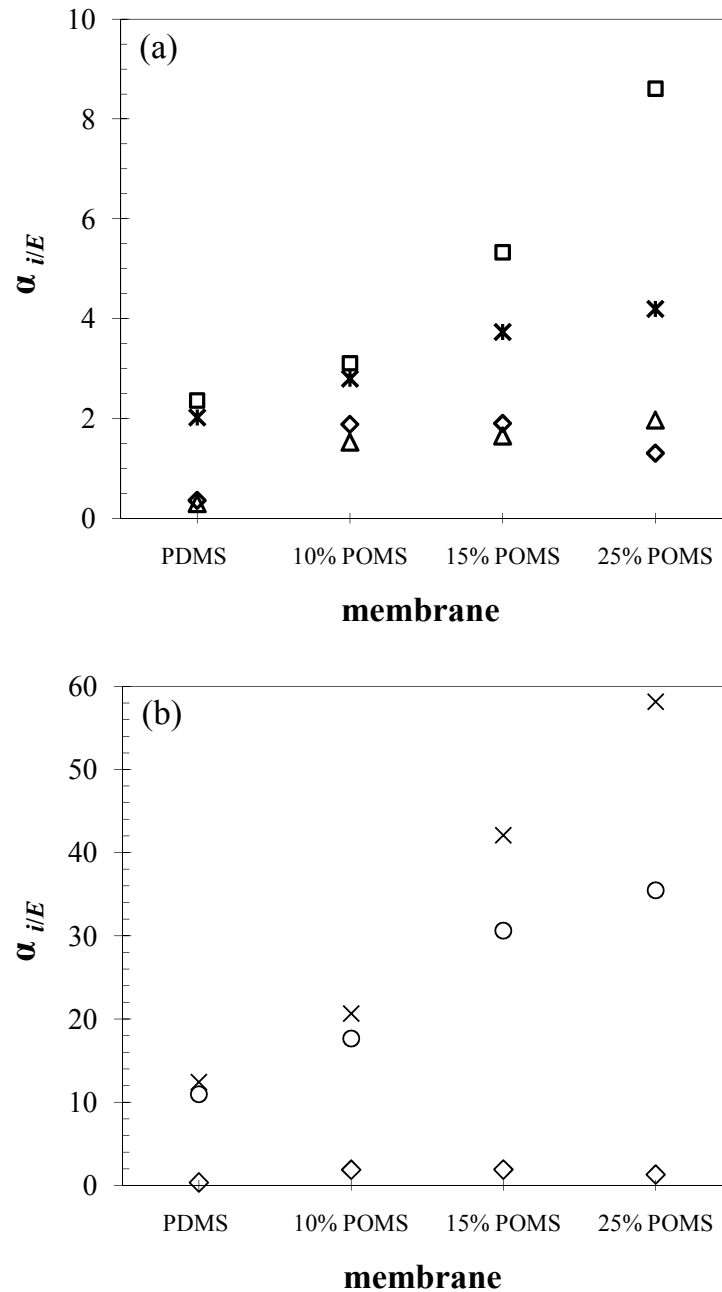


Figure 2.15. Membranes selectivity towards beer aroma compounds over ethanol ($\alpha_{i/E}$): (a) higher alcohols (Δ propanol, $\times$ isobutanol and $\square$ amyl alcohols) and $\diamond$ acetaldehyde; (b) esters ($\circ$ ethyl acetate and $\times$ isoamyl acetate) and $\diamond$ acetaldehyde, in lab scale.

Figure 2.15 shows that the membranes selectivity towards aroma compounds over ethanol is in most cases higher than the unit. This permits producing an aroma extract with a high concentration of aroma compounds, which when added to the depleted beer allows its enrichment.

The selectivity of the membranes towards beer aroma compounds is directly related to the concentration of the same aroma compounds on the pervaporated stream added to the dealcoholized beer. Thus, for a high quality product membranes with high selectivity are required. On the other hand, for industrial applications high permeate fluxes are preferable, because they demand smaller membrane areas. As it was observed, permeate flux and membrane selectivity show different trends as a function of the membrane nature and thickness. Taking into consideration the trade-off between permeate flux and selectivity there were pre-selected membranes 10% POMS and 15% POMS.

Besides the concentration of each aroma compound in the aroma extract, and consequently their concentration in the non-alcoholic beer after being enriched with the pervaporation aroma extract, the balance and interaction between some aroma compounds is also important. In order to select the most promising membrane for industrial recovery of aroma compounds, the aroma extracts obtained by 10% POMS and 15% POMS membranes were added to a base non-alcoholic beer (obtained by SCC dealcoholization) and the aroma recovery evaluated. Table 2.1 shows the aroma profiles of the standard original beer, the dealcoholized beer and the aroma profiles obtained after adding the aroma extract to the dealcoholized beer. Despite the recovery obtained with 15% POMS membranes being higher than the one obtained with 10% POMS (especially concerning esters recovery), the last membrane allowed to obtain a most balanced aroma profile (ratio between higher alcohols and esters – A/E). Besides, the recovery of aroma compounds can be improved increasing the amount of aroma extract added, making the 15% POMS extract more expensive because of the low permeate flux of this membrane. On the other hand, a panel of trained tasters recognized that the dealcoholized beer enriched with the aroma obtained using 10% POMS membrane was more balanced and did not reveal the unpleasant sensations resulted from the dealcoholization process. Moreover, 10% POMS shows the highest values of permeances towards beer aroma compounds. As a result, this membrane was selected for being used in the pervaporation industrial plant and for continuing the research work.

Table 2.1. Aroma profile of original beer, dealcoholized beer and enriched beers (with aroma extracted by 10% POMS and 15% POMS membranes).

Characteristics	Original beer	dealcoholized beer	10% POMS	15% POMS
$C_{p,E}$ (vol.%)	5.63	0.34	0.40	0.40
C_{Pr} (mg·L ⁻¹)	8.99	0.90	1.28	1.40
C_{iB} (mg·L ⁻¹)	11.52	0.77	1.29	1.65
C_{AA} (mg·L ⁻¹)	69.90	4.83	8.19	12.59
C_{EA} (mg·L ⁻¹)	17.57	1.26	5.18	11.59
C_{iAA} (mg·L ⁻¹)	1.65	0.10	0.49	1.30
C_{Ac} (mg·L ⁻¹)	2.43	1.68	1.80	1.75
A/E	4.70	4.78	1.90	1.21

2.3.1.1. Preliminary study about the influence of the operating conditions

A design of experiments (DoE) tool – *JMP 5.01* (SAS software) was used for assessing the relevant operating variables concerning the permeating flux and selectivity obtained with the 10% POMS/PEI membrane. The operating conditions or factors considered were the feed temperature (T_f), feed pressure (P_f), feed velocity (v_f) and permeate pressure (P_ℓ). Table 2.2 shows the design factors ranges; the temperature range corresponds to the ideal conditions for preserving the organoleptic quality of the product and, the feed pressure and the feed velocity interval were defined according to physical limitations of the pervaporation lab set-up. The upper limit of the permeate pressure was 20 mbar since above this value the amount of the collected permeate was too low and the lower permeate pressure was set for 1 mbar, limited by the vacuum pump used.

Table 2.2. Custom design factors and respective levels.

Factor	Level		
	-1	0	+1
T_f (°C)	5.0	10.0	15.0
P_f (bar)	3.0	4.0	5.0
v_f (m·s ⁻¹)	0.1	0.3	0.5
P_ℓ (mbar)	1.0	10.5	20.0

It was applied a second order interaction model with two levels and a central point. The central point was replicated three times for assessing the response precision but it was used in the DoE just the averaged value. Table 2.3 summarizes the process responses for the selected operating conditions. The beer used for all experiments was collected from a single production batch and stored in glass bottles at 5 °C. The water flux of the pervaporation unit was measured before and after this set of experiments, using Milli-Q ultrapure water ($0.054 \mu\text{S}\cdot\text{cm}^{-1}$). It was read a water flux of $6.24\times 10^{-5} \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ before the set of experiments and of $6.34\times 10^{-5} \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ afterwards (relative difference 0.9 %). It was then concluded that the membrane kept its integrity during the experimental runs (Table 2.3).

From the experimental values it was obtained a first order representation of the process responses as a function of the operating variables. Figure 2.16 shows the permeate flux and the membrane selectivity towards aroma compounds and their dependence with the operating conditions. Feed temperature has a positive influence on the permeate flux and higher alcohols selectivity, while it presents a negative effect on the esters and acetaldehyde selectivity. Feed pressure has no detrimental effect on the aroma compounds selectivity; it was though observed that permeate flux decreases with feed pressure. Feed velocity does not influences significantly the permeate flux, it has a positive effect on the aroma compounds selectivity, being more significant for esters than for higher alcohols and acetaldehyde. Permeate pressure has a negative influence on the permeate flux and higher alcohols selectivity, whereas it shows a positive effect on the esters and acetaldehyde selectivity. From these results, it was possible to conclude that the most important factors on the membrane properties are: feed temperature, feed velocity and permeate pressure. Feed pressure did not significantly affect the pervaporation responses and it was excluded from further experimentation.

From Figure 2.16 one can observe that the influence of operating conditions follows different trends concerning the permeate flux and aroma compounds selectivity. As a result the optimization of the permeate flux and the aroma profile of the beer aroma extract is a very complex problem. Chapter IV describes the effect of each operating condition on the process performance using 10% POMS/PEI membranes in order to maximize the permeate flux, the selectivity towards aroma compounds over ethanol and to optimize the aroma profile of the aroma extract. The last criterion is very important since the main goal of this thesis is to obtain a pervaporated extract intended to be added to a dealcoholized beer for improving its depleted aroma profile.

Table 2.3. Operating conditions of the experimental runs and respective responses.

Run #	T_f (°C)	P_f (bar)	v_f (m·s ⁻¹)	P_t (mbar)	$J_p \times 10^5$ (kg·m ⁻² ·s ⁻¹)	$\alpha_{Pr/E}$	$\alpha_{iB/E}$	$\alpha_{AA/E}$	$\alpha_{EA/E}$	$\alpha_{iAA/E}$	$\alpha_{Ac/E}$
1	5	5	0.1	1.0	4.67	1.70	3.08	3.60	19.33	19.70	3.19
2	5	3	0.5	20.0	2.63	1.50	2.40	2.38	26.52	35.05	5.31
3	15	3	0.1	1.0	8.50	1.59	3.04	3.73	11.47	11.83	2.74
4	15	3	0.1	20.0	4.79	1.39	2.65	2.85	16.56	19.72	4.23
5	5	5	0.1	20.0	1.53	1.19	2.12	2.10	19.13	23.07	3.73
6	15	5	0.5	1.0	8.87	1.59	3.27	4.06	15.65	18.27	3.22
7	10	4	0.3	10.5	4.19	1.45	2.72	2.98	18.11	22.20	4.02
8	15	5	0.1	20.0	3.32	1.23	2.54	2.61	15.38	18.68	3.55
9	5	3	0.1	20.0	1.58	1.11	1.90	1.86	18.74	24.92	4.16
10	5	5	0.5	20.0	1.66	1.20	1.99	1.97	22.93	33.98	4.83
11	5	3	0.5	1.0	5.33	1.63	2.84	3.40	22.34	26.76	3.00
12	15	5	0.5	20.0	4.13	1.37	2.63	2.82	20.36	29.50	3.42
13	5	5	0.5	1.0	4.84	1.46	2.84	3.34	21.90	26.55	2.58
14	15	3	0.5	20.0	4.21	1.46	2.77	2.96	18.21	24.14	3.76
15	5	3	0.1	1.0	6.00	1.39	2.57	3.08	15.26	16.79	2.79
16	15	3	0.5	1.0	8.83	1.69	3.31	4.13	15.87	18.71	3.16
17	15	5	0.1	1.0	8.75	1.59	3.08	3.76	11.77	12.01	3.35

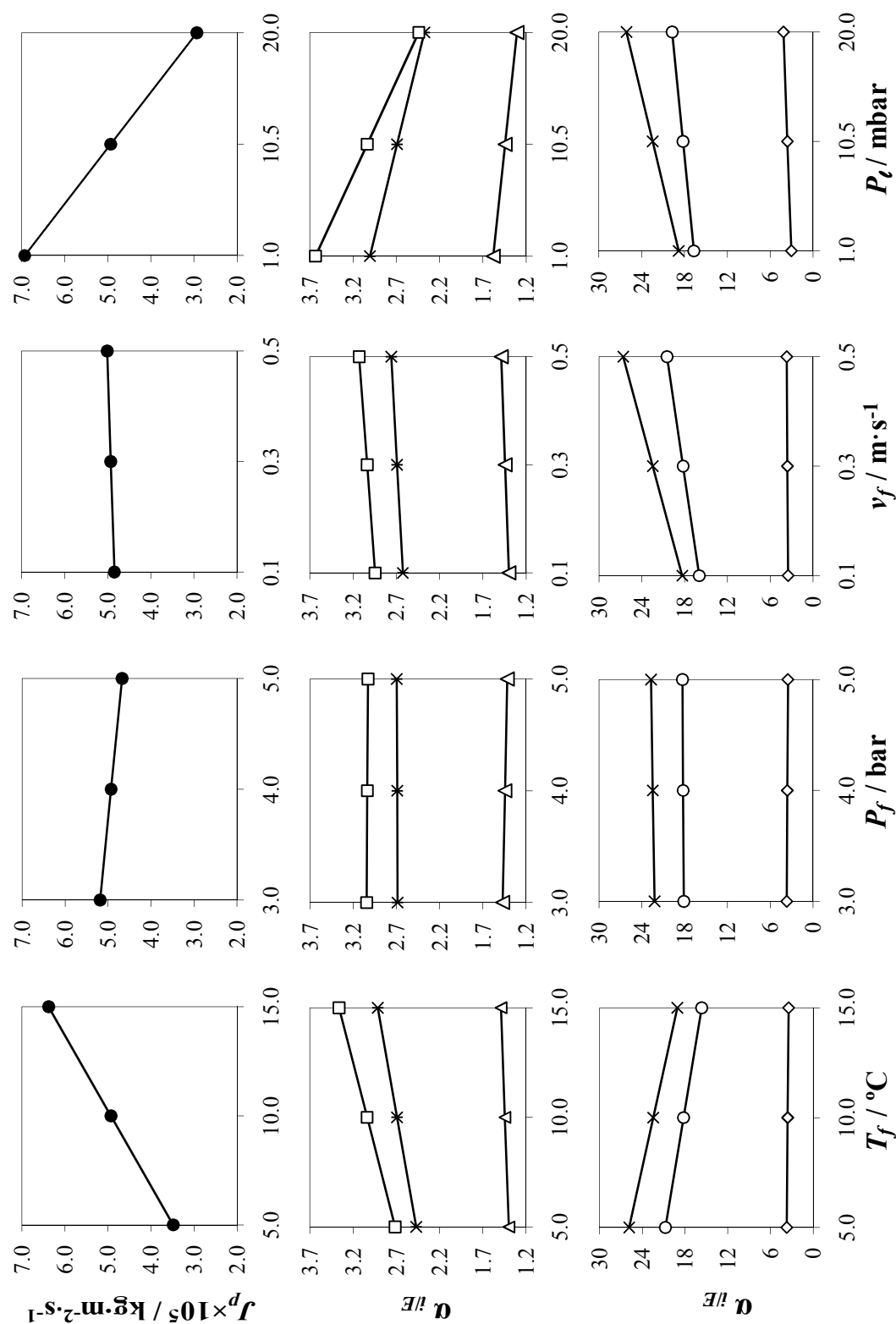


Figure 2.16. Permeate flux (J_p) and aroma compounds selectivity ($\alpha_{i/E}$) over ethanol (Δ), isopropanol ($\times$), isobutanol ($\square$), amyl alcohols ($\circ$), ethyl acetate ($\times$), isoamyl acetate ($\diamond$) and acetaldehyde ($\diamond$) as a function of the operating conditions.

2.3.2. Industrial results

The pervaporation industrial plant was designed, manufactured and assembled in the framework of the present research. Preliminary experimental runs were carried out for assessing the performance of the plant. Table 2.4 compares the lab with the industrial performances at close operating conditions.

Table 2.4. Comparison between pervaporation lab and industrial results.

		Lab set-up	Industrial plant
Operating conditions	T_f (°C)	10.0	10.0
	P_f (bar)	4.0	3.2
	v_f (m·s ⁻¹)	0.3	0.2
	P_t (mbar)	10.5	6.8
Results	$J_p \times 10^5$ (kg·m ⁻² ·s ⁻¹)	4.19	1.48
	$C_{p,E}$ (vol.%)	25.38	17.00
	$\alpha_{Pr/E}$	1.45	1.29
	$\alpha_{iB/E}$	2.72	2.42
	$\alpha_{AA/E}$	2.98	2.68
	$\alpha_{EA/E}$	18.11	13.09
	$\alpha_{iAA/E}$	22.20	32.55
	$\alpha_{Ac/E}$	4.02	0.46

The permeate flux as well as the ethanol concentration of the industrial extract are smaller than of those of the lab unit. Concerning the selectivity towards beer aroma compounds, the results from both plants are in the same order of magnitude. On the other hand, since ethanol concentration of the industrial extract is smaller, the concentration of the other aroma compounds is also smaller (similar selectivities) leading to a permeate with a less enriched aroma profile. These differences were assigned to the condensing system of the industrial plant, which presented a low condensation efficiency, especially of the more volatile compounds. The industrial plant has shown to perform within the design parameters and it was then decided to optimize the operating conditions for producing an equilibrated aroma extract. Again, the modelling and the optimization of the industrial plant are hard to achieve due to the same reasons pointed before for the lab set-up. Besides, as the performance of the industrial plant is influenced by some operating conditions,

additional criteria need to be considered. The optimization of the pervaporation industrial plant is described in Chapter V.

2.4. Conclusions

In this chapter, a new process for producing low alcohol beer enriched with natural aroma extract obtained by pervaporation of the original beer was proposed and described. This process was described, as well as the lab and industrial units and the main operating and design variables identified and briefly discussed.

It was concluded that the best membrane for aroma extraction was the 10% POMS supported in PEI composite membrane. This membrane showed the best permeances towards beer aroma compounds and good selectivity for the same aroma compounds. A pre-screening study of the operating conditions influences on the process performance was conducted. It was concluded that the most important factors are the feed temperature, feed velocity and permeate pressure. Feed pressure was concluded to have a minor influence on the pervaporation performance.

The results with the 10% POMS/PEI membrane were used for designing, manufacturing and assembling the industrial plant. The industrial plant was designed to operate continuously with two sets of two condensers each. Since the performance of the condensers was below the expected, mainly due to carbon dioxide desorption from beer, the pervaporation plant was reprogrammed to operate batch-wise concerning the freezing and defrosting steps.

The industrial plant extract characterization was within the designed characterization. However, due to the lower efficiency of the industrial condensing system, the optimized operating conditions would be different from the experimental ones. On the other hand, a pre-treatment of beer for extracting the carbon dioxide before pervaporation plant can be considered.

2.5. List of symbols

A/E	higher alcohols/esters ratio (–)
C	concentration ($\text{g}\cdot\text{cm}^3$ or vol.%)
J	flux ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
k	membrane permeance ($\text{m}\cdot\text{s}^{-1}$)
P	pressure (bar)
r	radius (mm)
T	temperature ($^{\circ}\text{C}$)
v	velocity ($\text{m}\cdot\text{s}^{-1}$)

Greek letters

α	membrane selectivity (–)
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Subscripts and superscripts

AA	amyl alcohols
Ac	acetaldehyde
c	concentration
E	ethanol
EA	ethyl acetate
f	feed
i	generic component
iAA	isoamyl acetate
iB	isobutanol
ℓ	low (permeate side)
m	membrane
p	permeate
Pr	propanol

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APPENDIX 2.A

The operation mode of each stage of the industrial pervaporation plant is described below.

Pre-start

The *Pre-start* step only occurs when the pervaporation plant is turned on after a period of inactivity; the operation time is 15 min and it considers the following tasks:

- Flowing the feed beer through the membrane modules by-pass in order to flush beer or water from this pipeline;
- Flushing water from the condensation line;
- Selecting the set-point for feed temperature (controlled by the plate heat exchanger which is fed with water at different temperatures) and feed flowrate (controlled by the feed pump); the optimal conditions of feed temperature and flowrate are reported in Chapter V;
- Heating the vacuum pump, with the outlet from the permeate side of the modules close, in order to achieve the highest performance (lowest permeate pressure and avoiding the condensation of non-permeate vapours inside the pump);
- Selecting the temperature set-point for the cooling/heating circulator at -89 °C, in order to cool the thermal fluid.

Start

During the *Start* step several goals are followed:

- Flowing beer through the feed side of the membrane modules (with no vacuum applied on the permeate side) in order to flush beer or water from the modules;
- Stabilization of the beer temperatures at the modules inlet and outlet; the last one should be similar to the first one in order to assure that the feed side of the modules is already flushed;
- Applying vacuum to the permeate side of the modules and stabilization of the permeate pressure below 10 mbar;
- Cooling the thermal fluid until -85 °C;

- Selection of the *Aroma extraction* operation time (optimum is 90 min).

The *Start* step ends when the above-cited tasks are achieved.

Aroma extraction

The *Aroma extraction* step aims the production of a beer aroma extract, which is intended to be added to a dealcoholized beer, in order to improve its aroma and flavour profile. During this step the following processes occur:

- Original beer flows in the feed side of the membrane modules and the vacuum applied on the permeate side allows the permeation of aroma compounds through the POMS/PEI membrane;
- Due to the low pressure, the permeate stream leaves the membranes as vapour and flows to the condensers;
- The cooling/heating circulator supplies the thermal fluid to the permeate condensers for condensing and frosting the permeate;
- The temperature of the thermal fluid tends to raise a few degrees due to the influence of the feed temperature and the presence of non-condensable gases, such as carbon dioxide, which are expelled through the vacuum pump vent;
- The previous effects together with the feed flowrate, affects the permeate pressure, which tends to increase too, although it is always kept below 10 mbar. The influence of operating conditions on the condensing system and vacuum pump performance is described in Chapter V;
- It is important to consider that the pressure drop between the feed and the retentate (after the outlet of the four modules) should not exceed 2 bar;
- The beer temperature decreases slightly (less than 5 °C due to low permeating rates) from the feed to the retentate side of the membrane modules because the latent heat of aroma compounds vaporization results from the sensible heat of the feed solution;
- The retentate stream consists of the feed fraction that does not permeate the membrane. This stream is a beer without a low fraction of its original aroma content and it is then fed to the dealcoholization unit.

The operation time of the *Aroma extraction* was optimized in order to maximize the productivity of the pervaporation plant, considering the balance between extraction and defrosting stages.

Aroma defrost and recovery

The last aroma production step aims the aroma permeate defrost in order to collect a liquid aroma extract and the storage of the permeate in containers for further addition to the dealcoholized beer. This step includes the following procedures:

- The permeate is defrosted by means of hot water, at 90 °C, which circulates in the condensers jacket. This water is supplied by the cooling system of the cooling/heating circulator and it is heated with vapour in a plate heat exchange;
- The set-point of the cooling/heating circulator is changed to 40 °C, in order to heat the thermal fluid and increase the aroma defrosting rate;
- During the aroma defrost no beer passes through the pervaporation plant and it is directed to the dealcoholization unit;
- Once defrosted, the aroma compounds are collected in the permeate reservoir;
- The permeate is then discharged through a dosing pump to containers and then stored at around 5 °C.

A new *Start* step begins at the same time of the permeate recovery.

Chapter III

3. Alcohol removal from beer by reverse osmosis¹

Abstract

In this chapter reverse osmosis technology was used for removing alcohol from beer. The process was carried out in diafiltration mode and it was possible to obtain a final beer with low ethanol content (less than 0.5 vol.%). Several cellulose acetate and polyamide membranes were tested with transmembrane pressures ranging from 20 to 40 bar. Temperature and feed flowrate varied from 5 to 20 °C and from 2 to 7 L·min⁻¹, respectively. It was observed that permeate flux and alcohols rejection increase with the feed pressure, whereas esters rejection decreases with pressure. Permeate flux increases with temperature, while rejections decrease with it. Concentration polarization occurs at low feed flowrates.

¹ *Adapted from:* M. Catarino, A. Mendes, L.M. Madeira, A. Ferreira, Alcohol removal from beer by reverse osmosis, *Separation Science and Technology* 42 (2007) 3011–3027.

3.1. Introduction

As referred in Chapter I (section 1.2), there is a suitable range of processes for producing non-alcoholic (ethanol content less than 0.5 vol.%) or low alcohol beer (ethanol content less than 1.0 vol.%). These can be divided in processes of restricted alcohol formation and in alcohol removal processes. The last ones include heat- and membrane-based processes. Concerning membrane separation processes, alcohol can be removed by reverse osmosis (cf. Figure 1.4).

In the reverse osmosis (RO) process, the product to be treated flows tangentially to the membrane surface and a portion of the feed flowrate (permeate) crosses selectively the membrane, while the other fraction (retentate) remains in the feed side. This kind of processes is called cross-flow filtration or tangential filtration [1]. The RO occurs when the transmembrane pressure exceeds the osmotic pressure [2]. This principle can be applied to remove alcohol from beer if a membrane semi-permeable to the ethanol is used. Ethanol (and water) permeates the membrane against the osmotic pressure and is recovered in the permeate side. On the other hand, larger molecules, such as beer aroma and flavour compounds, mostly remain at the retentate side (concentrated beer).

Beer aroma profile consists of a large group of volatile organic compounds (VOCs) at low concentration (ppm level), that are responsible for the odour and taste of beer [3–6]. These beer aroma compounds can belong to several functional group categories such as alcohols, esters, aldehydes, lactones, carboxyl acids, phenols and ethers [4,5]. Each aroma compounds group is responsible for a typical flavour. Higher alcohols, for example, which are the major group of aroma compounds in the beer (ethanol is the compound in highest quantity), provide an alcoholic, fruity and immature flavour. Esters confer a sweet and fruity flavour to the beer, while aldehydes are associated to the freshness (immaturity) of the beer [7].

The RO process has some advantages compared to other dealcoholization processes. RO requires low energy consumption compared to distillation processes and the feed beer can be processed at low temperatures (below room temperature). The low alcohol beer quality is similar to the standard beer because RO semi-permeable membranes are specific to retain the larger beer flavour and aroma compounds. These characteristics contrast with the ones assigned to the heat processes, where temperature sensitive compounds can suffer some damages (chemical alterations and physical losses), and with restricted alcohol processes, where the fermentation is stopped and the beer aroma does not

develop such as in a regular alcoholic beer [1]. Besides these advantages, RO is a very versatile process since various beer types can be dealcoholized in a given unit and various alcohol contents can be obtained. In addition, it is a modular technology, easy of scaling-up.

The RO process has been reported by several authors for removing ethanol from fermented beverages such as cider, wine and beer [8,9]. López et al. studied the use of RO for producing low alcohol content cider in both diafiltration and batch modes [8]. Several authors describe the economic feasibility of RO for ethanol removal processes. According with their results, RO is not viable for reducing the ethanol content from alcoholic beverages under 0.45 % [9]. On the other hand, RO is a profitable process for the recovery and purification of ethanol from fermentation beer, comparing with typical processes such as distillation [10,11]. RO has also been used in large scale to concentrate fruit juices and wine must [12,13].

The aim of this chapter is the evaluation of RO effectiveness for removing alcohol from a fermented beer with about 5.5 vol.% of ethanol content, in order to produce non-alcoholic beer with less than 0.5 vol.% of ethanol content. After selecting the most promising membrane, some tests were carried out in order to study the effect of the most critical operating conditions in the process performance.

3.2. Theory

The RO separation process can be described by the solution-diffusion theory [2]. According to it the solvent flux (J_A) can be represented by the following equation:

$$J_A = k_A (\Delta P - \Delta \pi) \quad (3.1)$$

where k_A is the solvent permeance factor, ΔP is the transmembrane pressure difference and $\Delta \pi$ is the osmotic pressure difference between both sides of the membrane.

When highly selective membranes are used the solvent flux is approximately equal to the permeate flux (J_p) which can be determined experimentally from the following equation:

$$J_A \approx J_p = \frac{m_p}{A \cdot t} \quad (3.2)$$

where m_p is the permeate mass, A is the effective membrane area and t is the permeation time. Although ethanol also permeates the membrane, its flux is relatively small compared to the overall one, which is mostly water.

The solute flux (J_s) is smaller than the solvent flux when membranes with high selectivity are used and can be written as:

$$J_s = k_B \Delta C_s \quad (3.3)$$

where k_B is the solute permeance factor and ΔC_s is the solute concentration difference between feed and permeate sides.

The selectivity of a membrane for a given solute is evaluated by the rejection coefficient (R):

$$R = \frac{C_b - C_p}{C_b} = 1 - \frac{C_p}{C_b} \quad (3.4)$$

where C_b and C_p are the solute concentrations, in the feed bulk and permeate sides, respectively.

Once the solute and solvent fluxes can be related by $J_s = C_p J_A$ and combining Eqs. (3.1) and (3.3), the rejection coefficient (R) can be expressed as:

$$R = \frac{k_A (\Delta P - \Delta \pi)}{k_A (\Delta P - \Delta \pi) + k_B} \quad (3.5)$$

3.3. Materials and methods

3.3.1. Experimental procedure

A lab reverse osmosis unit, which is sketched in Figure 3.1, was used for conducting the dealcoholization experiments. The beer stored in the feed tank (1 – Figure 3.1) is pumped batch-wise by means of a diaphragm pump (2) to the membrane module (3) with 155 cm² effective membrane area. A fraction of the feed stream was recycled to the feed tank through a plate heat exchanger (5). The retentate was also recycled to the feed reservoir through the same heat exchanger and its flowrate measured by a rotameter (6a). Water and ethanol permeate through the membrane against the osmotic pressure and are collected at the permeate side (4), which flowrate is measured using a graduated cylinder and a chronometer. On the other hand, the bulky molecules (such as beer aroma and flavour compounds) remain at the retentate side. The feed pressure, which is measured by a manometer (11), and the retentate flowrate are adjusted by regulating needle valves (8a, 8b and 8c). A PT100 (10a) and a thermocouple (10b) measure the feed and membrane module temperature, which is controlled by a diaphragm valve (9) that regulates the cooling water flowrate. Since water is also removed with ethanol the RO process was carried out in diafiltration mode: the volume of feed beer in the tank (1) was maintained approximately constant by adding deaerated deionized water every hour. By this way, the concentrations of non-permeable compounds, such as proteins, polyphenols, non-fermentable sugars, bitter species, colour substances and some aroma compounds are maintained approximately constant along with the osmotic pressure, whereas the ethanol content is continuously reduced. This is the principle of alcohol removal by means of RO.

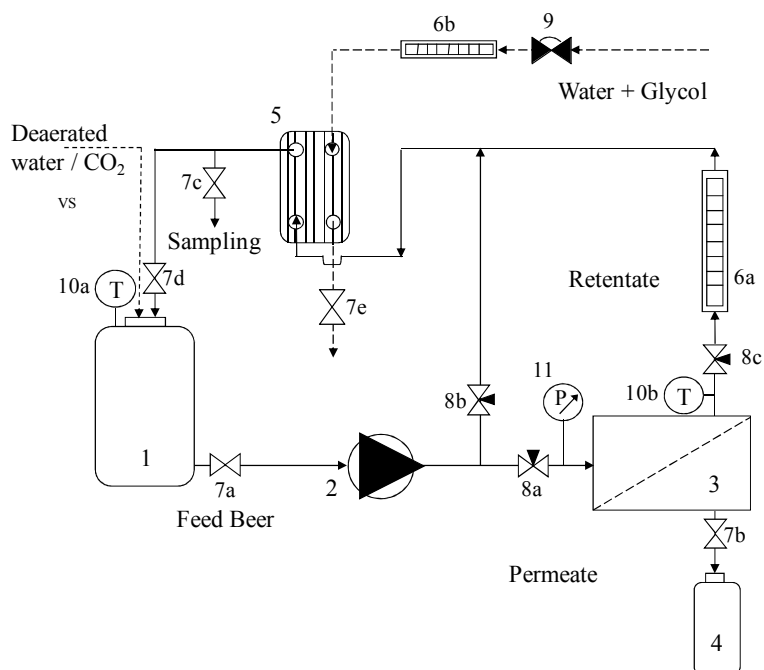


Figure 3.1. Sketch of the reverse osmosis unit used for removing alcohol from beer (1, feed tank; 2, diaphragm pump; 3, membrane module; 4, permeate reservoir; 5, plate heat exchanger; 6, rotameters; 7, on/off valves; 8, needle valves; 9, diaphragm valve; 10, temperature sensors; 11, manometer).

3.3.2. Membranes

The most used membrane in alcohol removal is made of cellulose acetate (CA), which has a high water and alcohol permeability and a high rejection to the compounds with high molecular weight such as proteins, polyphenols, sugars, bitter species, colour substances and aroma compounds.

In this work several membranes made of cellulose acetate and polyamide were used, provided by Alfa Laval (Sweden) and Centec (Germany), respectively. The membranes characteristics are given in Table 3.1.

Table 3.1. Characteristics of the RO membranes used for removing ethanol from beer.

Membrane reference	Supplier	Type	MMCO ^a (g·mol ⁻¹)	$P_{\max}^b$ (bar)	$T_{\max}^b$ (°C)
CA995PE	Alfa Laval	Cellulose triacetate/diacetate blend on polyester	200	50	30
BW RLC	Centec	Polyamide	N/A	41	45
BW 30 LE	Centec	Polyamide	N/A	41	45
SW 30 HR	Centec	Polyamide	N/A	41	45
ACM 4	Centec	Polyamide + Composite Fiberglass	N/A	41	45
ACM 2	Centec	Polyamide + Composite Fiberglass	N/A	41	45

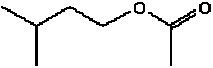
^a Molecular mass cut-off^b Maximum operating conditions

N/A – not available

3.3.3. Feed solution and aroma compounds

The beer used in the present study was a regular alcoholic beer, which ethanol content was about 5.5 vol.%. Eight aroma compounds, four alcohols (ethanol, propanol, isobutanol, and isoamyl alcohol), two esters (ethyl acetate and isoamyl acetate), one aldehyde (acetaldehyde) and one sulphur compound (dimethylsulphide) were followed using gas chromatography (GC). In this study only the permeation of alcohols and esters, the most important beer aroma compounds, are tracked. Their properties are given in Table 3.2.

Table 3.2. Beer aroma compounds properties.

Compound	Structure Formula	Molecular weight (g·mol ⁻¹)	Boiling point (°C)	Beer threshold ¹ (ppm)	Range of concentration ¹ in beer (ppm)	Typical aroma
Ethanol		46	78	14000	–	Alcoholic
Propanol		60	98	800	7.5 – 13.8	Alcoholic
Isobutanol		74	108	200	8.6 – 56.6	Alcoholic
Isoamyl alcohol		88	132	68	27 – 122	Alcoholic, banana
Ethyl acetate		88	77	30	8.2 – 47.6	Fruity, solvent
Isoamyl acetate		130	149	1.2	0.8 – 6.6	Banana

¹ Source: Meilgaard [14]

3.3.4. Analytical methods

A density meter (DMA 4500, Anton Paar) coupled to an Alcolyzer Plus (Anton Paar) was used to determine the density and the ethanol content of the solutions. For determining the aroma content on both feed and permeate streams, a GC (Varian Star 3400) was used; the method is described in Chapter II (section 2.2.1). These analytical methods correspond to the standard methods by EBC – the European Brewery Convention [15].

3.4. Results and discussion

3.4.1. Ethanol removal from beer

Experiments with fresh and clarified alcoholic beer were carried out in order to produce non-alcoholic beer (less than 0.5 vol.% of ethanol) by means of reverse osmosis. A restricted taste panel recognized a promising taste in the produced beer. Figure 3.2 shows the ethanol content during the dealcoholization process, from 5.4 vol.% of the initial feed beer to 0.49 vol.% of the final one, using the CA995PE membrane. This figure shows that the ethanol content decreases following a negative exponential, characteristic of the diafiltration operating mode [2]. It was observed that the permeate flux was maintained approximately constant ($5.06 \times 10^{-4} \text{ g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$) during the RO process because it was operated in diafiltration mode. The addition of deaerated deionized water to the feed tank is done in order to keep the beer osmotic pressure approximately constant.

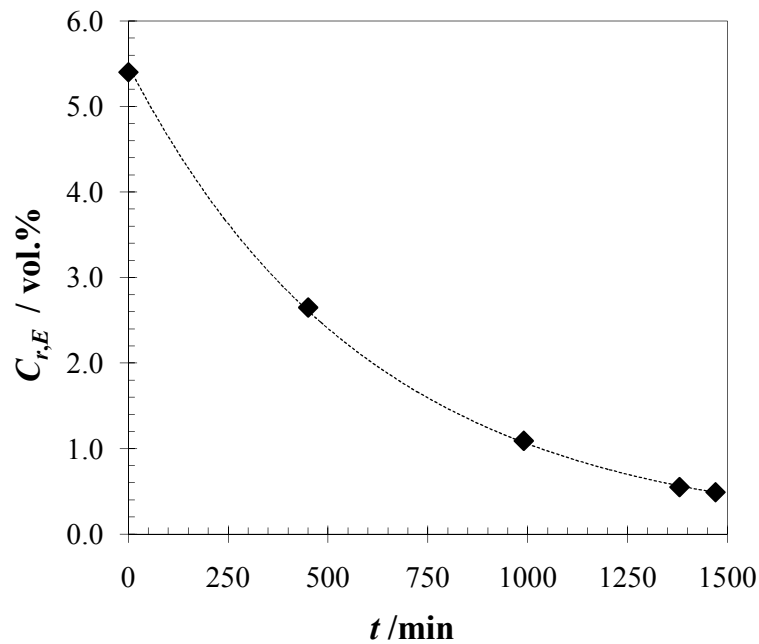


Figure 3.2. Ethanol content history at the retentate side for 5 °C, 40 bar and 7 L·min⁻¹ feed flowrate, using the CA995PE membrane (dot – experimental data, line – exponential fitting).

3.4.2. Membrane selection

The choice of the most promising membrane was made based on Figure 3.3. This figure shows, for each membrane, the normalized permeate flux as a function of the ethanol rejection. The best membrane should have the highest permeate flux and the lowest ethanol rejection (it is aimed to permeate the ethanol). The best performing membrane is the CA995PE, a cellulose acetate membrane by Alfa Laval – Table 3.1. The other membranes show very low permeate fluxes and also higher ethanol rejections. Similar results with cellulose acetate and polyamide membranes were observed by other authors [8].

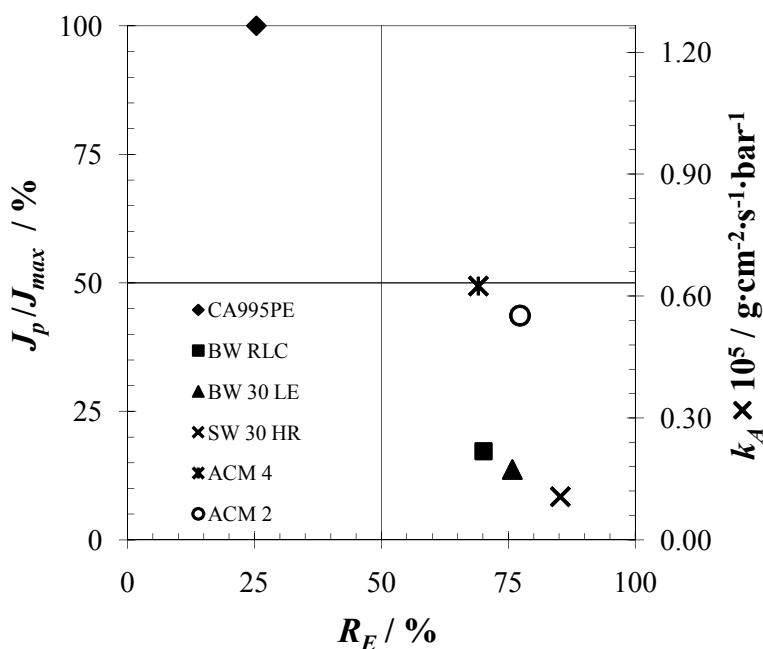


Figure 3.3. Normalized permeate flux and permeance as a function of the ethanol rejection for all tested membranes. Operating conditions: $T=5$ °C, $\Delta P=40$ bar and $Q_f=7$ L·min⁻¹.

3.4.3. Influence of the operating conditions

After selecting the membrane (CA995PE) several laboratory experiments were performed in order to study the performance of such membrane under a range of operating conditions. In order to guarantee the uniformity of the beer, beer from the same batch was stored at 5 °C in glass bottles and used for all the experiments. Table 3.3 summarizes the operating conditions employed as well as the membrane performance in terms of ethanol rejection, total permeate flux and permeate flux for each aroma compound. Experiments were performed at three pressure differences, five temperatures and three feed flowrates. It is worth nothing that, in these experiments, a more concentrated beer in non permeable compounds was used compared to that described in section 3.4.1, consequently the osmotic pressure is higher, which results in a decrease of the permeate flux (cf. Eq. (3.1)).

The membrane permeability towards water was measured before and after this set of experiments, using Milli-Q ultrapure water ($0.054 \mu\text{S}\cdot\text{cm}^{-1}$). The water permeance observed before beer experiments was $1.25\times 10^{-5} \text{ g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{bar}^{-1}$, while the permeance after was $1.30\times 10^{-5} \text{ g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{bar}^{-1}$ (relative difference 4.0 %). From these results, it can be assumed that the membrane keeps its performance during the whole set of experiments with beer (Table 3.3).

Run 9 was performed in triplicate in order to assess the experimental errors. The permeate mass flux and ethanol rejection relative standard deviations were 2.5 % and 4.2 %, respectively – Table 3.3. The relative standard deviations of the fluxes were 2.7 %, 3.4 %, 4.6 %, 4.5 %, 4.1 % and 6.0 % for ethanol, propanol, isobutanol, amyl alcohols, ethyl acetate and isoamyl acetate, respectively.

Table 3.3. Ethanol concentration in the permeate, rejection of ethanol, permeate and aroma compounds fluxes for membrane CA995PE.

Run #	P_f (barg)	T (°C)	Q_f (L·min ⁻¹)	$C_{0,E}$ (vol.%)	$C_{p,E}$ (vol.%)	R_E (%)	$J_p \times 10^4$ (g·cm ⁻² ·s ⁻¹)	$J_E \times 10^6$ (g·cm ⁻² ·s ⁻¹)	$J_{Pr} \times 10^9$ (g·cm ⁻² ·s ⁻¹)	$J_{iB} \times 10^9$ (g·cm ⁻² ·s ⁻¹)	$J_{AA} \times 10^9$ (g·cm ⁻² ·s ⁻¹)	$J_{EA} \times 10^9$ (g·cm ⁻² ·s ⁻¹)	$J_{iAA} \times 10^9$ (g·cm ⁻² ·s ⁻¹)
7	20	5	7.0	5.28	5.09	3.60	1.26	5.11	1.87	0.98	6.76	1.87	0.10
8	30	5	7.0	5.27	4.87	7.59	2.11	8.17	2.88	1.41	9.88	3.25	0.19
9.1	40	5	7.0	5.28	4.72	10.61	2.99	11.23	4.00	1.96	13.79	4.51	0.26
9.2	40	5	7.0	5.27	4.75	9.87	3.10	11.70	4.15	2.05	14.45	4.89	0.30
9.3	40	5	7.0	5.26	4.74	9.89	2.95	11.12	3.87	1.87	13.21	4.64	0.28
10	40	10	7.0	5.26	4.81	8.56	3.38	12.93	4.79	2.38	16.82	5.39	0.33
11	40	15	7.0	5.28	4.88	7.58	3.77	14.66	5.50	2.86	20.18	6.14	0.40
12	40	18	7.0	5.26	4.89	7.03	4.30	16.77	6.36	3.43	24.03	6.92	0.45
13	40	20	7.0	5.25	4.92	6.29	4.85	19.02	7.41	4.07	28.45	7.84	0.48
14	40	5	4.5	5.26	4.74	9.89	2.88	10.86	3.94	1.89	13.31	4.55	0.28
15	40	5	2.0	5.27	4.79	9.11	2.81	10.70	4.04	1.92	13.57	4.55	0.28

P_f – feed pressure, T – temperature, Q_f – feed flowrate, $C_{0,E}$ – initial feed concentration of ethanol, $C_{p,E}$ – 120 min permeate concentration of alcohol, R_E – ethanol rejection,

J – flux, p – permeate, E – ethanol, iB – propanol, Pr – propanol, AA – amyl alcohols, EA – ethyl acetate, iAA – isoamyl acetate

Influence of the feed pressure

Table 3.3 and Figure 3.4 show that the permeate flux increases linearly with the pressure difference. These results are in agreement with the solution-diffusion transport theory – Eq. (3.1). According to this equation, it is possible to determine the solvent permeance factor (k_A) and the osmotic pressure difference ($\Delta\pi$) across the membrane. Permeate flux should be zero when the osmotic pressure difference is equal to the pressure difference through the membrane, so, from the linear regression it was obtained the osmotic pressure difference, $\Delta\pi=5.70$ bar at 5 °C. From the plot slope it was obtained the solvent permeance factor, $k_A=8.75\times10^{-6}$ g·cm⁻²·s⁻¹·bar⁻¹, at 5 °C.

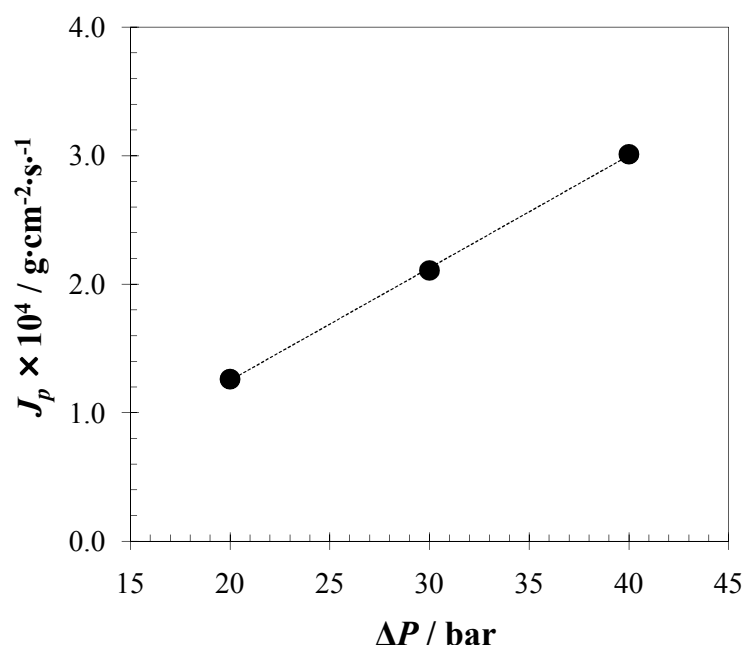


Figure 3.4. Permeate flux as a function of the pressure difference at 5 °C and 7 L·min⁻¹ feed flowrate (line – linear fitting).

Table 3.3 shows that ethanol exhibits the highest flux through the membrane, followed by amyl alcohols, ethyl acetate, propanol, isobutanol and isoamyl acetate. These fluxes order is in agreement with the order of the aroma compounds concentration in the feed beer. Regarding the dependence of the beer aroma compounds fluxes with pressure difference, it is possible to observe a linear increase of all fluxes with the pressure difference, although this increase is more noticeable for esters than for alcohols. For isoamyl acetate and ethyl acetate it was observed a flux increase of 185 % and 150 %, respectively.

respectively, from 20 bar to 40 bar (runs 7 and 9), while for alcohols the increments were 122 %, 115 %, 104 % and 99 % for ethanol, propanol, amyl alcohols and isobutanol, respectively (runs 7 and 9).

Figure 3.5 shows the influence of the pressure difference on the rejection of ethanol and other aroma compounds. For ethanol and higher alcohols, as the pressure difference increases the aroma rejection also increases, as well as their permeation fluxes (Table 3.3). However, the solvent (water) permeation increase (139 % from 20 to 40 bar – Figure 3.4) is higher than the alcohols one (with the exception of propanol), which causes a decrease in the permeate aroma concentration. As a result of the reduction of concentration, the C_p/C_b ratio decreases and the aroma rejection increases, according with Eq. (3.4). For esters the opposite behaviour was verified. Similar results concerning the influence of the feed pressure on the permeate flux and rejection coefficients were observed by other authors [8,12].

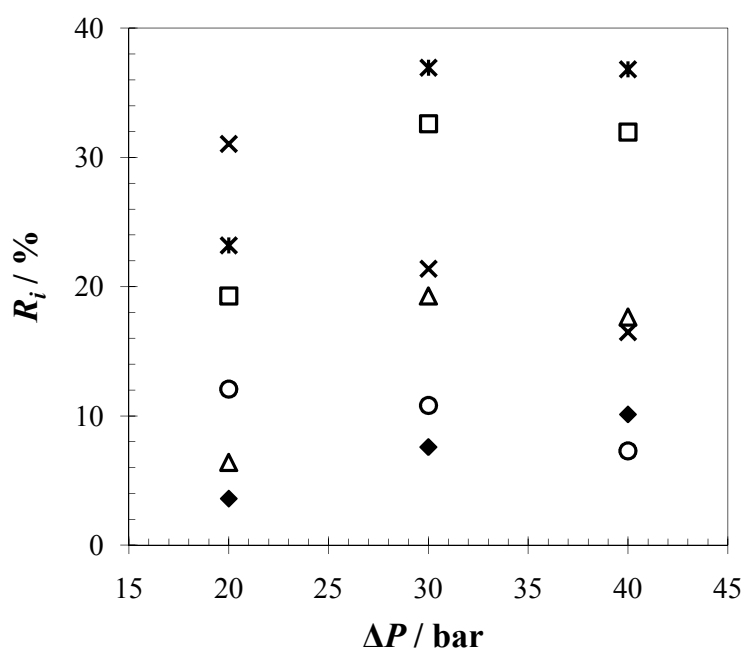


Figure 3.5. Ethanol and other aroma compounds rejection as a function of the pressure difference at 5 °C and 7 L·min⁻¹ feed flowrate (♦ ethanol, Δ propanol, × isobutanol, □ amyl alcohols, ○ ethyl acetate and × isoamyl acetate).

Since pressure affects the aroma compounds rejection in different ways, the optimal value should be determined in order to minimize the beer aroma losses and in order to improve the aroma profile of the dealcoholized beer. From Figure 3.5, the relative increase

of alcohols rejection, which is reached by increasing the pressure difference from 20 to 40 bar, is much higher than the relative decrease of esters rejection. Therefore, in the subsequent runs we will operate at 40 bar, the maximum pressure that the used lab setup allows to reach, once increasing the feed pressure results in higher aroma rejection, higher permeate and ethanol fluxes and besides that ethanol removal is high enough.

Influence of the temperature

Table 3.3 and Figure 3.6 show that the permeate flux increases with the temperature following an almost exponential behaviour – Arrhenius dependence. Table 3.3 shows that the fluxes of ethanol and aroma compounds also increase with the temperature. Again, the increase of the aroma fluxes depends on the compound's nature, with isobutanol and amyl alcohols being more affected by the temperature. For these compounds it was observed a flux increase of 108 % and 106 %, respectively, when changing the temperature from 5 °C to 20 °C (runs 9 and 13). For the other compounds the increments were 68 %, 85 %, 68 % and 72 %, for ethanol, propanol, ethyl acetate and isoamyl acetate, respectively. Figure 3.7 shows the effect of temperature on the rejection of the aroma compounds. For all compounds the rejection decreases with the temperature. As the temperature increases, the aroma permeation through the membrane increases. The solvent flux also increases with the temperature, but in a smaller extent (61 % from 5 °C to 20 °C – Figure 3.6). Consequently the ratio between aroma flux and permeate flux increases with the temperature as well as the C_p/C_b ratio, which causes a decrease in the rejection. Therefore, the lowest operating temperatures give the highest rejections (especially for esters), and despite the permeate flux decrease, in the subsequent runs we will operate at 5 °C.

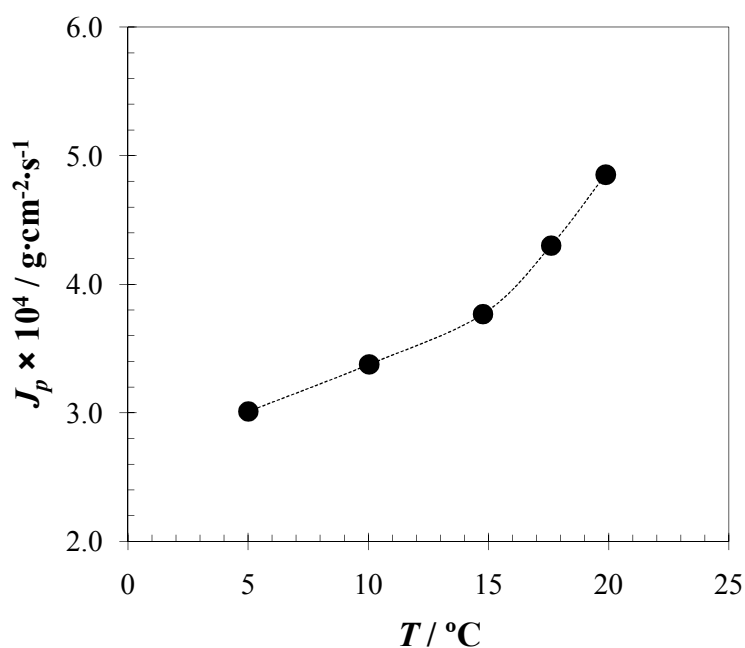


Figure 3.6. Permeate flux as a function of the temperature, at 40 bar and 7 L·min⁻¹ feed flowrate (lines are only for readability).

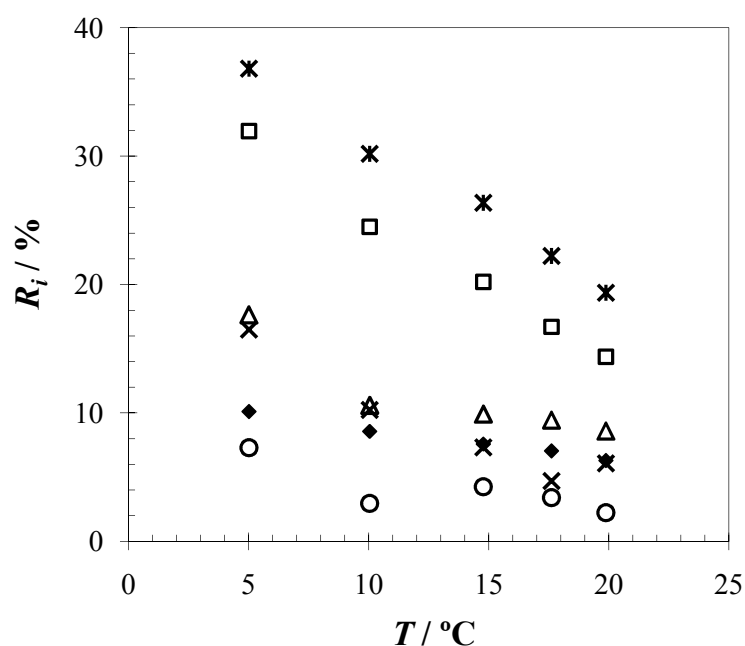


Figure 3.7. Ethanol and other aroma compounds rejection as a function of the temperature, at 40 bar and 7 L·min⁻¹ feed flowrate (♦ ethanol, Δ propanol, × isobutanol, □ amyl alcohols, ○ ethyl acetate, ✕ isoamyl acetate).

Influence of the feed flowrate

Some experiments were carried out at different feed flowrates in order to evaluate the concentration polarization effect. The feed flowrate was varied from 2 to 7 L·min⁻¹, the maximum flowrate allowed by the lab set-up used. From Table 3.3 and Figure 3.8 it is possible to conclude that the permeate flux increases with the feed flowrate. Table 3.3 shows that ethanol flux is the most affected by the concentration polarization. The increase observed in permeate and ethanol fluxes, by increasing the feed flowrate from 2 to 7 L·min⁻¹, were 7.2 % and 6.1 %, respectively, while for the other aroma compounds the increase was less than 3 % (runs 15 and 9).

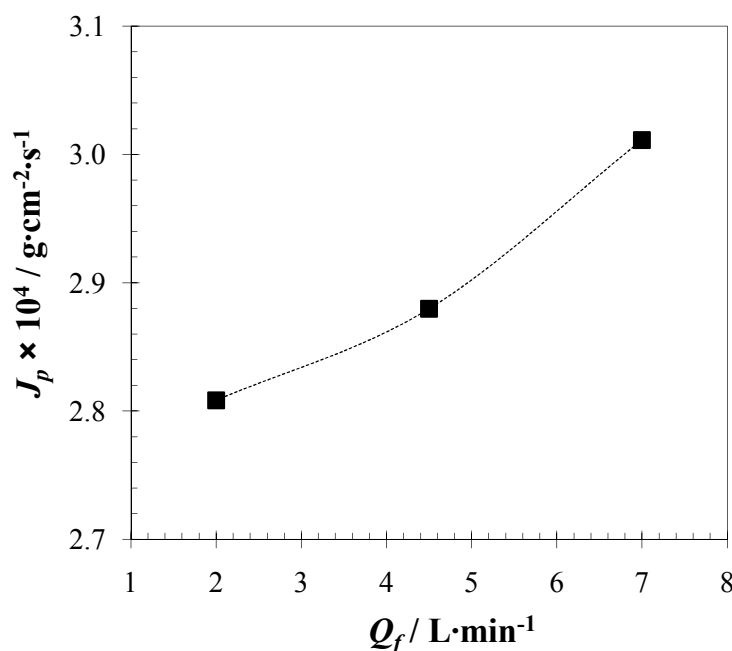


Figure 3.8. Permeate flux as a function of the feed flowrate, at 5 °C and 40 bar (lines are only for readability).

Figure 3.9 shows the effect of the feed flowrate on the permeate concentration of ethanol and other aroma compounds (a) and on their rejection (b). From Figure 3.9a one can see that the concentrations of the beer aroma compounds are approximately constant within the range of feed flowrates used. On the other hand the rejection of the aroma compounds increases, although only very slightly, with the feed flowrate (Figure 3.9b). The increment of the rejection for all the aroma compounds was in the range of 1 – 5 % (percentage points). This is mainly due to the permeate flux increase with the feed flowrate (Figure 3.8). As the feed flowrate increases, the concentration polarization decreases by

increasing the turbulence in the feed side. Other authors reported similar results for the influence of feed the flowrate on the permeate flux and rejection coefficients [12]. Consequently, high feed flowrates should be used in order to avoid the concentration polarization which causes a decrease of the permeate flux and a decrease of the rejection of the aroma compounds.

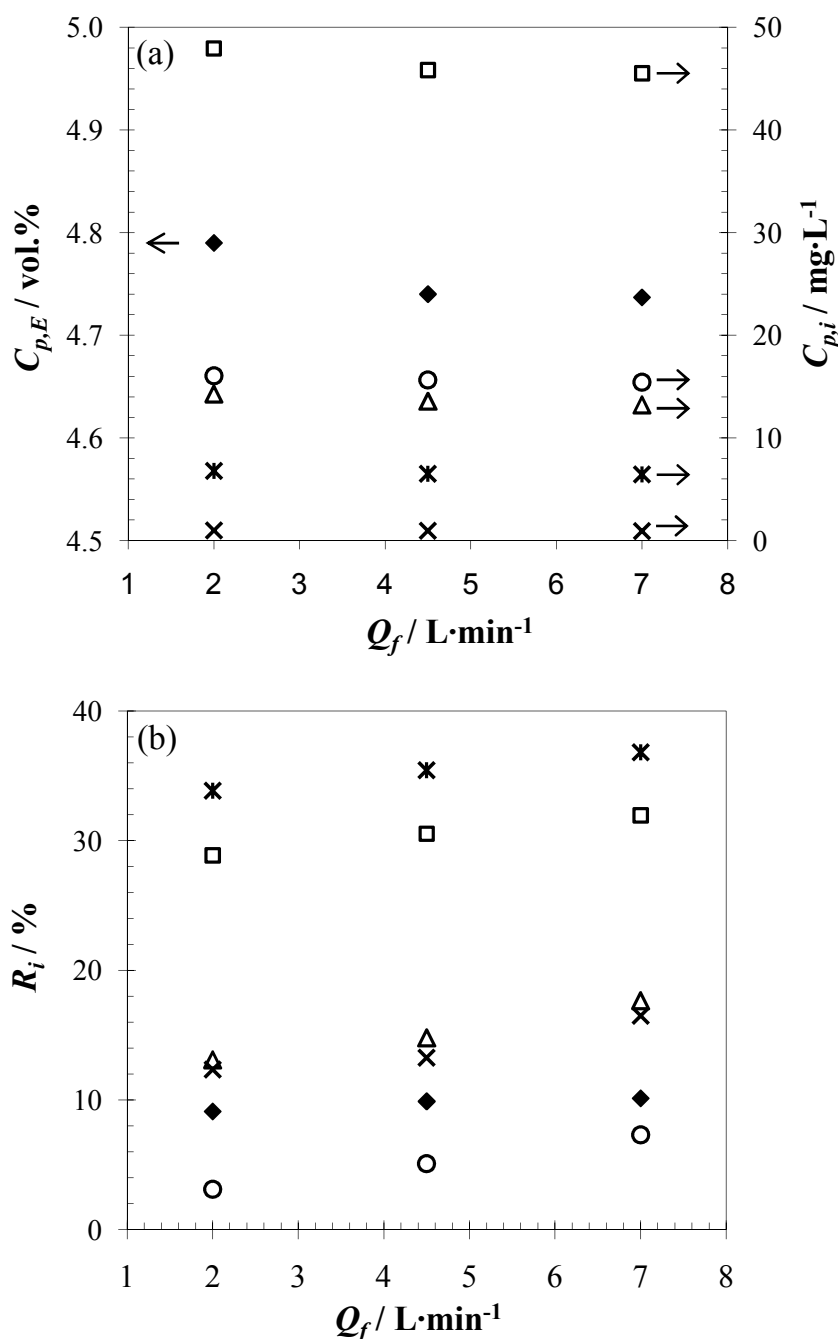


Figure 3.9. (a) Ethanol and other aroma compounds permeate concentration and (b) Ethanol and other aroma compounds rejection as a function of the feed flowrate, at 5 °C and 40 bar (♦ ethanol, Δ propanol, × isobutanol, □ amyl alcohols, ○ ethyl acetate, × isoamyl acetate).

3.5. Conclusions

In this chapter the reverse osmosis process was used in diafiltration mode for removing ethanol from an alcoholic beer. When operated at low temperatures, this process proved to be effective for producing non-alcoholic beer (ethanol content less than 0.5 vol.%) with high aroma content.

Six RO membranes made of cellulose acetate and polyamide were tested. The acetate cellulose membrane, CA995PE, was the one providing simultaneously a higher permeate flux and a lower ethanol rejection.

The most critical operating conditions were analysed, in order to evaluate their influence on the permeate flux and aroma compounds rejection. Higher pressures result in higher aroma rejection (although esters rejection slightly decrease with feed pressure) and in a higher permeate flux, despite ethanol rejection also increases. Low temperatures result in higher rejection to the aroma compounds, however ethanol rejection increases as well. High feed flowrates reduce the concentration polarization effect.

3.6. List of symbols

A	effective membrane area (cm^2)
C	concentration ($\text{g}\cdot\text{cm}^{-3}$)
J	flux ($\text{g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$)
k_A	solvent permeance ($\text{g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot\text{bar}^{-1}$)
k_B	solute permeance ($\text{cm}\cdot\text{s}^{-1}$)
m	mass (g)
P	pressure (bar)
Q	flowrate ($\text{cm}^3\cdot\text{s}^{-1}$)
R	rejection (–)
T	temperature ($^{\circ}\text{C}$)
t	time (s)

Greek letters

Δ	absolute difference (–)
π	osmotic pressure (bar)

Subscripts

A	solvent
AA	amyl alcohols
B	solute
b	feed bulk
E	ethanol
EA	ethyl acetate
f	feed
iAA	isoamyl acetate
iB	isobutanol
p	permeate
Pr	propanol
r	retentate
s	solute
W	water
0	initial conditions

3.7. References

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Chapter IV

4. Study and optimization of aroma recovery from beer by pervaporation¹

Abstract

This chapter studies the aroma extraction from beer by pervaporation, using a polyoctylmethylsiloxane/polyetherimide (POMS/PEI) composite asymmetric membrane. A response surface methodology (RSM) was used to describe the influence of the operating conditions (factors) on process performance. The factors considered for the design of experiments were the feed temperature, the feed velocity and the permeate pressure. The responses considered were the permeate flux, the selectivity towards aroma compounds over ethanol, the ethanol concentration and the ratio between higher alcohols and esters concentrations on the permeate.

It was concluded that the membrane flux increases with the temperature and cross feed velocity while it decreases with permeate pressure. The aroma selectivities are affected by the operating conditions according to their nature. RSM generated interpolating polynomial models that describe the relationship between the operating conditions and process responses. A good agreement between experimental and predicted values was observed. The optimal operating conditions were achieved using an objective function that weights the selected responses desirability. The optimal operating conditions were 12.4 °C for feed temperature, 0.45 m·s⁻¹ for feed velocity and 1.0 mbar for permeate pressure. For these conditions the permeate flux was predicted to be 7.26 kg·m⁻²·s⁻¹; the higher alcohols selectivity ranged from 1.31 to 3.39; the esters selectivity ranged from 14.46 to 17.10 and the higher alcohols/esters ratio was predicted to be 1.07. Experimental results for the runs performed at the optimal operating conditions mostly agreed with the predicted values.

¹ Adapted from: M. Catarino, A. Ferreira, A. Mendes, Study and optimization of aroma recovery from beer by pervaporation, Journal of Membrane Science 341 (2009) 51–59.

4.1. Introduction

Beer aroma profile is made by many volatile organic compounds at very low concentration (ppm level), which are responsible for its flavour [1–6]. Compounds from several chemical groups, such as alcohols, esters, aldehydes, lactones, carboxylic acids and phenols, can be found on beer composition, and they give to the beer a specific flavour [4,5]. Esters are responsible for sweet and fruity flavours of the beer, while higher alcohols, which are the major group of aroma compounds in this beverage, confer an alcoholic, fruity and immature flavour to the beer. The most important aldehyde in beer is the acetaldehyde and it is associated to the beverage freshness [7,8]. The relationship between total higher alcohols and total esters concentrations is an important indicator for evaluating the beer flavour, once it indicates if the beer has a more alcoholic or fruity character.

During beverage processing, such as dealcoholization, some aroma compounds are lost [1,4,9]. As a result, the sensorial quality is negatively affected, though low alcohol drinks are successful if their aroma profile is as close as possible to the original brew. In the beverage industry, it is usual to add aroma compounds for improving the aroma profile of dealcoholized beers. The aroma compounds can be commercial or originated from the processed beer. This last strategy is preferable because aroma compounds extracted from the original beverage have a higher commercial value [10,11]. This chapter deals about a newly developed process that considers the extraction of aroma species from the original beer, before dealcoholization, by pervaporation and their addition to the dealcoholized beer for minimizing the aroma depletion [2].

As referred in Chapter I (section 1.3), there is a range of processes that allows aroma recovery and among them, membrane processes such as pervaporation are the most attractive. Besides the high selectivity of membranes, the pervaporation can be carried out at low temperatures, which is relevant for treating thermo-sensitive beer compounds [3–6]. On the other hand, it requires low energy consumption and no chemical additives; it accomplishes a physical separation, which is preferable compared to other kind of separations [5,6,10,12].

Various authors studied the process of aroma extraction by pervaporation as well as the effect of the most critical operating conditions. Karlsson et al. studied the temperature effect on the Muscat wine pervaporation, using polydimethylsiloxane membranes [13]. Börjesson et al. investigated the performance of different membranes for recovering apple

juice aroma compounds by pervaporation [8]. Lipnizki et al. combined experimental data and simulation results for analysing the influence of pervaporation parameters such as total permeate pressure, feed temperature, degree of aroma folding and membrane area, using polydimethylsiloxane (PDMS) and polyoctylmethylsiloxane (POMS) membranes, targeting designing pervaporation units for food industry [10]. Pereira et al. studied the recovery of tropical fruit juice by pervaporation, testing different membrane materials as well as the influence of process parameters, using both experimental and simulations results [3]. She and Hwang analysed the effect of pervaporation operating conditions (concentration and temperature) and the membrane properties (PDMS and POMS) on the separation of multicomponent mixtures representing real flavour systems [14]. On the other hand, they reported the recovery of key flavour compounds (alcohols, esters and aldehydes) from real solutions (apple essences, orange aroma and black tea distillate), using different PDMS and POMS membranes [15]. Takács et al. considered the reduction of the alcohol content of wine by pervaporation and estimated the operating costs for pilot-scale production [16]. García et al. studied the effect of operating conditions, such as feed concentration, flowrate and feed temperature, on the extraction of bilberry aroma from a model solution of water/ethanol model, using PDMS hollow-fibre membranes [17]. Raisi et al. tested the pervaporation process to recover pomegranate aroma compounds from both real juices and aqueous solutions, using POMS and PDMS membranes [18]. These authors studied the influence of process parameters, such as membrane type and thickness, feed flowrate, feed temperature and permeate pressure, on the permeate flux and aroma enrichment.

In the present chapter, the beer aroma extraction by pervaporation using a POMS (polyoctylmethylsiloxane) membrane is studied. This beer aroma is intended to correct the aroma profile of the same beer after a dealcoholization process. A response surface methodology (RSM) with a central composite design (CCD) was used in order to evaluate the effect of independent variables on the process performance and to optimize the operating conditions. The RSM analysis was achieved with a commercially available software – *JMP 5.01* (SAS software). Second order models were fitted using the CCD results, which describe the effect of the operating conditions on the process responses. These models were used for interpolating the responses values for the experimental conditions and therefore compare the predicted values with the experimental ones. On the other hand, the models were used to evaluate the effect of the critical operating conditions on the responses and to optimize these conditions.

4.2. Materials and methods

4.2.1. Experimental procedure

Pervaporation experiments were carried out using a semi-batch laboratory set-up. Figure 4.1 shows a simplified sketch of this unit. The feed is pumped from the tank (1 – cf. Figure 4.1) to the membrane cell (3, radial geometry and 107.5 cm² effective membrane area) and the permeate recycled to the beer tank, through a plate heat exchanger (8). Before the inlet of the radial cell, a fraction of feed beer was also recycled to the beer tank, through the heat exchanger (8). The permeate side of the membrane is maintained at low pressure by means of a vacuum pump (6, Edwards V5); and the permeate condensed before the vacuum pump in a cold trap (4), immersed in liquid nitrogen at -196 °C (5). After the selected permeation elapsing time, the permeate was defrosted by placing the cold trap in cold water for melting the trapped aroma compounds, minimizing their evaporation. The amount of permeate was then weighted, analysed and stored in closed flasks in a freezer at 5 °C.

The detailed description of the experimental set-up and laboratory procedure is presented in Chapter II (section 2.2.3).

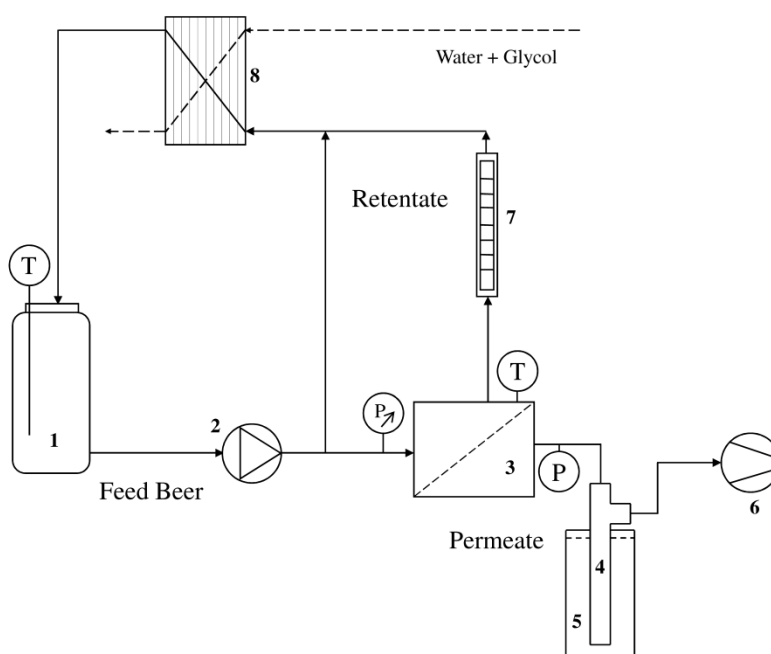
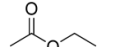
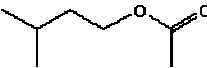


Figure 4.1. Pervaporation experimental set-up (1, feed tank; 2, centrifuge pump; 3, membrane cell; 4, permeate reservoir; 5, liquid nitrogen dewar; 6, vacuum pump; 7, rotameter; 8, plate heat exchanger).

4.2.2. Analytical methods

It was collected 100 L of a Pilsner type beer, with a regular alcohol content, from the same batch and stored at 5 °C in 0.33 L glass bottles. This sample was used in all pervaporation experiments hereafter reported. There were selected 7 aroma compounds for characterizing the beer profile, four alcohols (ethanol – *E*, propanol – *Pr*, isobutanol – *iB*, and isoamyl alcohol – *AA*), two esters (ethyl acetate – *EA* and isoamyl acetate – *iAA*) and one aldehyde (acetaldehyde – *Ac*). Table 4.1 shows the aroma properties and their average concentration in the feed beer. A gas chromatograph (Varian Star 3400) was used to determine the aroma contents on both feed and condensed samples. The method is described in Chapter II (section 2.2.1). A densitometer (DMA 4500, Anton Paar) and an ethanol analyser (Alcolyzer Plus, Anton Paar) were used to measure the feed and permeate densities, as well as the ethanol content. Both methods are recommended by European Brewery Convention [20].

Table 4.1. Beer aroma compounds properties.

Compound	Structure Formula	Molecular weight (g·mol ⁻¹)	Boiling point (°C)	Beer threshold ¹ (ppm)	Concentration in feed beer (ppm)	Typical aroma
Ethanol		46	78	14000	5.23 vol. %	Alcohol
Propanol		60	98	800	14.67	Alcohol
Isobutanol		74	108	200	12.67	Alcohol
Isoamyl alcohol		88	132	68	72.93	Alcohol, banana
Ethyl acetate		88	77	30	16.18	Fruity, solvent
Isoamyl acetate		130	149	1.2	1.38	Banana
Acetaldehyde		44	20	25	7.38	Green apples

¹ Source: Meilgaard [19]

4.2.3. Membranes

In the present work it was used a ca. 1 μm thick POMS (polyoctylmethylsiloxane) membrane supported in PEI (polyetherimide) (kindly offered by GKSS – Geesthacht, Germany).

4.2.4. Response surface methodology

Response surface methodology is a combination of mathematical and statistic tools that are effective for studying and modelling processes where responses are dependent on several operating variables [21]. The model parameters are estimated using the least square method and selecting adequate experiment designs for collecting data – response surface designs. In this work it was selected a central composite design (CCD), which is the most used method for fitting second order models [22]. The process responses selected are the permeate flux, aroma compounds selectivities over ethanol, permeate ethanol concentration and permeate higher alcohols/esters ratio. The factors considered are the feed temperature (T_f), feed velocity (v_f) and permeate pressure (P_t); preliminary runs showed that feed pressure has no significant effect on the responses considered (this studied is reported in Chapter II, section 2.3.1.1). Table 4.2 shows the design factors as well as their levels. The feed velocity interval was defined according to physical limitations of the pervaporation lab set-up. At that velocity range, laminar flow regime should be expected. The temperature range corresponds to the ideal conditions for preserving the organoleptic quality of the product. The dimensionless axial α values were chosen to be unitary ($\alpha=1$) to keep the factors inside the selected ranges (it avoids, e.g., the selection of negative feed temperatures). This approach favours the precision of empirical models when the central region is of interest, which is the case.

Table 4.2. CCD factors and respective levels.

Factor	Symbol	Level				
		$-\alpha$	-1	0	+1	$+\alpha$
T_f ($^{\circ}\text{C}$)	x_1	5.0	5.0	10.0	15.0	15.0
v_f ($\text{m}\cdot\text{s}^{-1}$)	x_2	0.1	0.1	0.3	0.5	0.5
P_t (mbar)	x_3	1.0	1.0	10.5	20.0	20.0

As CCD is built up from a two level factorial design, plus axial and central points [22], in the present case of three factors the total number of runs is 2^3 , plus 2×3 axial points and 3 central points (in order to assess the response precision), which corresponds to 17 runs. Table 4.3 shows the plan of runs that was generated by the RSM software used (*JMP 5.01*). This table includes both dimensionless (coded) and real (actual) values of the operating conditions. For generating design matrices, dimensionless (coded) factors (X_i), ranging from -1 to +1, are used [23]. These factors are computed from their actual values (x), range null value (middle) and the semi variation interval according to:

$$X_1 = \frac{T_f - 10}{5}; X_2 = \frac{v_f - 0.3}{0.2}; X_3 = \frac{P_t - 10.5}{9.5} \quad (4.1)$$

Table 4.3. Actual and coded values for the CCD run conditions.

Run #	Coded values			Actual values		
	X_1	X_2	X_3	x_1 (°C)	x_2 (m·s ⁻¹)	x_3 (mbar)
1	-1	+1	-1	5.0	0.5	1.0
2	0	0	$-\alpha$	10.0	0.3	1.0
3	+1	+1	+1	15.0	0.5	20.0
4	-1	-1	+1	5.0	0.1	20.0
5	0	$+\alpha$	0	10.0	0.5	10.5
6	0	0	0	10.0	0.3	10.5
7	0	$-\alpha$	0	10.0	0.1	10.5
8	0	0	0	10.0	0.3	10.5
9	0	0	$+\alpha$	10.0	0.3	20.0
10	0	0	0	10.0	0.3	10.5
11	$-\alpha$	0	0	5.0	0.3	10.5
12	+1	+1	-1	15.0	0.5	1.0
13	$+\alpha$	0	0	15.0	0.3	10.5
14	-1	-1	-1	5.0	0.1	1.0
15	+1	-1	+1	15.0	0.1	20.0
16	+1	-1	-1	15.0	0.1	1.0
17	-1	+1	+1	5.0	0.5	20.0

4.2.5. Process performance

As it was mentioned earlier the process performance was evaluated by the following responses: permeate flux, aroma compounds selectivities over ethanol, permeate ethanol concentration and permeate higher alcohols/esters ratio.

The steady-state permeate flux (J_p) is obtained from:

$$J_p = \frac{m_p^*}{A \cdot t} \quad (4.2)$$

where m_p^* is the condensed permeate mass, A is the effective membrane area and t is the permeation time. The membrane permselectivity towards a component i (e.g., aroma compound) compared to a component j (e.g., ethanol) is given by:

$$\alpha_{i/j} = \frac{w_{p,i}^* / w_{p,j}^*}{w_{b,i} / w_{b,j}} \quad (4.3)$$

where w_p^* and w_b are the mass fractions on the condensed permeate and on the feed bulk, respectively. The ratio between higher alcohols and esters (A/E) concentrations (C) is given by:

$$A/E = \frac{C_{total\ higher\ alcohols}}{C_{total\ esters}} \quad (4.4)$$

4.3. Results and discussion

4.3.1. Pervaporation process modelling

Table 4.4 summarizes the results for the CCD runs in terms of permeate flux (J_p), aroma compounds/ethanol selectivities ($\alpha_{i/E}$), ethanol concentration in the permeate side ($C_{p,E}$) and concentration ratio between higher alcohols and esters (A/E) in the permeate. Second order polynomial equations were fitted for each process response using the above experimental results:

$$y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \quad (4.5)$$

where y is the process response; X_1 , X_2 and X_3 are the dimensionless process factors; b_0 is the interception coefficient; b_1 , b_2 and b_3 are the equation coefficients related to the factors effects; b_{12} , b_{13} and b_{23} correspond to the cross interaction between factors and b_{11} , b_{22} and b_{33} are the coefficients related to the quadratic effects (curvature).

Table 4.4. Observed values of process responses.

Run #	$J_p \times 10^5$ ($\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)		$\alpha_{P/E}$	$\alpha_{B/E}$	$\alpha_{A/E}$	$\alpha_{E/E}$	$\alpha_{iA/E}$	$\alpha_{Ac/E}$	$C_{p,E}$ (vol.%)	A/E
	y_1	y_2	y_3	y_4	y_5	y_6	y_7	y_8	y_9	y_9
1	5.42	1.40	2.90	3.39	19.75	24.23	2.93	22.00	0.85	
2	6.81	1.43	2.97	3.52	15.35	17.58	2.91	26.50	1.13	
3	4.44	1.27	2.34	2.48	16.13	22.36	3.73	28.00	0.76	
4	1.66	1.20	2.11	2.01	20.15	27.90	4.11	25.50	0.51	
5	4.13	1.26	2.47	2.62	19.45	26.40	4.00	27.00	0.68	
6	3.84	1.29	2.51	2.64	17.74	22.86	4.06	28.00	0.74	
7	3.55	1.30	2.35	2.53	14.68	18.01	3.63	27.50	0.86	
8	3.71	1.34	2.52	2.72	19.09	25.28	4.39	28.00	0.73	
9	2.81	1.03	2.27	2.31	21.31	28.75	5.33	29.50	0.59	
10	3.47	1.23	2.41	2.49	17.84	23.42	3.89	28.00	0.70	
11	2.36	1.23	2.30	2.28	22.09	30.05	3.85	26.00	0.52	
12	8.56	1.44	2.97	3.55	15.23	18.35	3.52	28.50	1.15	
13	5.41	1.30	2.66	2.91	16.91	20.34	3.99	27.50	0.91	
14	3.80	1.37	2.71	3.15	15.27	16.82	3.08	27.00	1.05	
15	3.71	1.05	2.08	2.22	13.14	15.59	3.54	29.50	0.90	
16	8.25	1.45	2.95	3.60	11.51	12.02	3.09	29.50	1.63	
17	1.53	1.04	2.25	2.19	24.76	35.78	5.37	28.00	0.46	

It was performed an analysis of variance (ANOVA) of the model [21] (see Appendix 4.A; Tables 4.A1 – 4.A2). It was observed that p -values ($Prob > F$) of t -Student test for the modelled responses are lower than 0.05, except for ethanol concentration ($C_{p,E}$) which is 0.10; in this case the analytical method employed for quantifying ethanol had not enough resolution, within the space of factors, resulting in a smaller confidence level of the fitted model. p -Values smaller than 0.05 are a strong indication of the model's significance. On the other hand, determination coefficients (R^2) vary between 0.778 and 0.995, indicating that the models can explain most of the experimental variance (cf. Table 4.A1). It was observed that the models have no lack of fit (LOF) (cf. Table 4.A2).

The influence of the models parameters was assessed from the corresponding p -values. The smaller is the p -value the more significant is the influence of the respective parameter. p -Values smaller than 0.05 indicate that parameters have a significant effect on the response with a confidence level of more than 95 %; if the p -values are between 0.05 and 0.15, the factor has a marginal effect on the response. Finally, if p -values are higher than 0.15, the corresponding parameters have no significant effect on the response [21]. These criteria were followed in order to select the higher contributing factors and only parameters with significant p -values were selected into the final models (see values signed with “*” in Table 4.A3). The final parameters showed to be close to the original ones and to have smaller p -values, meaning that the selection criteria were appropriated (cf. Table 4.A6). The analysis of variance of the final models is also presented in Appendix 4.A (Tables 4.A4 – 4.A6).

After removing the negligible parameters from the original fitting polynomial equations, one obtained:

$$J_p \times 10^5 = 3.781 + 1.560X_1 + 0.311X_2 - 1.869X_3 - 0.329X_1X_3 + 0.918X_3^2 \quad (4.6a)$$

$$\alpha_{pT/E} = 1.272 + 0.027X_1 + 0.004X_2 - 0.150X_3 + 0.043X_1X_2 \quad (4.6b)$$

$$\alpha_{iB/E} = 2.460 + 0.073X_1 + 0.073X_2 - 0.354X_3 + 0.095X_3^2 \quad (4.6c)$$

$$\alpha_{AA/E} = 2.599 + 0.174X_1 + 0.072X_2 - 0.600X_3 + 0.243X_3^2 \quad (4.6d)$$

$$\alpha_{EA/E} = 18.619 - 2.910X_1 + 2.057X_2 + 1.838X_3 - 0.920X_1X_3 - 1.612X_2^2 \quad (4.6e)$$

$$\alpha_{iAA/E} = 24.040 - 4.612X_1 + 3.678X_2 + 4.138X_3 - 1.881X_1X_3 - 2.294X_2^2 \quad (4.6f)$$

$$\alpha_{Ac/E} = 3.848 - 0.147X_1 + 0.655X_3 - 0.351X_1X_3 \quad (4.6g)$$

$$C_{p,E} = 27.412 + 1.450X_1 - 0.550X_2 + 0.700X_3 + 0.875X_2X_3 \quad (4.6h)$$

$$A/E = 0.719 + 0.196X_1 - 0.105X_2 - 0.259X_3 - 0.046X_1X_2 - 0.024X_1X_3 + 0.061X_2X_3 + 0.052X_2^2 + 0.142X_3^2 \quad (4.6i)$$

The fitting models can be used to interpolate the response values, which can be compared with the experimental ones. Figure 4.2 compares the experimental vs. the fitting data for all responses. The parity graphs show that the data are plotted very close to the diagonals (where predicted are equal to observed), resulting in low residual values, which translates a good agreement between the experimental and the predicted values. On the other hand, determination coefficients R^2 were very close to the unit, except for acetaldehyde (Figure 4.2c) and ethanol concentration (Figure 4.2d), where R^2 values were smaller than 0.70. This fact can be due to the low variation of results for the acetaldehyde selectivity and ethanol concentration within the range of design operating conditions (see Table 4.4).

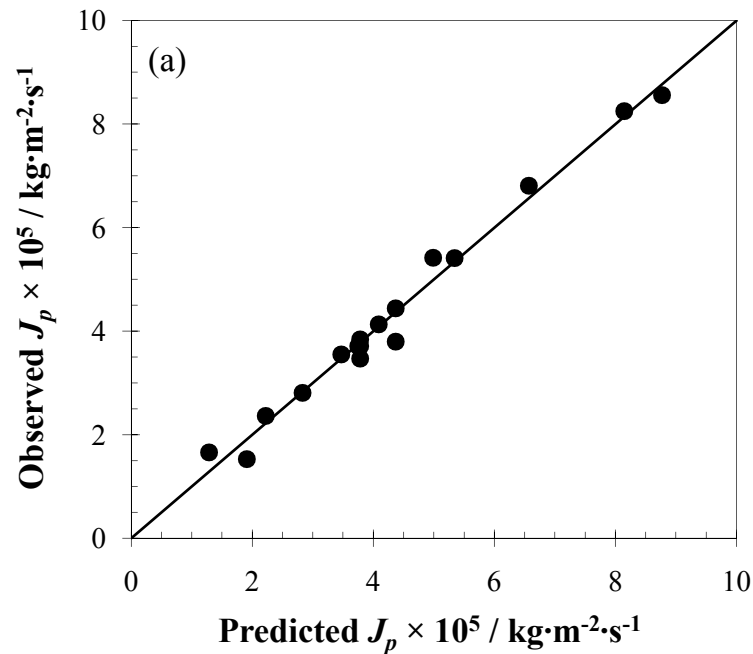


Figure 4.2. (a) Comparison between predicted values and experimental results of permeate flux ($R^2=0.984$).

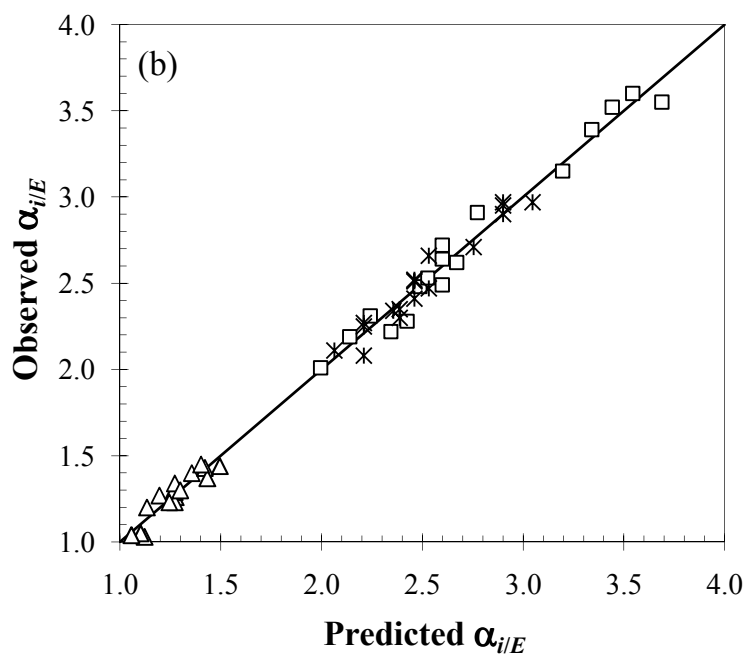


Figure 4.2.(b) Comparison between predicted values and experimental results of selectivity towards higher alcohols (Δ propanol ($R^2=0.858$), $*$ isobutanol ($R^2=0.945$) and $\square$ amyl alcohols ($R^2=0.971$)).

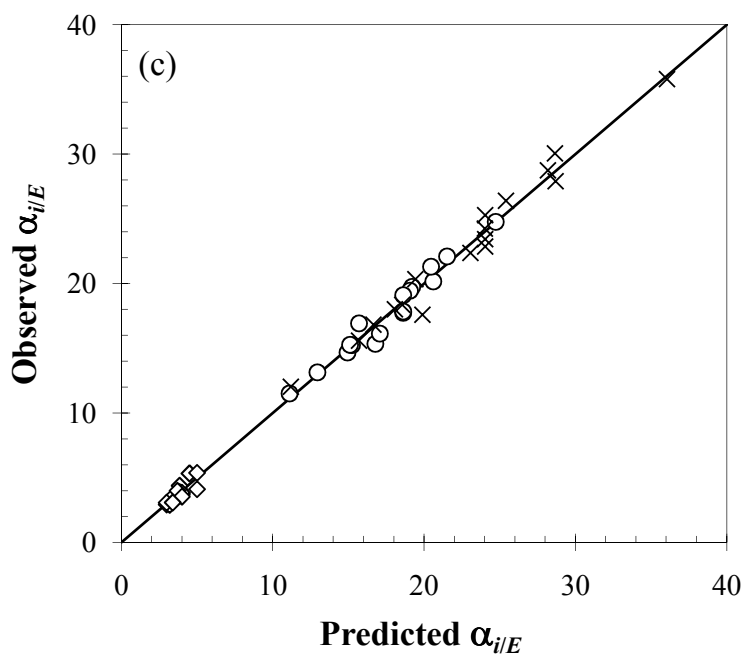


Figure 4.2.(c) Comparison between predicted values and experimental results of selectivity towards esters and acetaldehyde ($\circ$ ethyl acetate ($R^2=0.957$), $\times$ isoamyl acetate ($R^2=0.975$) and $\diamond$ acetaldehyde ($R^2=0.677$)).

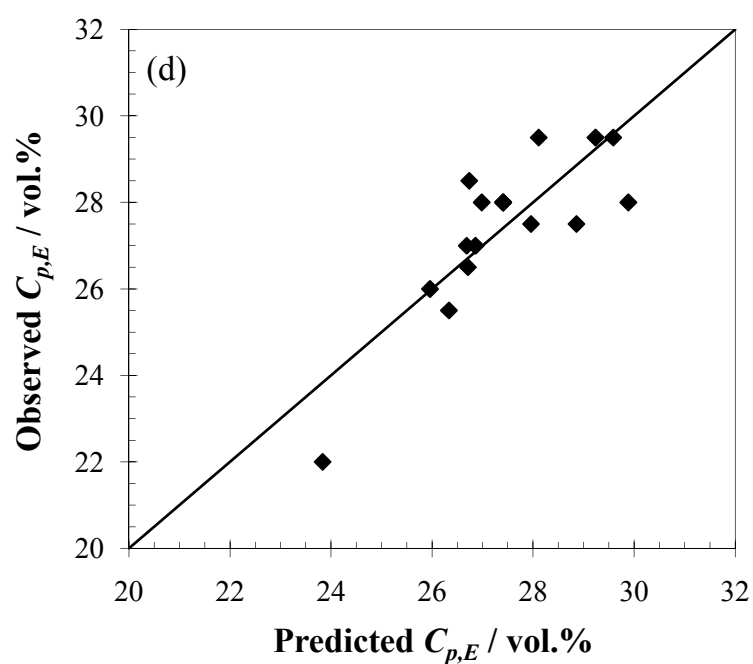


Figure 4.2. (d) Comparison between predicted values and experimental results of ethanol concentration ($R^2=0.673$).

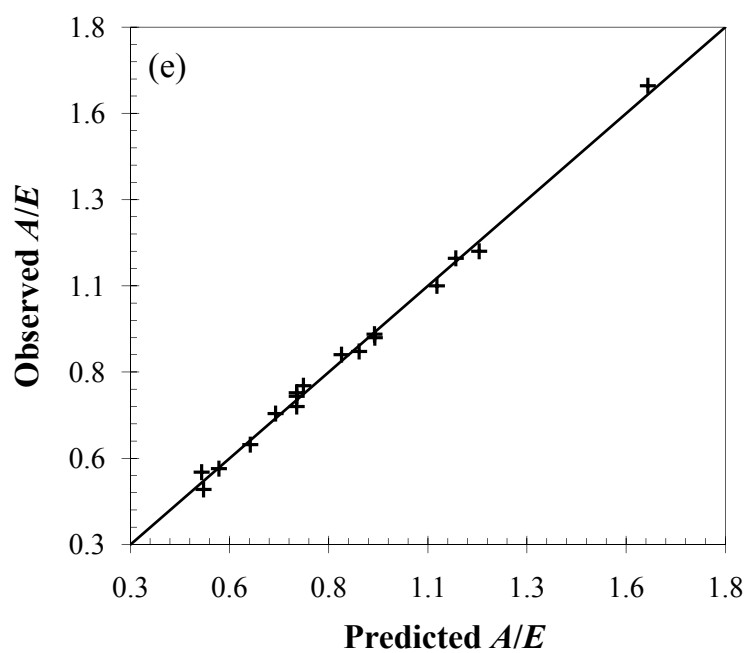


Figure 4.2. (e) Comparison between predicted values and experimental results of higher alcohols/esters ratio ($R^2=0.995$).

4.3.2. Influence of the operating conditions

The fitting models, represented by Eqs. (4.6a) to (4.6i), can also be used to interpolate the effect of the different operating parameters on the flux, aroma compounds selectivities, ethanol concentration and higher alcohols/esters ratio. Figures 4.3 to 4.6 show the permeate flux, the ethanol concentration on the permeate side, the selectivities of the selected key components, referred to the ethanol and the concentration ratio between higher alcohols and esters as a function of the operating variables.

According to Figure 4.3, one can conclude that most relevant factors on the permeate flux are the feed temperature (X_1) and the permeate pressure (X_3), being the feed velocity (X_2) less important. Permeate flux increases linearly with temperature due to the increase of the membrane permeability with temperature [24] and it increases very slightly with feed velocity due to the increase of turbulence over the membrane surface (Figure 4.3a and Eq. (4.6a)). On the other hand, permeate flux is negatively affected by the permeate pressure increase due to the decrease of the process driving force (Figure 4.3a and Eq. (4.6a)). Permeate pressure has a significant curvature effect (X_3^2) on the membrane flux (Figure 4.3b); the rate of flux decrease is higher for low permeate pressures. These results are consistent with other studies previously reported, using POMS/PEI membranes [10] and PDMS ones [13,25,26]. The factors with higher significance on the concentration of ethanol on the permeate side are the feed temperature (X_1), permeate pressure (X_3) and the cross interaction between feed velocity and permeate pressure (X_2X_3) (see Table 4.A3). When permeate pressure is maintained at the middle value, the ethanol concentration increases with temperature due to the increase of its permeability through the membrane. Ethanol concentration shows a slight decrease with feed velocity (X_2) due to concentration polarization. As the turbulence of feed flow on the membrane surface decreases, the amount of ethanol on the feed boundary layer increases due to its low permeability through the membrane, comparing to other compounds, and consequently the amount of ethanol on the permeate side also increases (Figure 4.3a). When feed temperature is maintained at the middle value, it is observed an interaction between feed velocity and permeate pressure (X_2X_3). At low feed velocity values, ethanol concentration decreases with the permeate pressure, whereas for high values of feed velocity (high turbulence) it increases with the permeate pressure; for low permeate pressure values, ethanol concentration decreases with feed velocity, while it increases with velocity at high permeate pressures (Figure 4.3b) (see Table 4.A3 and Eq. (4.6h)).

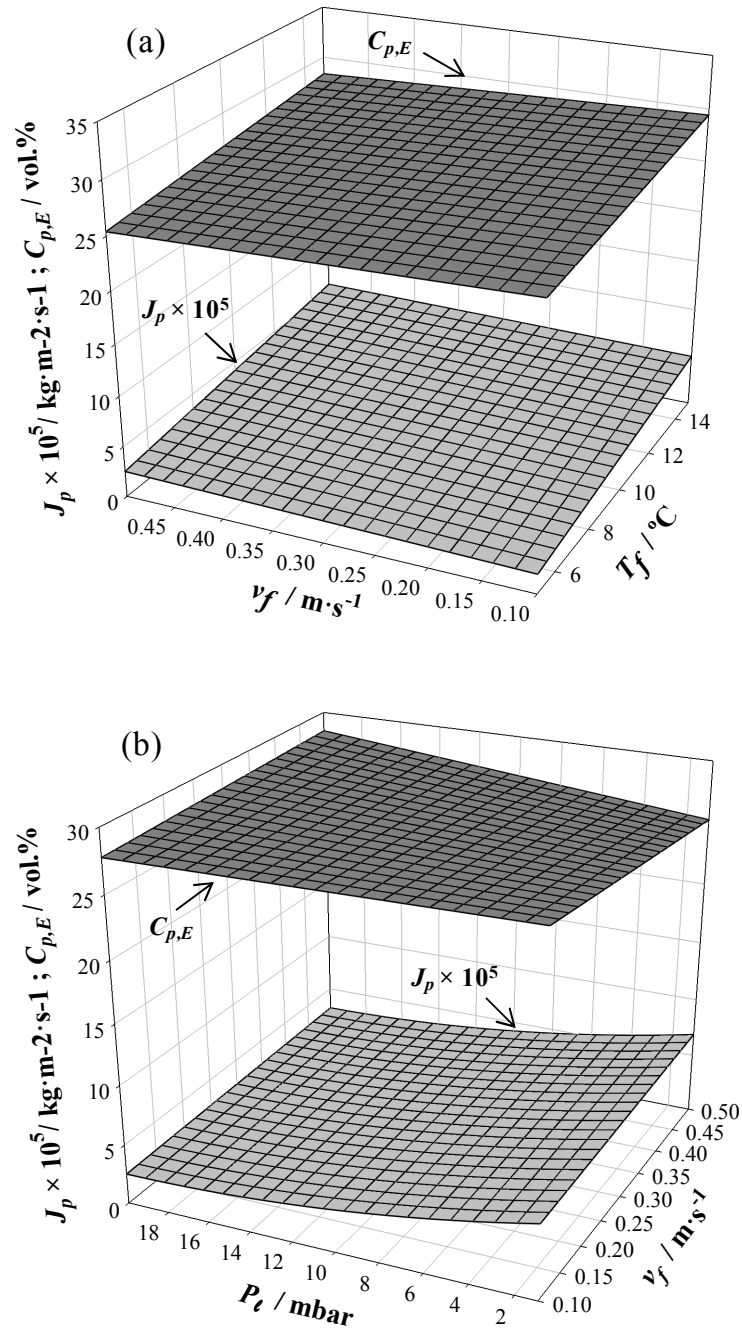


Figure 4.3. Permeate flux (J_p) and ethanol concentration ($C_{p,E}$) as a function of operating conditions: (a) feed temperature and feed velocity, keeping permeate pressure at middle value (10.5 mbar); (b) feed velocity and permeate pressure, keeping feed temperature at middle value (10 °C).

Operating conditions affect the mass transport of aroma compounds in different ways. As a result, their selectivities against ethanol assume different dependences according to each compound nature (see Figures 4.4 and 4.5). Figure 4.4 shows that amyl alcohol is the higher alcohol with the highest selectivity against ethanol, followed by isobutanol and propanol. For higher alcohols, which transport activation energy is higher than water [10], generally an increase in temperature (X_1) enhances their permeate concentration. On the other hand, ethanol concentration is less sensitive to temperature increase than the permeate (mostly water) flux (cf. Table 4.4, runs 11 and 13). Consequently the selectivity towards higher alcohols over ethanol increases. Higher alcohols selectivity shows a very slight increase with the feed velocity (X_2), meaning that concentration polarization affect them in a minor extent due to the low permeability of these compounds (see Figure 4.4a). On the other hand, an increase in the permeate pressure (X_3) – decrease in the vacuum – leads to a decrease in higher alcohols permeate concentration, because of their low saturated vapour pressures (low volatilities) [10]. As a result, the selectivity against alcohol decreases with the permeate pressure increase (see Figure 4.4b). These results are consistent with other studies previously reported [10,13,25,27]. From the individual higher alcohols, propanol is the aroma that suffers smaller variation within the range of design factors. Figure 4.4b shows that propanol selectivity is linearly affected by permeate pressure; while isobutanol and amyl alcohols show a quadratic dependence with permeate pressure (X_3^2) (see Table 4.A3 and Eqs. (4.6b) – (4.6d)).

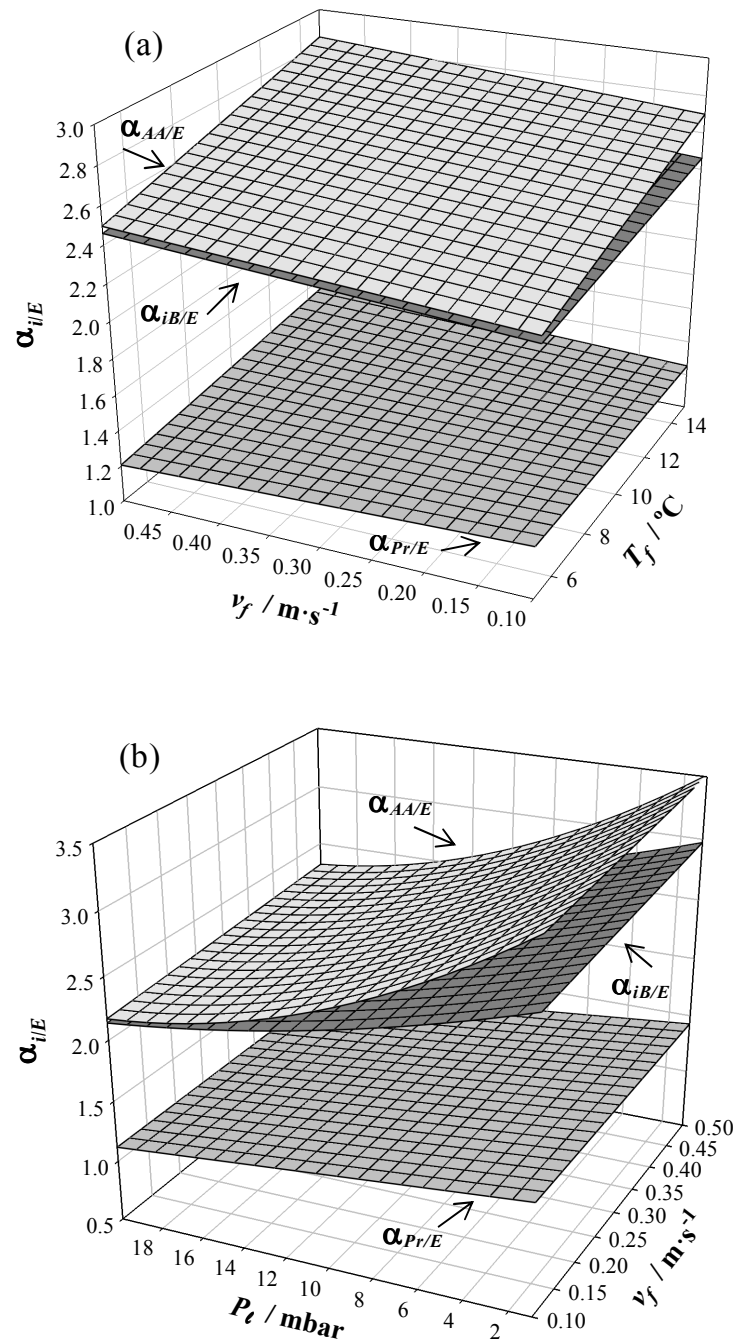


Figure 4.4. Higher alcohols selectivity as a function of operating conditions: propanol (Pr), isobutanol (iB) and amyl alcohols (AA): (a) feed temperature and feed velocity, keeping permeate pressure at middle value (10.5 mbar); (b) feed velocity and permeate pressure, keeping feed temperature at middle value (10 $^\circ\text{C}$).

Figure 4.5 shows the influence of operating variables on the esters and acetaldehyde selectivity. One can observe that isoamyl acetate shows the highest selectivity, followed by ethyl acetate and then by acetaldehyde. All three factors (X_1 , X_2 and X_3) have a high influence on the selectivity towards esters (see Table 4.A3 and Eqs. (4.6e) and (4.6f)). An increase in temperature (X_1) leads to a decrease in esters concentration on the permeate due to their transport activation energy being close to water (especially ethyl acetate) [10]. The increase of the ethanol concentration with temperature is less significant than the increase of the permeate (mostly water) flux (cf. Table 4.4, runs 11 and 13). Consequently, the selectivity towards esters compared to ethanol decreases linearly with the temperature. Feed velocity (X_2) has a strong influence on esters selectivity (Figure 4.5a), more than on higher alcohols, showing also a quadratic influence (X_2^2), which means that concentration polarization occurs and affects mostly these compounds due to their higher permeability through the membrane. Regarding the permeate pressure (X_3) effect, the concentration of esters increases with it. As a result, the esters selectivity increases with permeate pressure (Figure 4.5b). These results are in agreement with the results found by other authors [10,13,25]. Concerning the acetaldehyde behaviour, one can see that its selectivity remains constant with feed velocity (X_2) variation (Figure 4.5a). As the feed turbulence increases the trend of the acetaldehyde concentration at the permeate side is proportional to the ethanol concentration, resulting in a constant selectivity. This means that the acetaldehyde selectivity is not affected by concentration polarization. As it was observed for esters, acetaldehyde selectivity increases with permeate pressure (X_3) due to its high volatility (Figure 4.5b). On the other hand, a cross interaction between feed temperature and permeate pressure (X_1X_3) is observed. At low permeate pressure, the acetaldehyde selectivity increases with feed temperature; while at high values of permeate pressure it decreases with feed temperature (see Table 4.A3 and Eq. (4.6g)).

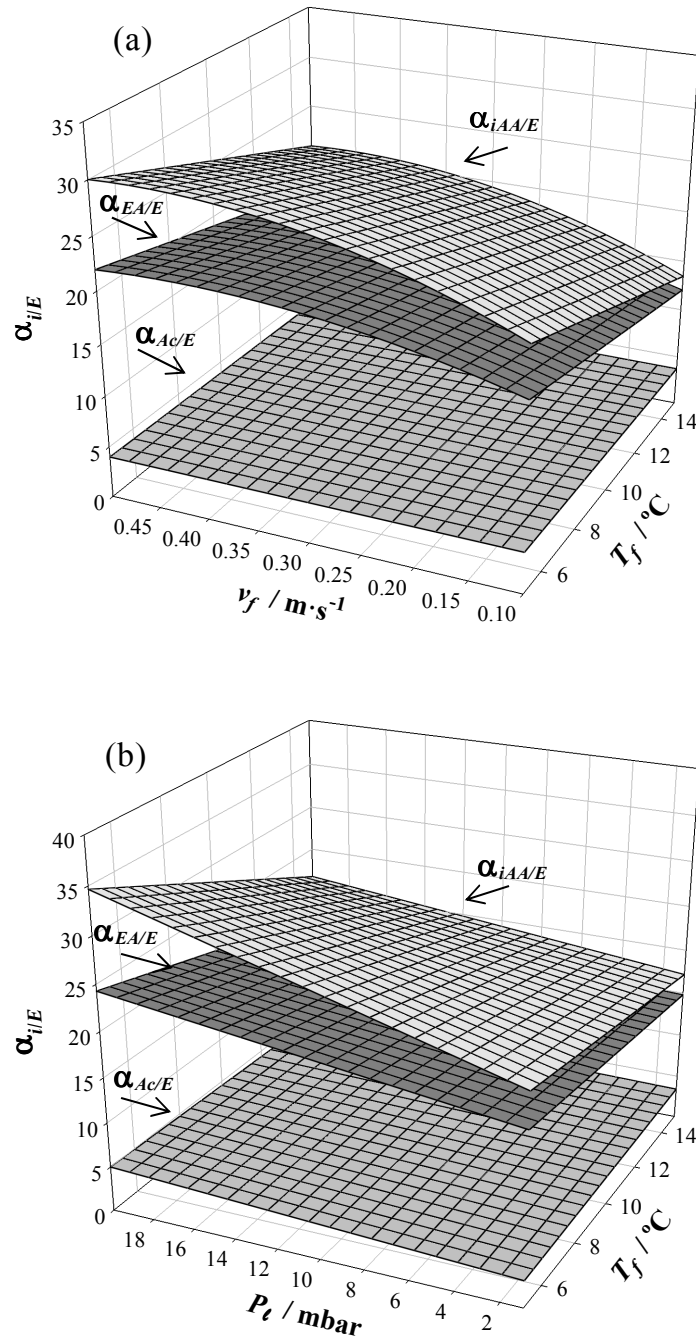


Figure 4.5. Selectivity towards esters and acetaldehyde as a function of operating conditions: ethyl acetate (*EA*), isoamyl acetate (*iAA*) and acetaldehyde (*Ac*): (a) feed temperature and feed velocity, keeping permeate pressure at middle value (10.5 mbar); (b) feed temperature and permeate pressure, keeping feed velocity at middle value ($0.3 \text{ m}\cdot\text{s}^{-1}$).

Observing all the aroma compounds (Figures 4.4 and 4.5), the esters exhibit the highest selectivity values (because of their higher sorption affinity), followed by the acetaldehyde and finally by the higher alcohols, which is in agreement with previous studies carried out by other authors [8,10,15].

Figure 4.6 presents the influence of operating variables on the concentration ratio between higher alcohols and esters (A/E) on the permeate side. The behaviour of the higher alcohols/esters ratio is dependent on the permeability of these classes of aroma compounds, which assumes different trends as a function of the operating conditions, as discussed above. From Figure 4.6, it is observed that A/E ratio increases with temperature (Figure 4.6a) and it decreases with feed velocity and permeate pressure (Figure 4.6b); it remains almost constant for high values of feed velocity and permeate pressure, keeping the other factors constant. According to ANOVA analysis (see Table 4.A3 and Eq. (4.6i)), all three factors (X_1 , X_2 and X_3) strongly affect the higher alcohols/esters response. Cross interactions between factors (X_1X_2 , X_1X_3 and X_2X_3) also have a significant influence and feed velocity and permeate pressure have a quadratic effect on the response (X_2^2 and X_3^2).

It is important to say that higher alcohols/esters ratio is a response which measures the equilibrium between aroma compounds and how close is the permeate profile to the original beer. The usual A/E value for Pilsner type beers is between 4 and 6 [28], which is the ideal ratio that the dealcoholized beer should have. However, due to the physical losses or chemical modifications that occur during the alcohol removal processes, the A/E ratio on the dealcoholized beer can be very different from the original one. The addition of the recovered aroma compounds is advantageous to overcome the aroma depletion of dealcoholized beers and to adjust the desired A/E ratio. Hence, by tuning operating conditions, with the same membrane, it is possible to optimize the aroma profile of the permeate solution in order to reach aroma concentrates with the A/E ratio according to the needs of the final product specifications.

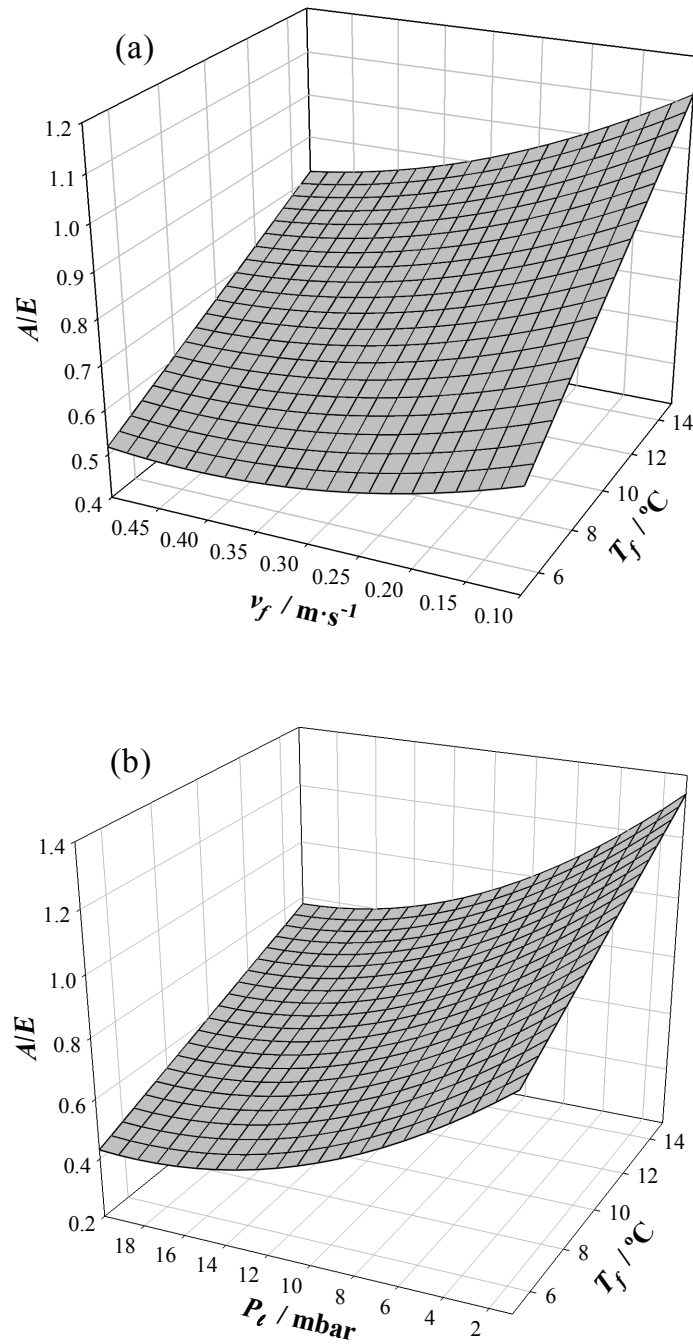


Figure 4.6. Higher alcohols and esters ratio (A/E) as a function of operating conditions: (a) feed temperature and feed velocity, keeping permeate pressure at middle value (10.5 mbar); (b) feed temperature and permeate pressure, keeping feed velocity at middle value ($0.3 \text{ m}\cdot\text{s}^{-1}$).

4.3.3. Optimization of the operating conditions

Since the operating variables influence the process responses in different ways, the optimization is a complex problem. Desirability function of *JMP* software was used to find the optimal conditions for multiple responses and to solve the trade-off between them [21,22]. The same importance (weight 1) was allocated to all responses and the optimization criteria were:

- maximize the permeate flux in order to increase the membrane productivity;
- maximize aroma compounds selectivities in order to increase their concentration over ethanol, on the permeate side;
- minimize ethanol concentration, once one goal of this study was obtaining a beer aroma for adding to a dealcoholized beer and ethanol legal content must be respected;
- maximize higher alcohols/esters ratio in order to improve the aroma quality towards the original beer profile.

The optimal operating conditions were found to be 12.4 °C for feed temperature (x_1), 0.45 m·s⁻¹ for feed velocity (x_2) and 1.0 mbar for permeate pressure (x_3), and a desirability of 0.54 was achieved, meaning that 54 % of the goals were satisfied. The models previously developed were used to predict the process responses for the optimal operating conditions. These values are given in Table 4.5 together with new experimental results, averaged from a run made in triplicate. It can be seen that the model agrees with the experimental data, except for amyl alcohols selectivity and higher alcohols/esters ratio, although they show acceptable values.

Table 4.5. Predicted optimal results, respective interval of variation and experimental results.

Response	Predicted values			Experimental values
	target	min	max	
$J_p \times 10^5$ (kg·m ⁻² ·s ⁻¹)	7.82	7.26	8.38	8.15
$\alpha_{Pr/E}$	1.44	1.31	1.56	1.53
$\alpha_{iB/E}$	3.01	2.87	3.14	3.11
$\alpha_{AA/E}$	3.59	3.39	3.78	3.89
$\alpha_{EA/E}$	15.97	14.46	17.48	15.50
$\alpha_{iAA/E}$	19.06	17.10	21.03	18.31
$\alpha_{Ac/E}$	3.40	2.67	4.14	3.53
$C_{p,E}$ (vol.%)	27.16	25.02	29.30	28.67
A/E	1.12	1.07	1.17	1.26

4.4. Conclusions

The extraction of beer aroma compounds by pervaporation was studied using RSM. A central composite design was used for evaluating the effect of main operating conditions, such as feed temperature, feed velocity and permeate pressure, on the process responses. The optimized process parameters (selected responses) were the permeate flux, beer aroma compounds selectivities against ethanol, concentration of ethanol on the permeate side and relationship between higher alcohols and esters concentrations on the permeate. Analysis of variance and surface plots showed that the factor with higher effect on the permeate flux is the feed temperature followed by the permeate pressure and the feed velocity. Permeate flux increases with temperature and feed velocity, whereas it decreases with permeate pressure. On the other hand, factors have different significance on the aroma compounds selectivities according to their nature. In general, higher alcohols selectivity is positively affected by temperature and, in a minor extent, by feed velocity, while permeate pressure affects negatively their selectivity. On the other hand, esters selectivity decreases with temperature and it increases with permeate pressure and velocity, being strongly affected by feed velocity, which corresponds to a strong concentration polarization effect. As a result, the higher alcohols/esters ratio increases with temperature and it decreases with feed velocity and permeate pressure. Once factors affect differently the process responses, an objective function was used for optimizing the trade-off between these responses. The model response of the pervaporation system for the calculated optimal conditions was compared with new experimental results showing a generally good agreement. These results show that pervaporation is an effective process for recovering aroma compounds from beer. Moreover, manipulating the operating conditions it is possible to obtain different A/E ratios and then to better correct the depleted dealcoholized beer targeting the A/E equilibrium.

4.5. List of symbols

A	effective membrane area (m^2)
b	polynomial model coefficient (–)
A/E	higher alcohols/esters ratio (–)
C	concentration ($\text{g}\cdot\text{cm}^3$ or vol.%)
J	flux ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
m	mass (kg)
P	pressure (bar)
R^2	determination coefficient (–)
T	temperature ($^{\circ}\text{C}$)
t	time (s)
v	velocity ($\text{m}\cdot\text{s}^{-1}$)
w	mass fraction (wt.%)
X	coded value of factor (–)
x	actual value of factor (–)
y	process response (–)

Greek letters

α	membrane selectivity (–)
α	axial value (–)

Subscripts and superscripts

AA	amyl alcohols
Ac	acetaldehyde
b	feed bulk
E	ethanol
EA	ethyl acetate
f	feed
i	generic component
iAA	isoamyl acetate
iB	isobutanol
j	generic component
ℓ	low (permeate side)
p	permeate
Pr	propanol
$*$	relative to condensed form

4.6. References

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APPENDIX 4.A

The ANOVA results for each process response are shown in Tables 4.A1 to 4.A6.

Table 4.A1. Analysis of variance of the modelled responses (all parameters considered).

Response	<i>F</i> Ratio	Prob > <i>F</i>	<i>R</i> ²
$J_p \times 10^5$ (kg·m ⁻² ·s ⁻¹)	63.3	<0.0001	0.988
$\alpha_{Pr/E}$	5.13	0.0212	0.868
$\alpha_{iB/E}$	22.5	0.0002	0.967
$\alpha_{AA/E}$	34.2	<.0001	0.978
$\alpha_{EA/E}$	24.5	0.0002	0.969
$\alpha_{iAA/E}$	45.7	<0.0001	0.983
$\alpha_{Ac/E}$	3.87	0.0442	0.832
$C_{p,E}$ (vol.%)	2.72	0.1001	0.778
<i>A/E</i>	165	<0.0001	0.995

Table 4.A2. Lack of fit (LOF) for the modelled responses (all parameters considered).

Response	<i>F</i> Ratio	Prob > <i>F</i>
$J_p \times 10^5$ (kg·m ⁻² ·s ⁻¹)	4.121	0.207
$\alpha_{Pr/E}$	2.100	0.353
$\alpha_{iB/E}$	2.144	0.348
$\alpha_{AA/E}$	1.012	0.565
$\alpha_{EA/E}$	1.624	0.423
$\alpha_{iAA/E}$	0.817	0.631
$\alpha_{Ac/E}$	3.807	0.221
$C_{p,E}$ (vol.%)	—	—
<i>A/E</i>	2.520	0.308

Note: *p*-values are higher than 0.1, meaning that the lack of fit is not significant; in the case of the lack of fit of the ethanol concentration, this value was not generated because the response values were the same for the three central points runs (runs 6, 8 and 10 from Table 4.4).

Table 4.A3. Analysis of variance for the models parameters of the responses (all parameters considered).

Response	Intercept	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	X_1^2	X_2^2	X_3^2
$J_p \times 10^5$ ($\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)	Estimate Prob > t	3.790 <0.0001*	1.560 <0.0001*	0.311 0.023*	-1.869 <0.0001*	-0.056 0.652	-0.329 0.028*	0.008 0.971	-0.037 0.862	0.933 0.003*
$\alpha_{Pr/E}$	Estimate Prob > t	1.270 <0.0001*	0.027 0.284*	0.004 0.868*	-0.150 0.0004*	0.043 0.146*	0.005 0.853	0.008 0.860	0.023 0.621	-0.027 0.570
$\alpha_{iB/E}$	Estimate Prob > t	2.483 <0.0001*	0.073 0.026*	0.073 0.026*	-0.345 <0.0001*	-0.006 0.836	-0.031 0.317	-0.004 0.932	-0.074 0.181	0.136 0.030*
$\alpha_{AA/E}$	Estimate Prob > t	2.623 <0.0001*	0.174 0.0022*	0.072 0.093*	-0.600 <0.0001*	-0.026 0.547	0.031 0.476	-0.033 0.662	-0.053 0.486	0.287 0.005*
$\alpha_{EA/E}$	Estimate Prob > t	18.551 <0.0001*	-2.910 <0.0001*	2.057 0.0002*	1.838 0.0004*	-0.298 0.383	-0.075 0.821	0.703 0.244	-1.732 0.017*	-0.467 0.426
$\alpha_{iAA/E}$	Estimate Prob > t	24.130 <0.0001*	-4.612 <0.0001*	3.678 <0.0001*	4.138 <0.0001*	-0.274 0.533	0.114 0.793	0.858 0.273	-2.132 0.021*	-1.172 0.148*
$\alpha_{Ac/E}$	Estimate Prob > t	4.104 <0.0001*	-0.147 0.327*	0.210 0.176	0.655 0.002*	-0.061 0.706	0.146 0.379	-0.176 0.533	-0.281 0.331	0.024 0.933
$C_{p,E}$ (vol.%)	Estimate Prob > t	27.718 <0.0001*	1.450 0.009*	-0.550 0.218*	0.700 0.129*	0.000 1.000	0.875 0.096*	-0.757 0.367	-0.257 0.753	0.493 0.550
A/E	Estimate Prob > t	0.720 <0.0001*	0.196 <0.0001*	-0.105 <0.0001*	-0.259 <0.0001*	-0.046 0.003*	0.061 0.0007*	-0.002 0.906	0.053 0.024*	0.143 0.0001*

Table 4.A4. Analysis of variance of the modelled responses (after parameters selection).

Response	<i>F</i> Ratio	Prob > <i>F</i>	<i>R</i> ²
$J_p \times 10^5$ (kg·m ⁻² ·s ⁻¹)	135.7	<.0001	0.984
$\alpha_{Pr/E}$	18.1	<.0001	0.858
$\alpha_{iB/E}$	51.8	<.0001	0.945
$\alpha_{AA/E}$	99.8	<.0001	0.971
$\alpha_{EA/E}$	49.3	<.0001	0.957
$\alpha_{iAA/E}$	84.6	<.0001	0.975
$\alpha_{Ac/E}$	9.08	0.0017	0.677
$C_{p,E}$ (vol.%)	6.17	0.0062	0.673
<i>A/E</i>	212	<.0001	0.995

Table 4.A5. Lack of fit (LOF) for the modelled responses (after parameters selection).

Response	<i>F</i> Ratio	Prob > <i>F</i>
$J_p \times 10^5$ (kg·m ⁻² ·s ⁻¹)	3.0788	0.2692
$\alpha_{Pr/E}$	1.1518	0.5509
$\alpha_{iB/E}$	1.887	0.3957
$\alpha_{AA/E}$	0.726	0.7038
$\alpha_{EA/E}$	1.3409	0.4985
$\alpha_{iAA/E}$	0.802	0.6673
$\alpha_{Ac/E}$	1.8394	0.2114
$C_{p,E}$ (vol.%)	—	—
<i>A/E</i>	2.1054	0.3566

Note: *p*-values are higher than 0.1, meaning that the lack of fit is not significant.

Table 4.A6. Analysis of variance for the models parameters of the responses (after parameters selection).

Response	Intercept										X_1^2	X_2^2	X_3^2
	Estimate	Prob > t	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	X_1^2	X_2^2	X_3^2		
$J_p \times 10^5$ ($\text{kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)	3.781	<.0001	1.560	0.311	-1.869	—	-0.329	—	—	—	—	—	0.918
													<.0001
$\alpha_{Pr/E}$	1.272	<.0001	0.027	0.004	-0.150	0.043	—	—	—	—	—	—	—
													—
$\alpha_{iB/E}$	2.460	<.0001	0.073	0.073	-0.345	—	—	—	—	—	—	—	0.095
													0.033
$\alpha_{AA/E}$	2.599	<.0001	0.174	0.072	-0.600	—	—	—	—	—	—	—	0.243
													0.0004
$\alpha_{EA/E}$	18.619	<.0001	-2.910	2.057	1.838	—	-0.920	—	—	-1.612	—	—	—
													—
$\alpha_{iAA/E}$	24.040	<.0001	-4.612	3.678	4.138	—	-1.881	—	—	-2.294	—	—	—
													—
$\alpha_{Ac/E}$	3.848	<.0001	-0.147	—	0.655	—	-0.351	—	—	—	—	—	—
													—
$C_{p,E}$ (vol.%)	27.412	<.0001	1.450	-0.550	0.700	—	—	0.875	—	—	—	—	—
													—
A/E	0.719	<.0001	0.196	-0.105	-0.259	-0.046	-0.024	0.061	—	0.052	0.142	—	—
													<.0001

Chapter V

5. Non-alcoholic beer – a new industrial process¹

Abstract

This chapter studies a new industrial process for producing non-alcoholic beer with a corrected natural flavour profile. The aroma compounds are obtained by pervaporation of the original beer. The operating conditions of this unit, using polyoctylmethysiloxane/polyetherimide (POMS/PEI) composite membranes, are investigated. High permeation temperature and low feed flowrate are the most effective for maximizing the permeation flux and the equilibrium of the flavour profile. The aroma depleted beer stream is then added to the feed stream of an industrial unit of spinning cone column distillation for dealcoholization. In this unit, the beverage contacts counter-currently with a water vapour stream that strips the ethanol and other volatile aroma compounds from beer. After dealcoholization, the beer is blended with the extracted aroma compounds and with a fraction of original beer to achieve a non-alcoholic beer (ethanol lower than 0.5 vol.%) with a good flavour profile. This new industrial process proved to originate a dealcoholized beer with a taste very close to the original one.

¹ *Adapted from:* M. Catarino and A. Mendes, Non-alcoholic beer – a new industrial process, *Submitted*

5.1. Introduction

The market of non-alcoholic brews has experienced a significant increase during the past years. However, most of the available non-alcoholic beverages present a poor flavour profile that is not well accepted by the consumers. Hence, it becomes important to adjust the flavour of non-alcoholic beverages to the typical alcoholic ones, to fill the lack in this market supply. Typical non-alcoholic brews, such as beer or wine, are produced interrupting the fermentation of sugars from the cereals or grapes juice to ethanol. This method leads to a lack of aroma compounds in the final product, as referred in Chapter I. Alternatively, non-alcoholic beverages can be produced by removing the ethanol from a completely fermented beverage using separation processes (cf. Figure 1.4). Most common separation processes for beverages dealcoholization are heat treatment or membrane-based processes [1–4]. Heat treatment processes comprise evaporation and distillation or vapour stripping, both under vacuum conditions [5,6], while membrane-based processes include reverse osmosis, nanofiltration, dialysis and pervaporation [7–14].

Spinning cone column (SCC) distillation is a worldwide popular method for removing ethanol from alcoholic beverages. SCC consists in a gas-liquid counter-current device where the stripping medium (e.g., water vapour) extracts the ethanol from the beverage [15]. This technology has been applied for dealcoholizing wine with aroma compounds recovery, for adjusting ethanol content of high alcohol wines and for removing ethanol from beer. SCC distillation is also applied for recovering flavour compounds from fruit juices, tea or coffee [3,5,6,16–18].

The main advantages of SCC distillation comprise low residence time, high contact area between liquid and vapour, low pressure drop in the column and moderate temperatures, which minimizes the thermal impact on the beverage [3,19]. However, as in most of the dealcoholization processes, SCC has also some drawbacks related to the decrease in the quality of the final product flavour, mainly because some of the volatile aroma compounds are removed together with the ethanol [5] and, on the other hand, ethanol itself contributes to the beverage flavour.

Regarding the loss of aroma compounds during beverages processing, the recovery of natural aroma compounds plays an important role in brews industry because of their high commercial value [20–22]. In order to improve the flavour profile of the treated beverages, the aroma compounds can be recovered from the alcoholic stream of the dealcoholization process or, instead, they can be extracted from the original beverages

before the dealcoholization and added back to the dealcoholized brews. Membrane-based processes proved to be effective for aroma recovery before beverage processing (e.g., pasteurization, concentration and dealcoholization) [23,24]. Membrane processes show several advantages over traditional heat or solvent extraction processes; their energy consumption is normally lower and there is no need of chemical additives. Otherwise, they can be operated at low temperatures, which is essential when sensitive aroma compounds are intended to be separated [25–27]. One of the most effective membrane processes for aroma recovery is pervaporation. Besides the above-mentioned advantages, suitable pervaporation membranes are very selective for several chemical groups that constitute typical beverages aroma profiles [28–31]. During last years, pervaporation process was successfully applied for recovering aroma compounds from fruit juices for subsequent addition to the same juice, after concentration by evaporation [32–37]. Pervaporation has been also applied for ethanol removal and aroma recovery from alcoholic beverages [13,14,38,39]. The extraction of beer aroma compounds by pervaporation, using the response surface methodology (RSM) for evaluating the effect of operating conditions on the membrane flux and selectivity, is described in Chapter IV [40]. Moreover, the integrated process that considers the extraction of beverages aroma compounds before the dealcoholization and subsequent addition to the treated beverage was patented [41].

This chapter studies the industrial process for producing non-alcoholic beer (ethanol < 0.5 vol.%) with improved flavour profile. The beer dealcoholization is performed by spinning cone column distillation, according to the process described elsewhere [42]. The dealcoholized beer is blended with fresh alcoholic beer and natural extracted aroma compounds. These aroma compounds are obtained by pervaporation of the original beer, using POMS/PEI membranes. The effect of feed temperature and feed flowrate on the pervaporated aroma profile was assessed. The operating conditions were selected to originate dealcoholized beer with the most equilibrated flavour profile.

5.2. Materials and methods

Figure 5.1 shows the block diagram of the process for producing non-alcoholic beer by integrating pervaporation (PV) for extracting aroma compounds and spinning cone column (SCC) distillation for removing ethanol. In the first step of the process, a stream fraction of non-carbonated alcoholic beer is pervaporated for extracting the aroma compounds. The retentate stream from the pervaporation unit is added to the feed stream of the SCC distillation unit. In the SCC unit, the feed contacts counter-currently with a water vapour stream that strips ethanol (and other volatile compounds). Finally, the aroma compounds from the pervaporation unit and a fraction of fresh alcoholic beer are added to the dealcoholized beer for balancing its lack of aroma compounds.

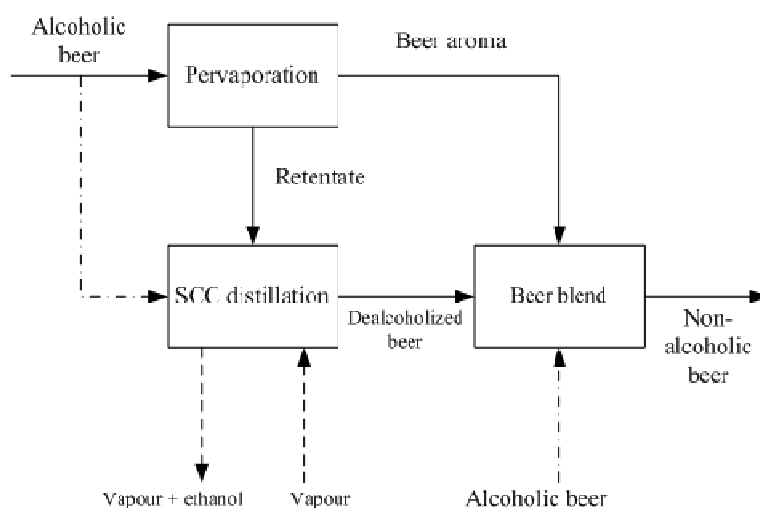
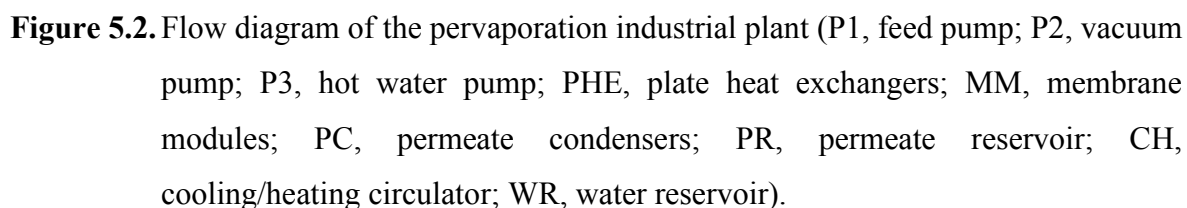


Figure 5.1. Block diagram of the industrial process for producing non-alcoholic beer by SCC distillation and pervaporation of a regular alcoholic beer.

5.2.1. Aroma extraction by pervaporation (PV)

The extraction of aroma compounds from beer is performed in an industrial plant as illustrated in Figure 5.2. A fraction of the original beer stream is pumped continuously to four membrane modules organized in two sets of two modules (MM, cf. Figure 5.2), using plate-and-frame POMS/PEI composite membranes with a total effective area of 40 m². The feed pump (P1) controls the inlet flowrate to a maximum pressure difference between the inlet (feed) and outlet (retentate) of membrane module of 2 bar. Before the inlet of the set of membrane modules, the feed stream passes through a plate heat exchanger (PHE1) for controlling the temperature. A rotary vane vacuum pump (P2) keeps the permeate side of the membrane module set under sub-atmospheric pressure. The vacuum provides the mass transfer of aroma compounds from the beer to the permeate side and the subsequent evaporation at the downstream side of the membranes. The plant was set to operate in batch-wise mode concerning the permeate recovery. In this embodiment, the permeate stream is conducted to the set of four condensers (PC1 – PC4), where it is condensed at around -85 °C. A cooling/heating circulator (CH) supplies the thermal fluid that condenses the permeate. After the extraction step, the thermal fluid is warmed up to 40 °C and hot water is made circulating in the condensers for defrosting the permeate, which is collected in the aroma tank (PR) and then discharged and stored in containers. The non-condensable compounds, such as carbon dioxide, are expelled through the vacuum pump (P2) vent. The retentate stream (stage cut of approximately 0.1 to 1.1 %), which corresponds to semi-depleted beer, is then fed to the SCC dealcoholization unit. The detailed operation mode of pervaporation industrial plant is described in Chapter II (section 2.2.4).



The beer dealcoholization is performed in a SCC plant (Flavourtech) sketched in Figure 5.3. The retentate stream from the pervaporation plant and a fraction of the original beer (not fed to the pervaporation unit) are pumped continuously through a plate heat exchanger (PHE3, cf. Figure 5.3) to the top of the spinning cone column (SCC). SCC is a stripping unit made of spinning cones attached to a rotating vertical central shaft, intercalated with static cones, fixed to the column wall. The feed beer flows down through the fixed cones, under gravity force, and flows up through the spinning cones, due to the centrifugal force, forming always a thin layer of liquid. The stripping stream, which consists in deaerated water vapour, flows up the column in turbulent regime and collects the ethanol and other volatile aroma compounds from beer. The vapour containing ethanol and other volatiles is carried out through the top of the column and then it is condensed in a plate heat exchanger (PHE5). The condensate passes through a cyclone (C) and is stored in

a tank. The distillate and vapour line are kept under vacuum by means of a vacuum pump (P6). The dealcoholized beer travels down the column and is discharged from the column bottom by a pump (P5). The dealcoholized beer passes through the feed heat exchanger (PHE3), where it is cooled by the feed beer, and then through a second heat exchanger (PHE4) for a final adjustment of the temperature.

The dealcoholized beer is then blended with fresh alcoholic beer (around 5 - 10 vol.%) and the extracted aroma compounds (around 0.3 vol.%) from the pervaporation unit, and finally it is carbonated. The blended beverage is a non-alcoholic beer with an aroma profile close to the original one.

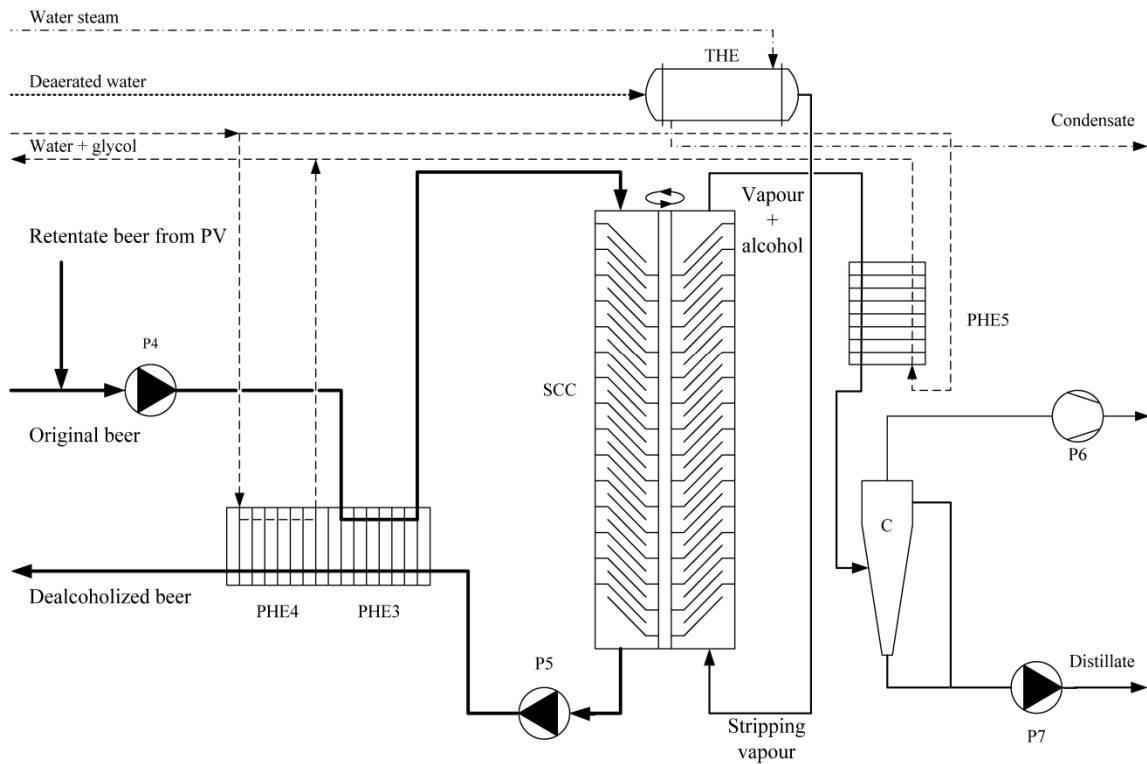


Figure 5.3. Flow diagram of the SCC industrial plant (P4, feed pump; P5, discharge pump; P6, vacuum pump; P7, distillate pump; SCC, spinning cone column; PHE, plate heat exchangers; THE, tubular heat exchanger; C, cyclone) (adapted from [42]).

5.2.3. Analytical methods

The experiments were performed with an alcoholic Pilsner type beer containing ca. 5.5 vol.% of ethanol and residual carbon dioxide of ca. 3.5 g·L⁻¹. The original extract, real extract, ethanol and aroma compounds concentrations were quantified in the original beer, in the dealcoholized beer, in the extracted aroma and in the final beer. It was used a densitometer coupled to an ethanol analyser (DMA 4500 and Alcolyzer Plus, Anton Paar) to measure the density, the original and real extract of beer and the ethanol content of beer and pervaporated samples. A gas chromatograph was used to determine the aroma compounds concentrations. The analysis method is described in Chapter II (section 2.2.1). Table 5.1 shows the properties of the selected volatile aroma compounds studied: ethanol (*E*), propanol (*Pr*), isobutanol (*iB*), amyl alcohols (*AA*), ethyl acetate (*EA*), isoamyl acetate (*iAA*) and acetaldehyde (*Ac*).

Table 5.1. Properties of beer volatile compounds.

Compound	Molecular formula	Molecular weight (g·mol ⁻¹)	Boiling point (°C)	Beer threshold ¹ (ppm)	Concentration in feed beer (ppm)	Typical flavour
Ethanol	C ₂ H ₆ O	46	78	14000	5.67 vol.%	Alcohol
Propanol	C ₃ H ₈ O	60	98	800	20.30	Alcohol
Isobutanol	C ₄ H ₁₀ O	74	108	200	12.87	Alcohol
Amyl alcohols	C ₅ H ₁₂ O	88	132	68	83.86	Alcohol, banana
Ethyl acetate	C ₄ H ₈ O ₂	88	77	30	20.27	Fruity, solvent
Isoamyl acetate	C ₇ H ₁₄ O ₂	130	149	1.2	1.37	Banana
Acetaldehyde	C ₂ H ₄ O	44	20	25	5.06	Green apples

¹ Source: Meilgaard [43]

5.3. Results and discussion

The efficiency of the pervaporation process was evaluated in terms of productivity (permeate flux) and quality of the extracted aroma (membrane selectivity, concentration of permeate and equilibrium between aroma compounds on the permeate).

At steady-state, the permeate flux (J_p) is given by:

$$J_p = \frac{m_p^*}{A \cdot t} \quad (5.1)$$

where m_p^* is the permeate mass collected after defrosting, A is the effective membrane area and t is the time of the permeation cycle.

The selectivity of the membranes ($\alpha_{i/E}$) towards a generic aroma compound i compared to ethanol (E) was obtained from:

$$\alpha_{i/E} = \frac{w_{p,i}^* / w_{p,E}^*}{w_{f,i} / w_{f,E}} \quad (5.2)$$

where $w_{p,i}^*$ and $w_{p,E}^*$ are the condensed permeate mass fractions of the aroma compound and ethanol, respectively; $w_{f,i}$ and $w_{f,E}$ are the mass fractions of the aroma compound and ethanol on the feed.

The enrichment factor (β_i) of a generic aroma compound i was computed using:

$$\beta_i = \frac{C_{p,i}}{C_{f,i}} \quad (5.3)$$

where $C_{p,i}$ and $C_{f,i}$ are the concentrations of the aroma compound on the permeate and feed side, respectively.

The equilibrium of the extracted permeate was assessed dividing the total amount of higher alcohols by the total amount of esters on the collected permeate:

$$A/E = \frac{C_{total\ higher\ alcohols}}{C_{total\ esters}} \quad (5.4)$$

where A/E is the ratio between higher alcohols and esters and C is the concentration of the species on the permeate.

5.3.1. Operation of the industrial plant of pervaporation

It was concluded in Chapter IV that the critical operation variables of the pervaporation plant are the feed temperature, feed flowrate and permeate pressure. In this study, the feed temperature was investigated in the range of 7 °C to 25 °C and the feed flowrate in the range of 500 L·h⁻¹ to 1500 L·h⁻¹. The permeate pressure was maintained below 8 mbar. The industrial unit uses a cooling/heating circulator that produces a refrigeration stream at ca. -90 °C used for condensing the permeate stream. Figures 5.4 and 5.5 show the influence of the feed temperature and flowrate on the permeate pressure and condensation temperature, respectively. The permeate pressure and condensation temperature increase with the feed temperature; as the feed temperature increases, the permeate flowrate also increases which leads to an increase of the permeate pressure (Figure 5.4). The increase of permeate flowrate also influences the performance of the condensers, leading to a smaller contact time and then to a decrease of the condensation rate. This originates the condensing temperature to increase with the feed temperature (Figure 5.5).

It was observed that the permeate pressure increased with the feed flowrate (Figure 5.4). This should be related to the increase of carbon dioxide permeation, as concluded using degassed beer. On the other hand, the feed flowrate has a minor influence on the condensation temperature (Figure 5.5).

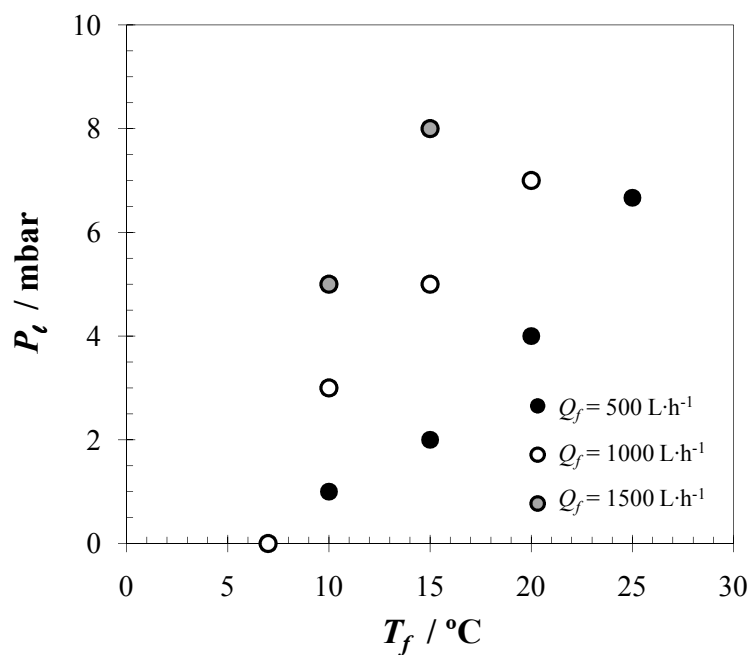


Figure 5.4. Permeate pressure (P_t) as a function of feed temperature (T_f) for three different feed flowrates (Q_f).

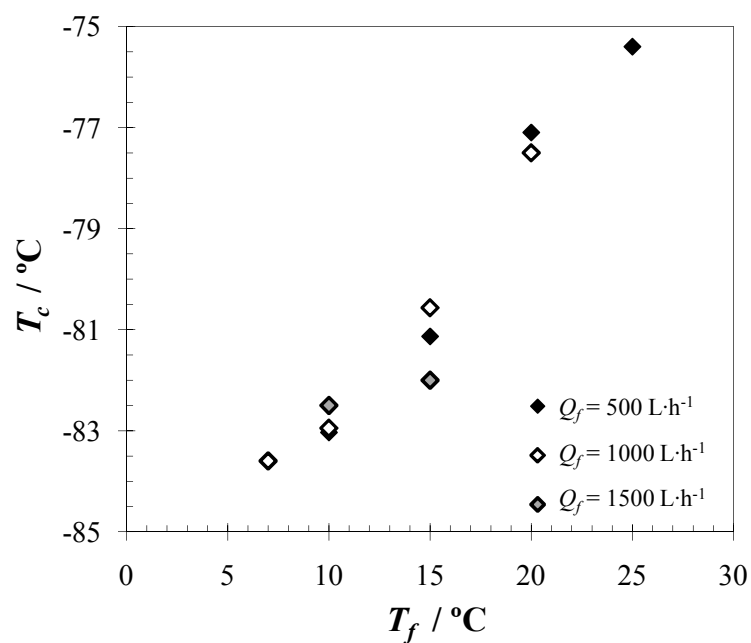


Figure 5.5. Condensation temperature (T_c) as a function of feed temperature (T_f) for three different feed flowrates (Q_f).

Influence and selection of feed temperature and flowrate

As mentioned before, the experiments in the industrial pervaporation plant were performed at different feed temperatures and flowrates. Despite the influence of these conditions on the permeate pressure, all runs were operated below 8 mbar. Figures 5.6 to 5.10 show the influence of the feed temperature and flowrate on the flux, selectivity and equilibrium between aroma compounds on the permeate stream. The permeate flux increases with feed temperature and is mostly not affected by the feed flowrate (Figure 5.6); this indicates a small or negligible concentration polarization effect. On the other hand, the selectivity towards higher alcohols remains almost constant as a function of the feed temperature and flowrate (Figure 5.7), while the selectivity towards esters decreases with the feed temperature and it shows a maximum for the middle value of feed flowrate (1000 L·h⁻¹, cf. Figure 5.8). Concerning acetaldehyde selectivity, it increases with the feed temperature and flowrate (Figure 5.9).

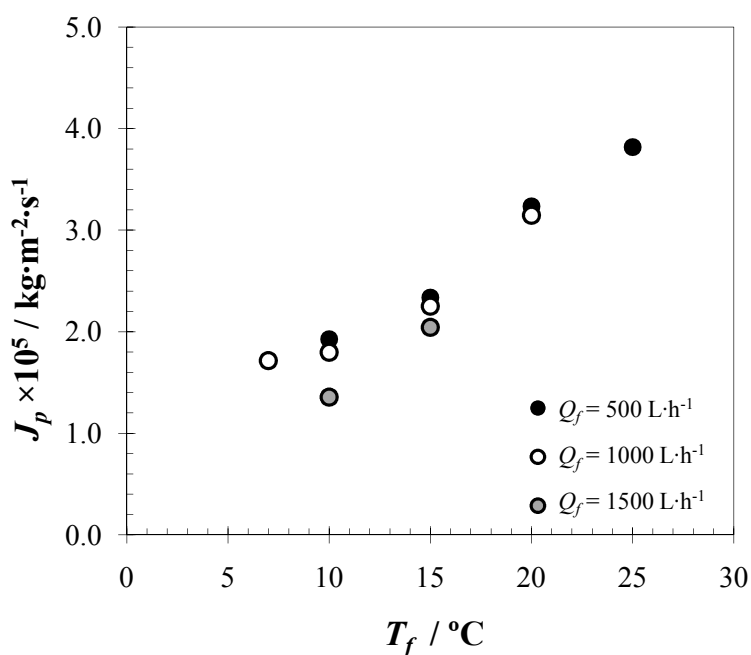


Figure 5.6. Permeate flux (J_p) as a function of feed temperature (T_f) and flowrate (Q_f).

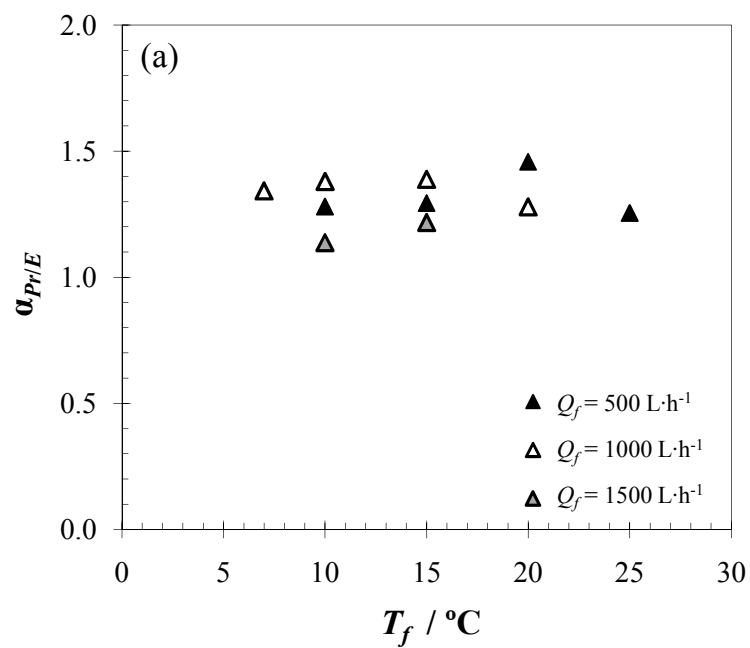


Figure 5.7. (a) Propanol selectivity as a function of feed temperature (T_f) and flowrate (Q_f).

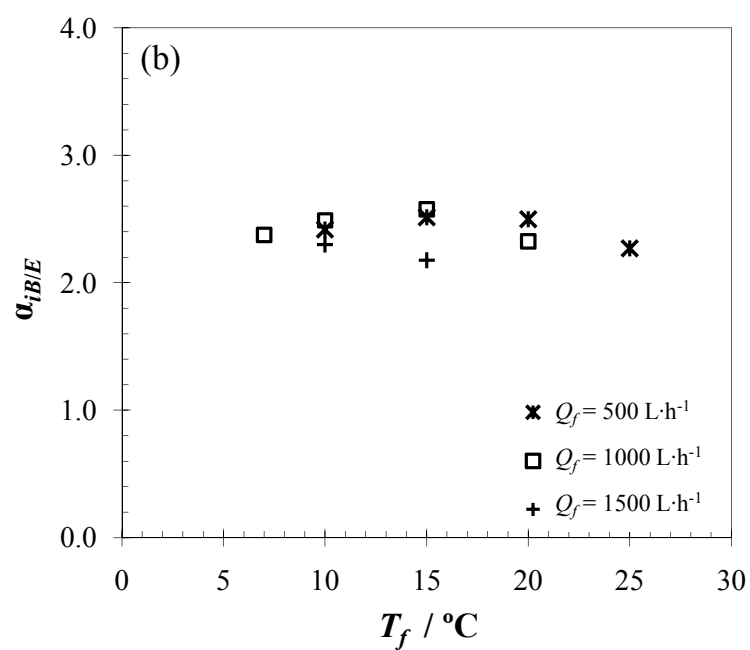


Figure 5.7. (b) Isobutanol selectivity as a function of feed temperature (T_f) and flowrate (Q_f).

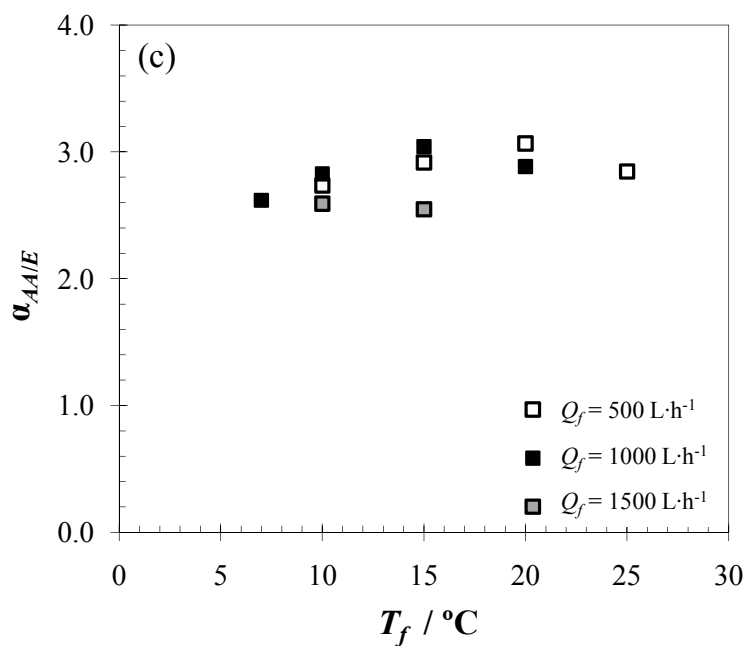


Figure 5.7.(c) Amyl alcohols selectivity as a function of feed temperature (T_f) and flowrate (Q_f).

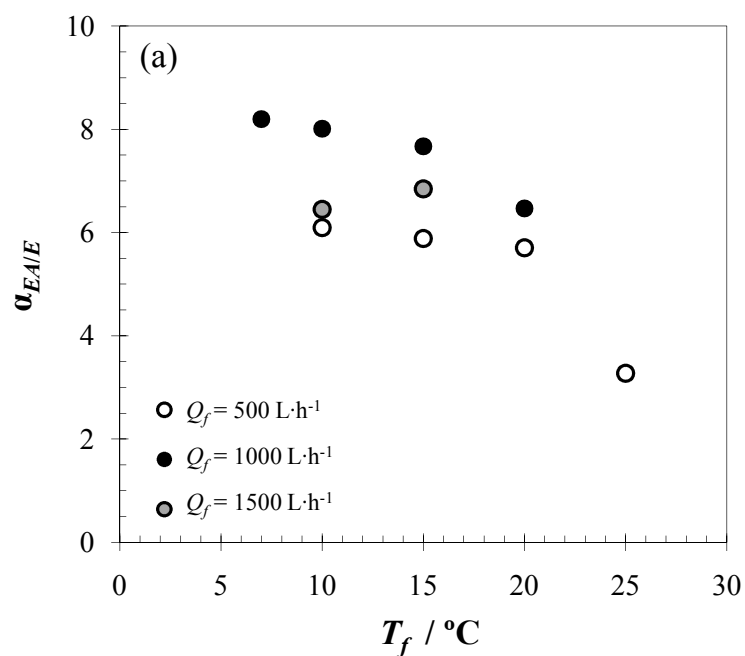


Figure 5.8.(a) Ethyl acetate selectivity as a function of feed temperature (T_f) and flowrate (Q_f).

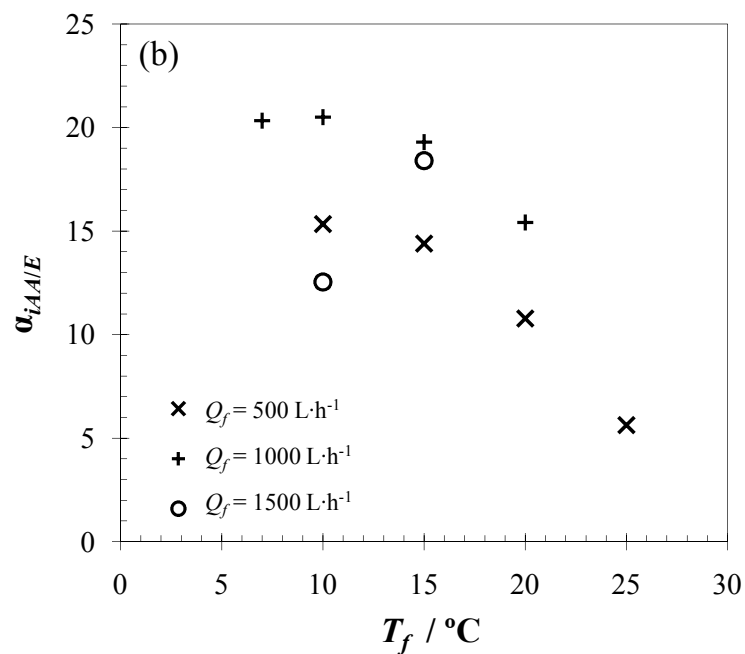


Figure 5.8. (b) Isoamyl acetate selectivity as a function of feed temperature (T_f) and flowrate (Q_f).

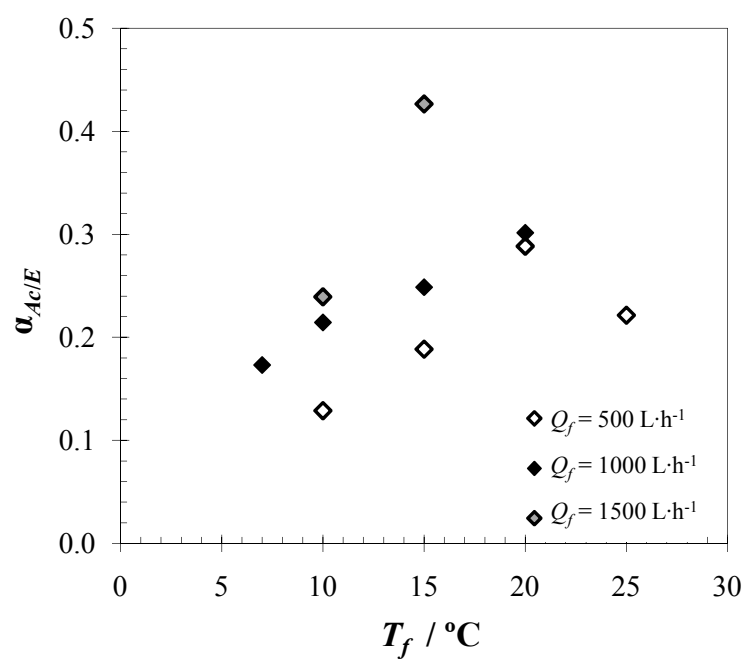


Figure 5.9. Acetaldehyde selectivity as a function of feed temperature (T_f) and flowrate (Q_f).

Figure 5.10 plots the ratio between higher alcohols and esters on the permeate as a function of the feed temperature and flowrate, showing that A/E increases with the temperature and decreases with the feed flowrate. It can be observed that for high feed temperature and low feed flowrate, the A/E ratio is closer to the typical value of Pilsner beers, which is placed between 4 and 6 [44].

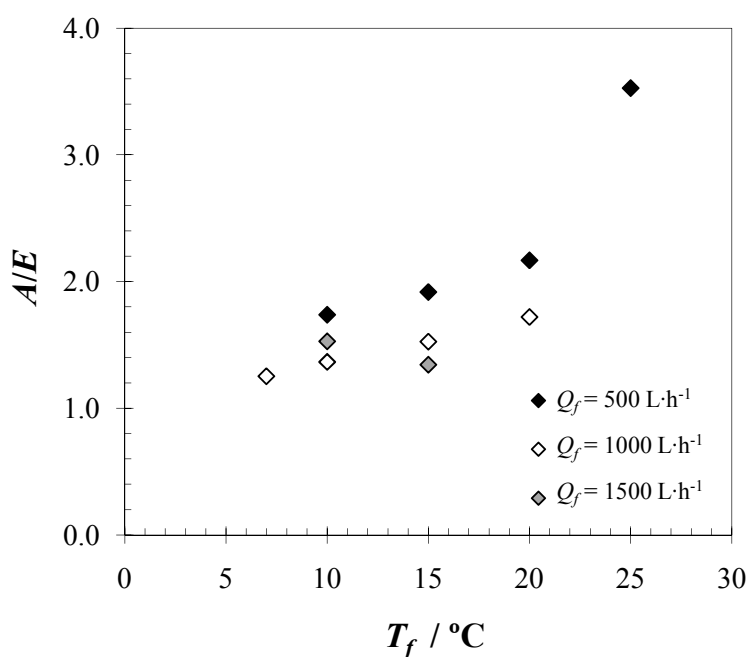


Figure 5.10. Higher alcohols and esters ratio (A/E) as a function of feed temperature (T_f) and flowrate (Q_f).

Chapter IV describes a similar study at laboratory level. In this study, the beer was stored in a tank, recirculating through the membrane cell originating the rapid degassing of the beer. On the other hand, the pervaporated stream was condensed using a liquid nitrogen trap. Comparing with the results obtained industrially, the higher alcohols selectivity behaves similarly as a function of the feed flowrate and differently as a function of the feed temperature. In the lab unit, there is an increase on higher alcohols selectivity with the feed temperature (cf. section 4.3.2), due to the transport activation energy of the higher alcohols being higher than of water [20] and also because ethanol concentration is less sensitive to the temperature than the permeate (water) flux. Higher alcohols selectivity also increases slightly with feed flowrate since higher alcohols are less permeable compared to esters and, as a result, they are less affected by the concentration polarization (cf. section 4.3.2). It was verified at lab level that higher alcohols selectivity decreases with permeate pressure

increase (cf. section 4.3.2), due to their low saturated vapour pressures (low volatilities) [20]. This trend was not observed in the industrial plant. In the industrial plant, a cooling/heating circulator provides the thermal fluid that condenses the permeate and the condensing temperature is influenced by the feed temperature, increasing with it (cf. Figure 5.5); this makes the condensing system to selectively condense the heaviest components. On the other hand, as the vacuum pump in the industrial plant is proportionally smaller than the one in the laboratory unit, the permeate pressure increases significantly with the feed temperature (cf. Figure 5.4), since the permeate flowrate increases; in this case an increase on the feed temperature makes the selectivity towards the heaviest permeating components to decrease. Finally, it should be expected an increase on the permeating flux of the higher alcohols with the feed temperature. The final trend should be the balance of these three effects and it was observed that the feed temperature mostly does not affect the higher alcohols selectivity.

Concerning the effect of the feed temperature and flowrate on the esters selectivity, the industrial results are in agreement with the lab ones. According to lab results, esters selectivity increased with feed flowrate. As described in Chapter IV esters present higher permeability through the membrane compared to higher alcohols and thus they are more sensitive to polarization concentration (cf. section 4.3.2). The membrane selectivity towards esters should decrease with the feed temperature (cf. section 4.3.2) due to their transport activation energy being closer to the water [20] and also because ethanol concentration is less affected by the temperature increase than permeate (water) flux. Esters selectivity increases with the permeate pressure increase (cf. section 4.3.2) due to their higher saturated vapour pressures [20]. However, in the industrial unit as the feed temperature increases, the condensing temperature increases and selectivity towards esters decreases; as the permeate pressure increases with the feed temperature, the selectivity towards esters should increase. The observed balance of these effects resulted in a decrease of esters selectivity with the feed temperature. On the other hand, the membrane selectivity towards esters was expected to increase with the feed flowrate (cf. section 4.3.2). Also, as the permeate pressure increases with the feed flowrate (cf. Figure 5.4), the selectivity towards esters should also increase (cf. section 4.3.2). On the other hand, the performance of the condensers is affected by the increase of feed flowrate (reduction of contact time), which reduces the condensation efficiency. At the end, it was observed that the selectivity towards esters shows a maximum for $1000 \text{ L}\cdot\text{h}^{-1}$ of feed flowrate.

Comparing the industrial permeate aroma profile with the one reported in the Chapter IV, for a lab unit, the industrial profile is less concentrated in aroma compounds, especially in esters and acetaldehyde – Table 5.2. It was observed that ethanol concentration is slightly lower in the industrial plant also. Regarding the selectivity towards aroma compounds, the selectivity towards higher alcohols is similar in both cases, while selectivity towards esters and acetaldehyde is lower, compared to the lab study. As referred before, in the lab unit, the permeate was collected and condensed batch-wise with liquid nitrogen at -196 °C, which allows the total condensation of the aroma compounds. In the industrial plant, the condensing system works at higher temperatures and it is affected by the permeation flowrate and the permeation of the residual carbon dioxide present in the feed. This less effective condensing system makes light compounds, mostly esters and aldehydes, to be selectively lost through the vacuum pump. On the other hand, the most permeable compounds, such as isoamyl acetate, are poorly condensed, due to the decrease of the contact time in the condensers. As a result, the ratio between higher alcohols and esters concentration becomes higher in the industrial plant (see Table 5.2). The limitations of the condensing system also affects the permeate condensing flux, which is lower than the one obtained for the lab unit – Table 5.2.

Table 5.2. Comparison between lab and industrial results of beer pervaporation.

Characteristics	Lab results ¹		Industrial results	
	min	max	min	max
$J_p \times 10^5 \text{ (kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1})$	1.53	8.56	1.35	3.82
$C_{p,E} \text{ (vol.}\%)$	22.00	29.50	12.75	20.00
$\alpha_{Pr/E}$	1.03	1.45	1.14	1.46
$\alpha_{iB/E}$	2.08	2.97	2.18	2.58
$\alpha_{AA/E}$	2.01	3.60	2.55	3.07
$\alpha_{EA/E}$	11.51	24.76	3.27	8.20
$\alpha_{iAA/E}$	12.02	35.78	5.63	20.50
$\alpha_{Ac/E}$	2.91	5.37	0.13	0.33
A/E	0.46	1.63	1.25	3.53

¹ Results reported in Chapter IV

As it can be seen from Figures 5.6 and 5.10 the highest permeate flux and aroma ratio was obtained for 25 °C of feed temperature and 500 L·h⁻¹ of feed flowrate (stage cut of ca. 1.1 %). For high feed temperatures and low feed flowrates the membrane productivity is higher (higher permeate flowrate) and the aroma profile becomes more equilibrated (higher alcohols and esters ratio closer to the original beer value). Besides, the taste of the blended non-alcoholic beer obtained by adding the pervaporation extract produced at 25 °C of feed temperature and 500 L·h⁻¹ of feed flowrate was the best one.

5.3.2. SCC operating conditions

The main operating parameters of SCC distillation that affect the ethanol removal from beer and hence the dealcoholized beer quality are the feed flowrate, the internal stripping ratio (ratio between vapour and feed flowrate) and the vacuum pressure. In this study, the beer dealcoholization was performed at 2200 L·h⁻¹ of feed flowrate, 18 % of stripping ratio and 50 mbar of vacuum pressure. The temperature of SCC for these conditions was 45 °C on the column top and 55 °C on the bottom. Table 5.3 shows the composition of the original beer (before any processing), dealcoholized beer (product from SCC, with an ethanol concentration of ca. 0.0 vol.%) and non-alcoholic beer (product from SCC blended with pervaporated aroma and fresh alcoholic beer, with an ethanol concentration < 0.5 vol.%). During alcohol removal by SCC distillation water vapour strips the ethanol as well as a great fraction of volatile aroma compounds. By adding fresh original beer and the permeate from the pervaporation unit, the aroma profile improves within the maximum allowable ethanol concentration of 0.5 vol.%. Despite the concentration of aroma compounds in the non-alcoholic beer being smaller than in the original one, the ratio between each aroma concentration and ethanol ($R_{i/E}$) is close to the original beer – Table 5.3. Moreover, a trained taste panel considered that the flavour profile of this non-alcoholic beer is similar to the original one.

Table 5.3. Composition of beer and pervaporated aroma during the process of dealcoholization and aroma recovery.

Characteristics	Original beer	Dealcoholized beer	Pervaporated aroma	Non-alcoholic beer	Original beer $R_{i/E}$	Non-alcoholic beer $R_{i/E}$
C_E (vol.%)	5.67	0.02	19.50	0.45		
Original Extract (wt.%)	14.65	6.24	–	6.79		
Real Extract (wt.%)	6.22	6.21	0.00	6.21		
C_{Pr} (mg·L ⁻¹)	20.3	n.d.	72.64	1.54	3.58	3.45
C_{IB} (mg·L ⁻¹)	12.87	n.d.	106.36	1.16	2.27	2.59
C_{AA} (mg·L ⁻¹)	83.86	n.d.	841.70	7.99	14.79	17.88
C_{EA} (mg·L ⁻¹)	20.27	n.d.	249.67	2.07	3.57	4.63
C_{IAA} (mg·L ⁻¹)	1.37	n.d.	39.82	0.21	0.24	0.47
C_{Ac} (mg·L ⁻¹)	5.06	2.17	6.24	2.37	0.89	5.31
A/E	5.41	–	3.53	4.69		

n.d. – not detected

5.3.3. Membrane ageing

After selecting the optimum feed temperature and flowrate for extracting aroma compounds from beer, the industrial pervaporation plant was set to work continuously. After 8 months of operation, it was verified a decrease on permeate flowrate and concentration. Figure 5.11 shows the history of permeate flowrate and permeate concentration of ethanol during these 8 months.

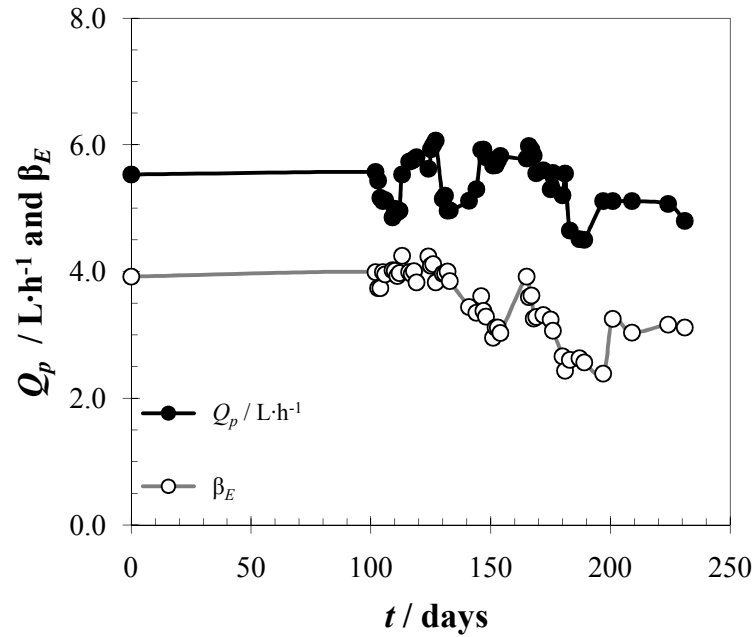


Figure 5.11. History of permeate flowrate (Q_p) and enrichment factor of ethanol (β_E) during 8 months of beer aroma compounds extraction (lines were introduced for improving readability).

To regenerate the original performance it was decided to test several cleaning solutions and cleaning conditions. First, it was developed a laboratory method to simulate this ageing phenomenon. Membrane samples were immersed in various ageing solutions, namely in ultrapure water, aqueous ethanol solutions (about 10 vol.%) and Pilsner type beer (about 5.5 vol.%) – Table 5.4. Besides the immersion of membranes in the ageing solutions, membrane samples were submitted to several pervaporation lab cycles with beer. The performance of aged membranes were then assessed by determining the pervaporation permeate flux and selectivity of an ethanol aqueous solution of ca. 10 vol.% – Table 5.4. The results in Table 5.4 indicate that immersing membranes in ultrapure water, ethanol solution or beer did not result in significant ageing of the membranes (runs *b*, *c* and *d*). The

use of membranes in pervaporation cycles with beer resulted in a slight decrease of the permeate flux and a significant decrease of the ethanol selectivity (run *e*). It was also observed that membrane samples (originally white – cf. Figure 5.A1) submitted to the pervaporation of beer showed an intense brown coloration in both surfaces (membrane fouling – cf. Figure 5.A2).

Table 5.4. Effect of ageing conditions on POMS/PEI membranes flux and ethanol selectivity (laboratory study).

Run #	Ageing conditions	Ageing time (days)	$J_p \times 10^5$ (kg·m ⁻² ·s ⁻¹)	δ_{J_p} (%)	$\alpha_{E/W}$	$\delta_{\alpha_{E/W}}$ (%)
a	Fresh membrane		7.10	0.00	5.24	0.00
b	Milli-Q ultrapure water	30	7.07	-0.32	5.54	5.82
c	Ethanol 10 vol.%	30	7.09	-0.11	5.24	-0.02
d	Beer 5.5 vol.% of ethanol	30	7.29	2.75	5.29	0.91
e	Beer PV runs	30	6.62	-6.75	4.56	-12.86
f	Membrane <i>e</i> after dry	30	10.5	47.97	3.36	-35.82
g	Beer PV and kept in ultrapure water	30	7.50	-2.73	5.23	0.64
h	Beer PV and kept in beer	45	7.49	-2.82	5.36	3.08
i	Beer PV and kept in beer	80	7.70	-0.18	5.33	2.52

After carefully analysing the industrial procedure, it was verified that the pervaporation membranes were let to dry periodically, when not used. It was then assessed in the laboratory unit the role of drying the pervaporation membranes periodically. It was concluded that the membranes showed a significant decrease in ethanol selectivity and an increase of membrane flux (see Table 5.4, run *f*). This ageing should be related to micro ruptures in the membrane selective film, which becomes more fragile. On the other hand, maintaining the membranes in water or beer between pervaporation runs resulted in a negligible ageing effect after 80 days of operation (Table 5.4, runs *g* – *i*).

Figure 5.12 shows electronic pictures of a fresh and an aged membrane samples. Aged membrane sample shows an increasing amount of particles at the selective surface.

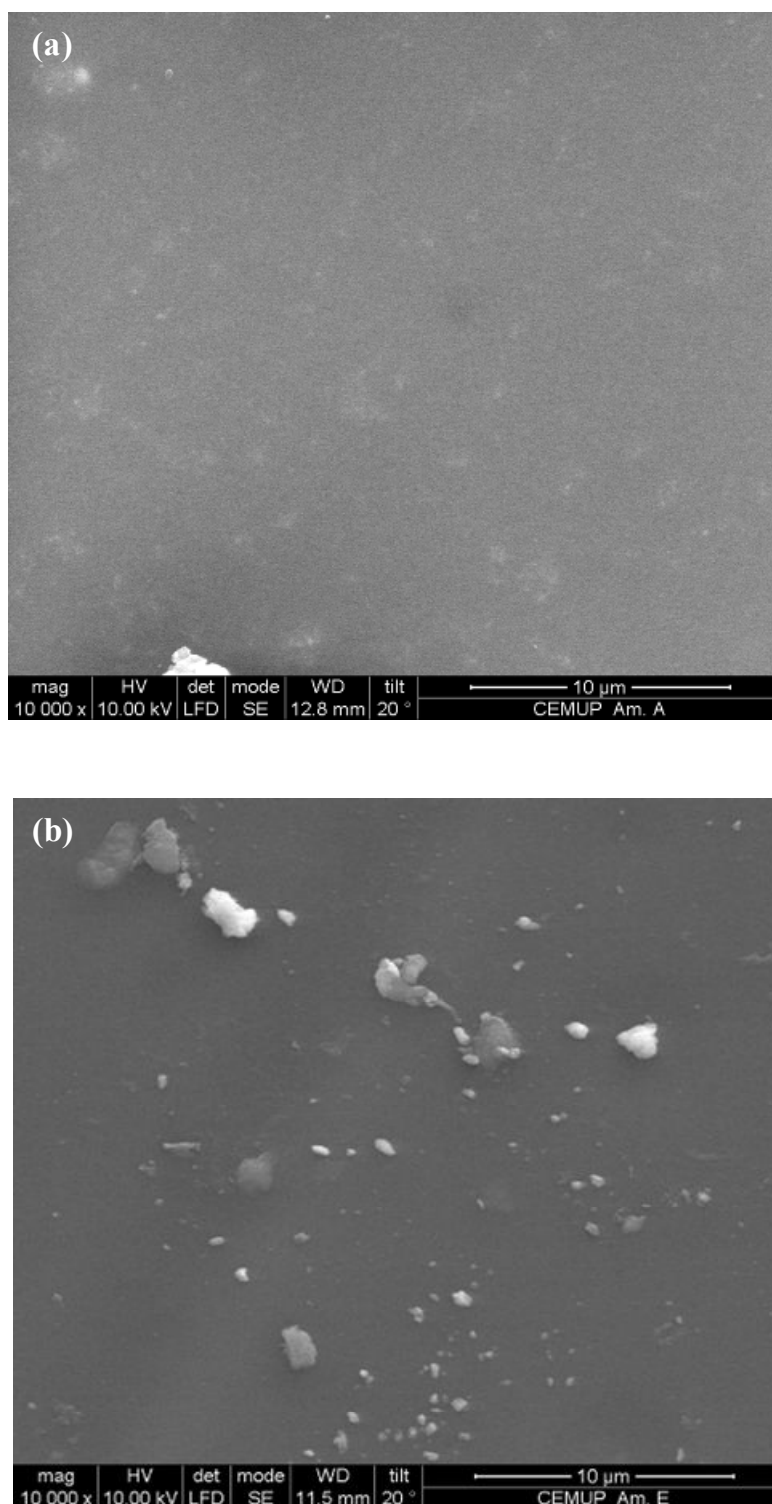


Figure 5.12. SEM micrographs of selective surface of POMS/PEI membrane samples: (a) fresh membrane; (b) aged membrane in PV runs.

Several cleaning solutions were tested for reducing the membrane fouling and restoring the original properties of the membranes. The membrane samples were submersed in the cleaning solutions at room temperature and concentrations as specified by the suppliers. Table 5.5 shows the characteristics of cleaning solutions, as well as the concentration applied.

Table 5.5. Characteristics of cleaning solutions.

Solution	Type of solution	Supplier	Concentration (wt.%)
TFD4	Alkaline	Franklab	1.00
Actinet	Surfactant	Imporquímica	5.00
Decal	Alkaline surfactant	Imporquímica	1.00
Divos 120CL	Chlorinated alkaline	Johnson Diversey	1.00
Divos 123	Alkaline	Johnson Diversey	1.50
Booster	Hydrogen peroxide additive	Johnson Diversey	0.25
Divos 98PE	Enzymatic	Johnson Diversey	1.00

Figure 5.13 shows the behaviour of the cleaning solutions in the removal of membrane fouling. The fouling removal was evaluated based on the intensity of the brown coloration and the contact angle of the membrane samples surface (originally white), before and after immersing in the cleaning solution. The results were compared with fresh (reference) and aged membrane samples. The solution of alkaline reagent *Divos 123* plus additive *Booster* (Johnson Diversey) showed the best removal of membrane fouling (see Figure 5.A3). On the other hand, the pervaporation flux and ethanol selectivity of a 10 vol.% aqueous solution of ethanol did not change after membrane immersion on this cleaning solution.

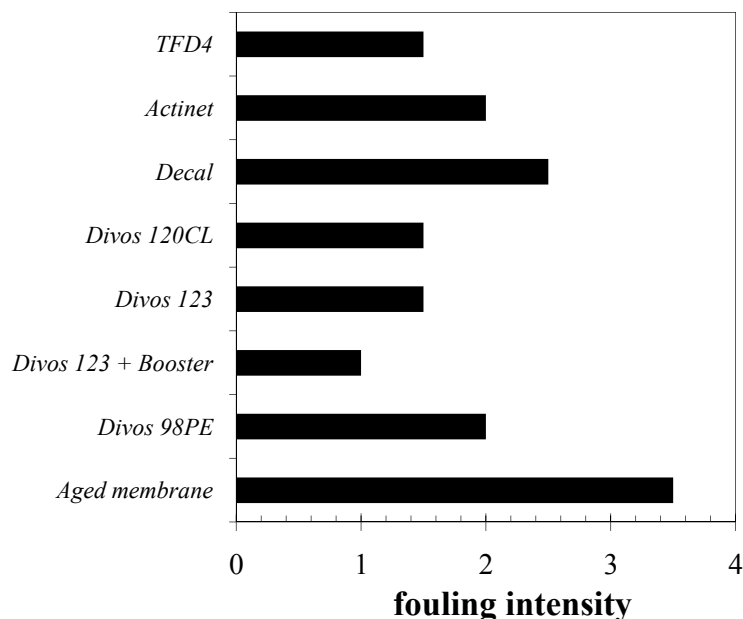


Figure 5.13. Effect of cleaning solutions (at specified concentrations) in the removal of fouling (0 – reference, 4 – maximum fouling).

5.4. Conclusions

In this study it was investigated the production of non-alcoholic beer (ethanol concentration < 0.5 vol.%) using an industrial plant. The process comprises two technologies: a pervaporation unit that extracts the aroma compounds from the feed beer and a SCC distillation unit that removes the ethanol, after pervaporation. The dealcoholized beer is then blended with original fresh beer and with the extracted aroma compounds, in order to improve its flavour profile.

SCC distillation proved to be an effective process to remove ethanol from beer. This extraction unit operates under vacuum (50 mbar, average temperature of 50 °C) and uses a water vapour stream for promoting the ethanol removal. However, SCC distillation also strips the beer feed from other aroma compounds.

The pervaporation unit uses four plate-and-frame membrane modules of POMS/PEI (40 m²) and operates between 1 mbar and 8 mbar of permeate pressure and between -75 °C and -85 °C of condensing temperature. Several pervaporation experiments were performed to assess the influence of the feed temperature and flowrate on the aroma compounds extraction. It was found that these operating variables affect the permeate pressure and the condensation temperature; the obtained best operating conditions were 25 °C of feed

temperature and $500 \text{ L}\cdot\text{h}^{-1}$ of feed flowrate (stage cut of ca. 1.1 %), allowing the maximum permeate delivery and a good equilibrium of the aroma profile. Around 0.3 vol.% of aroma extract and 5 vol.% to 10 vol.% of fresh beer are added to the dealcoholized beer to balance the lack of aroma, without overcoming the ethanol concentration limit of 0.5 vol.%.

During the industrial extraction of aroma compounds from beer it was observed a decline in the permeate flowrate and concentration after 8 months of operation. This ageing process was reproduced at laboratory level. It was concluded that the membrane ageing could be prevented if membranes were not let to dry. On the other hand, various cleaning solutions for removing the pervaporation membranes fouling were evaluated. The best performing solution was *Divos 123* with *Booster* (Johnson Diversey); this solution showed no detrimental effect on the membrane pervaporation flux and selectivity.

5.5. List of symbols

A	membrane effective area (m^2)
A/E	higher alcohols and esters ratio (–)
C	concentration (vol.%, wt.% or $\text{mg}\cdot\text{L}^{-1}$)
J	flux ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
m	mass (kg)
Q	flowrate ($\text{L}\cdot\text{h}^{-1}$)
R	ratio between aroma compounds and ethanol (–)
T	temperature ($^{\circ}\text{C}$)
t	time (s, min or days)
w	mass fraction (wt.%)

Greek letters

α	membrane selectivity (–)
β	enrichment factor (–)
δ	relative difference (%)

Subscripts and superscripts

AA	amyl alcohols
Ac	acetaldehyde
c	condensation
E	ethanol
EA	ethyl acetate
f	feed
i	generic aroma compound
iAA	isoamyl acetate
iB	isobutanol
p	permeate
Pr	propanol
$*$	relative to condensed form
W	water

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APPENDIX 5.A

Figures 5.A1 – 5.A3 show pictures of a POMS/PEI membrane samples during ageing laboratory study.

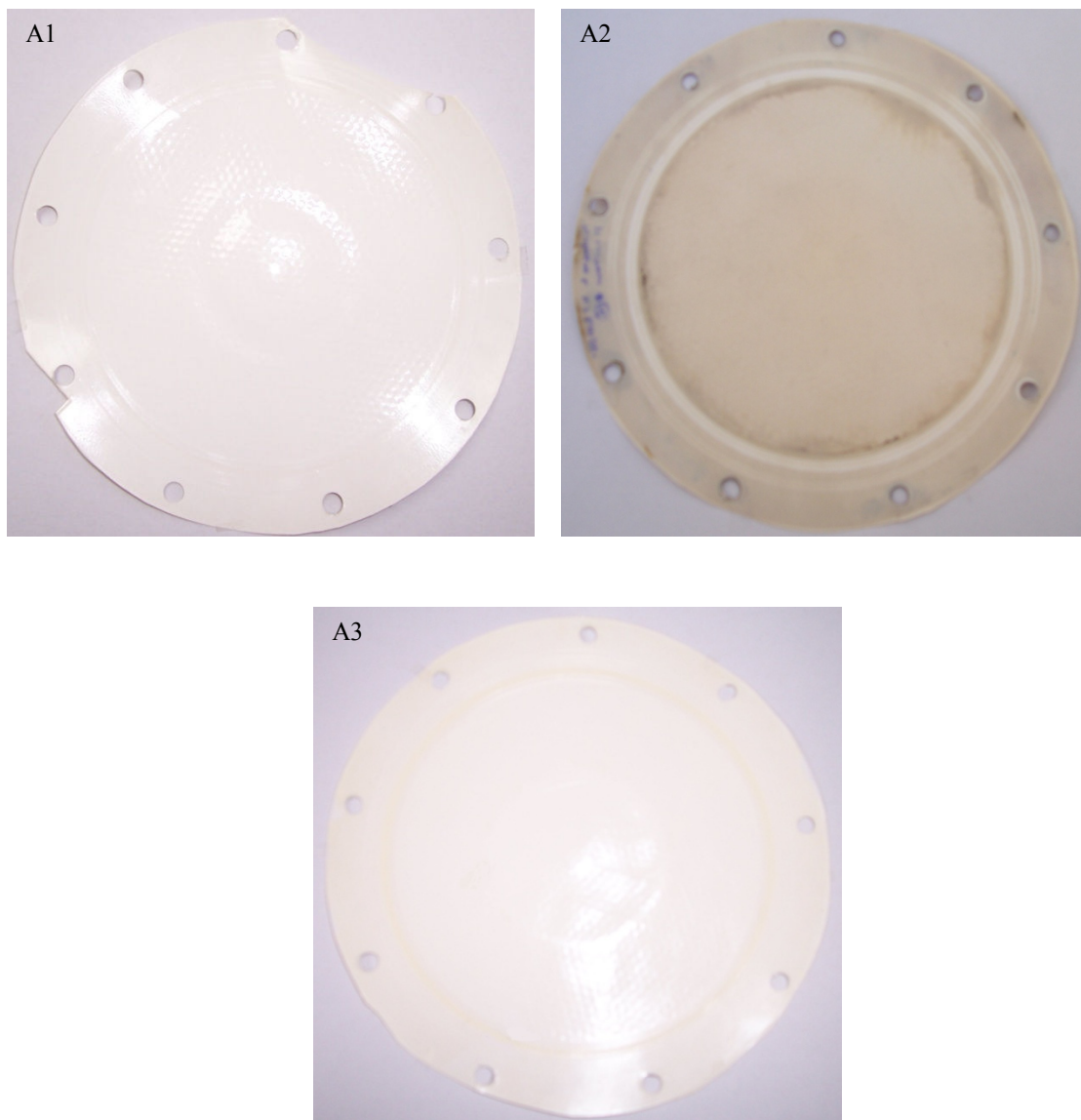


Figure 5.A. Photographs of selective surface of POMS/PEI membrane samples: (A1) fresh membrane; (A2) aged membranes in PV runs; (A3) aged membrane after immersing in cleaning solution *Divos 123* plus additive *Booster*.

Chapter VI

6. New perspectives:

Dealcoholizing wine by membrane separation processes¹

Abstract

The present chapter studies the use of membrane separation processes for producing wine with low alcohol content. Several membranes of reverse osmosis (CA995PE from Alfa Laval) and nanofiltration (NF99 HF, NF99, NF97 from Alfa Laval and YMHLSP1905 from Osmonics) were used for removing ethanol from a 12 vol.% red wine, in diafiltration mode. Pervaporation membranes of polyoctylmethylsiloxane supported in polyetherimide (POMS/PEI) from GKSS were used to recover the aroma compounds before the dealcoholization step, and adding them back to the dealcoholized wine. YMHLSP1905, NF99 and NF99 HF nanofiltration membranes showed higher effectiveness in alcohol removal from wine, due to their good permeability to ethanol and high aroma compounds rejection, resulting in dealcoholized wine samples with promising organoleptic properties. The addition of pervaporated aroma compounds to the dealcoholized wine samples increased the aroma and flavour sensations during the wine tasting, making this combined process the one that originates the best dealcoholized wine samples.

¹ *Adapted from:* M. Catarino and A. Mendes, Dealcoholizing wine by membrane separation processes, *Submitted*

6.1. Introduction

According to European Commission (EC) regulation, wine is defined as an alcoholic beverage resulted from fermentation of grapes or grape must, having an ethanol content higher than 8.5 vol.% [1]. Wine is one of the most consumed alcoholic drinks in the world. Moderate consumption of alcoholic beverages, especially red wine, is related to the decrease of cardiovascular diseases. Red wine consumption has higher antioxidant and cardiovascular protection benefits than other common alcoholic beverages. This high protective effect is related to the high concentration of polyphenolic compounds such as flavonoids [2–5]. Despite health benefits of red wine, the alcoholic beverages consumption has been reduced due to civil restrictions and also health reasons. It was also reported that the removal of ethanol from red wine does not decrease its health beneficial properties, namely its antioxidant and cardiovascular protection effects [6,7]. On the other hand, the ethanol content of wine in some countries increased in the last decades due to namely the global warming and winemaking practices, despite in some countries winemakers have to pay taxes when wine ethanol content is over 14.5 vol.% [8,9].

Several techniques have been applied for producing low alcohol wine. The use of grape juice with low sugar content allows to produce wine with low ethanol content. That approach can be accomplished by using unripe grapes or enzymes that reduce the sugar content of the grape juice. The earlier interruption of the fermentation or the use of special yeasts also results in a wine of low alcohol content [10]. Besides these techniques, physical separation processes for removing ethanol from wine, have been also used. Although the European Commission allows wine dealcoholization, it should not be removed more than 2 percentage points of ethanol and the minimum ethanol concentration should not be less than 8.5 vol.% [11]. Deeper dealcoholization originates a beverage that can not be called “wine”. For removing ethanol from wine, heat or membrane-based processes can be employed. Heat-based processes can produce wines with very low alcohol content (< 0.5 vol.%), however most of the volatile aroma compounds are also lost during the ethanol removal [12]. Membrane-based processes seem to be the more promising for obtaining low alcohol wine. These processes can be carried out at low temperatures, minimizing the thermal impact on the wine; there are available membranes very selective to ethanol that also preserve the volatile aroma compounds on the final beverage [13–15]. Nanofiltration (NF) and reverse osmosis (RO) are the most popular membrane-based processes used for beverage dealcoholization. Usually the dealcoholization is performed by diafiltration. In

diafiltration mode, as the permeate (formed mainly by water and ethanol) is been withdrawn from the feed, water is added to the retentate to balance the permeated flow [10]. Diafiltration improves the ethanol removal selectivity. By adding continuously water to the retentate, the concentration of non-permeable species remains approximately constant, as well as the osmotic pressure, avoiding the decrease of the membrane flux; on the other hand, the concentration polarization is minimized [14,16,17]. However, adding water in oenological practices is strictly forbidden by European Commission regulation [1]. To overcome this regulation, the permeate stream can be subject to a second ethanol removal step and the hence dealcoholized stream reintroduced in the filtration retentate [10].

Wine flavour and aroma profile results from a combination of non-volatile and volatile aroma compounds. The first group is present on the grape juice and it is responsible for the basic taste sensations (sweetness, acidity, saltiness, bitterness and astringency). The second group is made of primary aroma compounds (present in the grapes juice and then in the wine), secondary aroma compounds (formed during fermentation) and tertiary aroma compounds (formed during maturation) and is responsible for the wine aroma sensations. These compounds correspond to several chemical species, such as esters (related to fruity sensations), aldehydes (related to ageing notes) and higher alcohols (related to fruity and immature aroma) [18,19].

Several authors have reported dealcoholization of alcoholic beverages based on membrane processes. López et al. applied the reverse osmosis, in batch and diafiltration modes, for producing low alcohol apple cider, preserving the desirable aroma compounds [14]. Pilipovik and Riverol reported the advantages and disadvantages of reverse osmosis for removing ethanol from beverages down to 0.45 % of ethanol. They found that reverse osmosis is not economically feasible for producing this low alcohol brews [20]. Diban et al. evaluated the mass transfer of ethanol and aroma compounds during wine dealcoholization by osmotic distillation and they found loss of aroma compounds in the process; however, they did not detect any lack of aroma during wine tasting, when a original wine sample was submitted to an ethanol reduction of 2 vol.% [21]. Varavuth et al. also studied wine dealcoholization by osmotic distillation, founding that some wine aroma compounds (ethyl acetate and isoamyl alcohol) show higher losses [22]. Labanda et al. studied the removal of ethanol from a model white wine using membranes of reverse osmosis and nanofiltration. Their analysis was directed to the permeation of aroma compounds during the concentration process and they found high rejections of these

compounds [4]. Meillon et al. used two different types of partially dealcoholized wine by reverse osmosis, in order to study the effect of the dealcoholization on the sensory properties of wines; wine treatment decreased some odour sensations, revealing some unpleasant aroma compounds [8].

This study concerns the comparison of several reverse osmosis and nanofiltration membranes for removing ethanol from a 12 vol.% red wine, for obtaining a beverage with ethanol content of ca. 7 – 8 vol.%, as requested by the company. The wine partial dealcoholization was performed by diafiltration. Water, ethanol and some aroma compounds permeate the membrane and are collected afterwards. The retentate (concentrated wine) is recycled back to the feed tank. The volume on the feed tank is maintained constant by adding water, batch-wise, in the same amount of the collected permeate. It was determined the permeate flux, ethanol and aroma compounds retention and assessed the organoleptic properties of the produced beverages. Finally, it was considered the extraction of aroma compounds from the original wine for adding them back to the dealcoholized wine samples; the aroma compounds were extracted by pervaporation [23,24]. According to EC regulation the beverage obtained by diafiltration of wine below 8.5 vol.% should not be called “wine”; although, for simplicity we refer to hereafter “dealcoholized wine” the resulting beverages.

6.2. Theory

NF and RO processes are used for separating solvents from salts or sugars and their basic principles of separation are the same [16]. Because NF and RO membranes are permeable to solvents and impermeable or less permeable to solutes, the pressure difference across the membrane thickness should be higher than the osmotic pressure difference in order to allow the permeation of water and ethanol from the concentrated solution to the diluted phase. Accordingly, solvent flux (J_A) on NF and RO membranes is given by [16]:

$$J_A = K_A(\Delta P - \Delta\pi) \quad (6.1)$$

where K_A is the permeance towards solvents (also defined as the hydrodynamic permeability coefficient), ΔP is the pressure difference between both sides of the membrane and $\Delta\pi$ is the osmotic pressure difference.

The selectivity of RO and NF membranes can be quantified based on rejection or retention coefficient (R):

$$R_i = 1 - \frac{C_{p,i}}{C_{r,i}} \quad (6.2)$$

where $C_{p,i}$ and $C_{r,i}$ are the concentrations of the compound i in the permeate and retentate sides, respectively.

When the process is carried out by diafiltration, the permeate (made mostly of water and ethanol) crosses the membrane and is continuously removed. The retentate is recycled to the feed tank and the amount of permeate is replaced by the same amount of water, in order to maintain constant the volume and the concentration of non-permeable compounds in the feed tank. According to this, water and ethanol mass balances are given by [16]:

$$Q_w = Q_p \quad (6.3)$$

$$Q_p C_{p,E} = -V_f \frac{dC_{r,E}}{dt} \quad (6.4)$$

where Q_w and Q_p are the flowrates of water and permeate, respectively, $C_{p,E}$ and $C_{r,E}$ are the concentrations of ethanol in the permeate and retentate sides, respectively, V_f is the

feed solution volume and t is the permeation time. Once ethanol concentrations at the permeate and retentate sides are related by the retention coefficient (R) (cf. Eq. (6.2)):

$$C_{p,E} = C_{r,E}(1-R) \quad (6.5)$$

Inserting Eqs. (6.3) and (6.5) into Eq. (6.4) and integrating the last one between the boundary conditions:

$$\begin{cases} t=0; & C_{r,E} = C_{f,E} \\ t=t; & C_{r,E} = C_{r,E}(t) \end{cases}$$

and assuming constant the retention coefficient along the diafiltration process, one obtain:

$$C_{r,E}(t) = C_{f,E} e^{\left[-\frac{Q_w t}{V_f} (1-R) \right]} \quad (6.6)$$

where $C_{f,E}$ is the ethanol concentration in the original feed solution. The total volume of water required (V_w) in a diafiltration time (t) is given by:

$$V_w(t) = Q_w t \quad (6.7)$$

substituting Eq. (6.7) in Eq. (6.6) it gives:

$$C_{r,E}(V_w) = C_{f,E} e^{\left[-\frac{V_w}{V_f} (1-R) \right]} \quad (6.8)$$

Eqs. (6.6) and (6.8) are the ethanol history concentration in the retentate (dealcoholized wine) as a function of the diafiltration time (Eq. (6.6)) or as a function of the amount of water added to the retentate to balance the permeating flux (Eq. (6.8)).

6.3. Materials and methods

6.3.1. Experimental procedure

Alcohol removal experiments from wine were carried out in the experimental set-up sketched in Figure 6.1. This set-up is similar to the one used in Chapter III for dealcoholizing beer by reverse osmosis. The differences are assigned to the separation modules and feed pumps used. In this work a flat-sheet membrane cell from Osmonics (SEPA® CF, with 155 cm² effective membrane area) and a multistage centrifugal pump (P1, Osmonics Tonkoflo, Model SS526X) were used. The original alcoholic wine is pumped from the feed tank (FR) to the membrane cell (MC – cf. Figure 6.1) using a multistage centrifugal pump (P1). A fraction of the feed solution, split from the main stream before entering the membrane cell, was recycled back to the wine tank, through a plate heat exchanger (HE), in order to control the feed flowrate and the temperature. The retentate was also recycled to the wine tank through the same heat exchanger (HE). The permeate was removed continuously from the membrane cell and stored in a glass flask (PR) immersed in an ice bath (B1) in order to avoid the volatilization of the permeate compounds. The permeate flowrate was determined using a graduate cylinder and a stopwatch. The detailed experimental procedure is described in Chapter III (section 3.3.1).

The separation was carried out in semi-continuous mode – diafiltration. Deaerated and deionized water was added batch-wise, after a diafiltration period, to balance the permeation volume. With this procedure the concentration of the non-permeable compounds remained approximately constant in the retentate while the concentration of permeable compounds, such as ethanol (and some aroma compounds), decreased. Samples of wine retentate and permeate were collected for analysis during the diafiltration period.

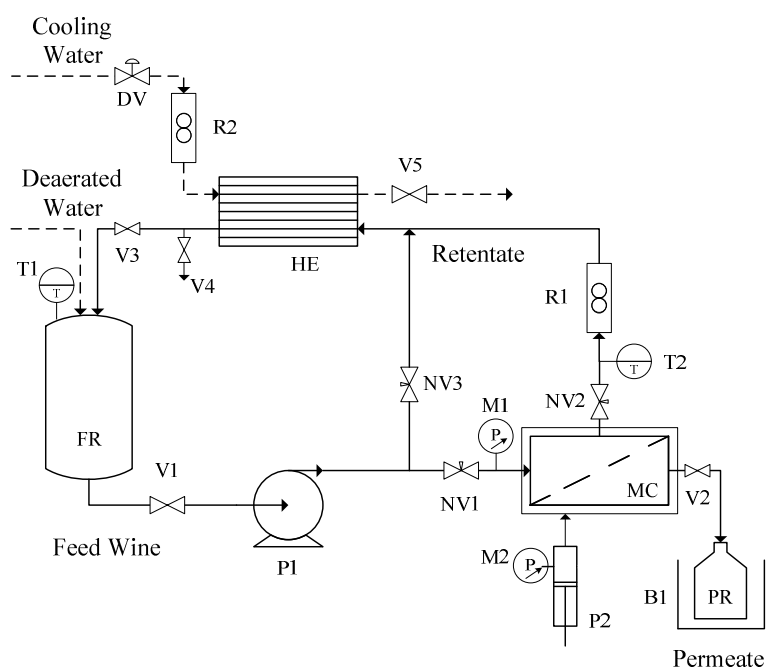


Figure 6.1. Sketch of the dealcoholization lab unit (FR, feed reservoir; P1, multistage centrifugal pump; MC, membrane cell; HE, heat exchanger; PR, permeate reservoir; B1, ice bath; R1 and R2, rotameters; NV1, NV2 and NV3, needle valves; DV, diaphragm valve; V1 to V5; on/off valves; T1, PT100; T2, thermocouple; M1 and M2, manometers; P2, pneumatic sealing pump).

Pervaporation experiments were performed using a POMS/PEI membrane with an effective area of 107.5 cm^2 . The aroma compounds from the feed wine were selectively permeated through the membrane due to the vacuum that was applied on the downstream side of the membrane. Once the aroma compounds leave the membrane as vapour, they have to be condensed and collected under cryogenic temperatures. The extracted aroma compounds were then added to the dealcoholized wine samples, previously obtained in alcohol removal experiments. The detailed operation of the pervaporation set-up is described in Chapter II (section 2.2.3).

6.3.2. Membranes

In the present work, one reverse osmosis and four nanofiltration membranes were evaluated for removing ethanol from wine; Table 6.1 shows the membranes properties. A POMS/PEI membrane was used for pervaporating wine aroma compounds (cf. Chapter IV, section 4.2.3).

Table 6.1. Properties of the membranes used for removing alcohol from wine.

Membrane	Supplier	Process	Type	MMCO ^a (g·mol ⁻¹)	R_{NaCl} / R_{MgSO_4} (%)	P^b (bar)	T^b (°C)	pH ^b
CA995PE	Alfa Laval	RO	Cellulose triacetate/diacetate blend on polyester	200	>95 (2000 ppm NaCl, 29.3 bar, 25 °C)	1 – 50	0 – 30	5 – 6.5
NF99 HF	Alfa Laval	NF	Polyamide type thin film composite on polyester	200	>98 (2000 ppm MgSO ₄ , 9 bar, 25 °C, pH 8, 15% recovery)	1 – 55 (30 °C)	0 – 50 (33 bar)	3 – 10 (25 °C)
NF97	Alfa Laval	NF	Polyamide type thin film composite on polyester	200	>97 (2000 ppm MgSO ₄ , 9 bar, 25 °C, pH 8, 15% recovery)	1 – 55 (30 °C)	0 – 50 (33 bar)	3 – 10 (25 °C)
NF99	Alfa Laval	NF	Polyamide type thin film composite on polyester	200	>98 (2000 ppm MgSO ₄ , 9 bar, 25 °C, pH 8, 15% recovery)	1 – 55 (30 °C)	0 – 50 (33 bar)	3 – 10 (25 °C)
YMHLSP1905	GE Osmonics	NF	N/A	N/A	>98 (MgSO ₄)	N/A	N/A	3 – 9 (25 °C)

^a Molecular mass cut-off^b Recommended operation limits

N/A – not available

6.3.3. Analytical methods

The dealcoholization experiments were performed with red wine from the same fermentation batch, stored in 20 L barrels at 5 °C. It was determined the ethanol concentration (Alcolyzer Plus and DMA 4500 densitometer, Anton Paar) in the original feed wine, in the permeate and retentate as a function of the permeation time. The residual sugar, which corresponds to the amount of sugars remaining in wine after fermentation, were analysed with a densitometer (DMA 4500, Anton Paar) in the original and dealcoholized wine samples. The aroma compounds were analysed by gas chromatography, in the original wine, in the retentate and permeate, for evaluating their loss. Different volatile aroma compounds, representing different chemical groups, were analysed. The aroma compounds controlled were: acetaldehyde – *Ac*, propanol – *Pr*, isobutanol – *iB*, amyl alcohols – *AA* (2-methylbutanol plus 3-methylbutanol), ethyl acetate – *EA* and isoamyl acetate – *iAA*; the analytical method is described in Chapter II (section 2.2.1). Tartaric acid, the main compound responsible for the wine acidity and which contributes to the flavour and freshness of the wine, was analysed by titration with a sodium hydroxide solution ($0.25 \text{ mol}\cdot\text{L}^{-1}$), in the original and dealcoholized wine samples.

The sensorial analysis of the final products was performed by a trained panel of seven tasters. The beverage samples were presented in glasses, at room temperature and each member was asked to characterize the samples in terms of colour, aroma, taste, body, acidity, astringency and to compare with the original alcoholic wine. The scale used reflected the proximity of the dealcoholized beverage quality to the original wine (100 is the maximum and corresponds to original wine).

6.4. Results and discussion

The main objective of this study is obtaining a low alcohol wine (alcohol content of ca. 7 – 8 vol.%) from a natural red wine with an alcohol content of ca. 12 vol.%, using a simple or combined membrane process. Various membranes of reverse osmosis and nanofiltration were evaluated for removing ethanol from the original wine. In a first step, all membranes were used for alcohol removal experiments, at 15 bar of feed-permeate pressure difference (the maximum allowed by the multistage centrifugal pump), $2 \text{ L}\cdot\text{min}^{-1}$ of feed flowrate (the maximum flowrate provided by the feed pump at the selected pressure) and 30 °C. At this temperature, wine is not subject to thermal degradation,

preserving its sensorial characteristics [25]. Besides, higher temperature also originates higher permeate flowrates. During these experiments the membranes were evaluated according to their permeate flux, ethanol and aroma compounds rejection and the organoleptic properties of the obtained dealcoholized wine samples; from now on named single step dealcoholized wine samples. The most promising membranes were selected and a second batch of alcohol removal experiments was performed at the same operating conditions as before. However, in this second step the ethanol removal time was extended to obtain dealcoholized wine samples of ca. 5 vol.% of ethanol. These dealcoholized wine samples were then blended with fresh original wine, for producing a low alcohol beverage with ca. of 7 – 8 vol.% of ethanol; from now on called reconstituted wine samples.

6.4.1. Ethanol rejection and permeate flux

The performance of the selected membranes was evaluated based on the permeation flux, rejection of ethanol and aroma compounds and based on the sensorial analysis. An ideal membrane for producing low alcohol wines should present a high permeation flux, have a low ethanol and high aroma compounds rejections and the dealcoholized beverage should exhibit an excellent sensorial analysis, comparing to the original wine. Table 6.2 shows the concentration of ethanol in the permeate, the ethanol rejection and permeate flux obtained after 150 min of operation; there were performed replicates with three membranes. Replicates with the same membrane originated similar results, except for NF99 HF flux, which can be related to some membrane fouling after the first run. Figure 6.2 shows the normalized membrane flux as a function of the normalized ethanol rejection for all membranes; the maximum values of membrane flux and ethanol rejection are given in Table 6.2. The evaluated membranes show very similar ethanol rejection except membrane CA995PE that shows the lowest ethanol rejection (see Table 6.2 and Figure 6.2). Concerning the permeate flux, membrane NF99 HF shows the highest permeation while membrane CA995PE shows the lowest one. Membranes NF99 and YMHLS1905 present the best compromise between permeate flux and ethanol rejection (see Table 6.2 and Figure 6.2); as a result, they seem to be the most promising membranes for wine dealcoholization. NF99 HF is also a promising membrane for dealcoholizing wine. Although it presents high rejection to ethanol, this membrane allows high rates of ethanol removal, due to its higher flux. Despite the producers suggesting that all

membranes have the same molecular mass cut-off (cf. Table 6.1), polyamide nanofiltration membranes showed higher ethanol retention than the RO cellulose acetate membrane.

Table 6.2. Ethanol concentration in the permeate, ethanol rejection and permeate flux, after 150 min of operation.

Membrane	$C_{p,E}$ (vol.%)	R_E (%)	$J_p \times 10^3$ ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
NF99 HF – 1	10.5	10.3	7.10
NF99 HF – 2	10.9	9.1	5.90
NF97	10.9	9.0	1.48
CA995PE	11.6	2.5	1.41
NF99 – 1	10.9	8.4	5.15
NF99 – 2	10.9	8.0	4.83
YMHLS1905 – 1	11.2	7.1	4.55
YMHLS1905 – 2	11.1	6.7	4.13

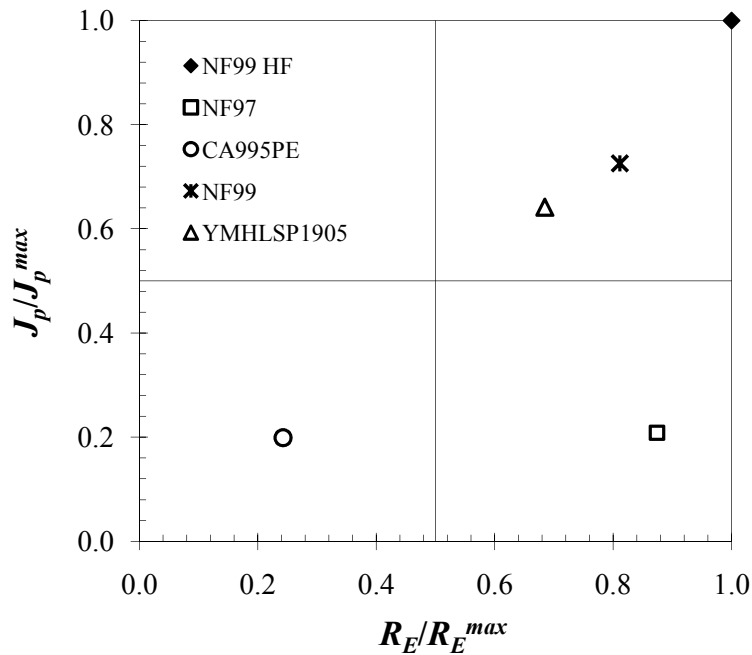


Figure 6.2. Normalized membrane flux and ethanol rejection for membrane comparison.

Figures 6.3 and 6.4 show the ethanol concentration history on the retentate, during the diafiltration process. Ethanol concentration is represented as a function of the volume of added diafiltration water (or collected permeate volume) (Figure 6.3 and Eq. (6.8)) and

as a function of the diafiltration time (Figure 6.4 and Eq. (6.6)). It can be observed that Eq. (6.8) describes well the experimental results for all membranes (see Figure 6.3). The results are consistent with the ones presented in Table 6.2, for lower flux membranes; membrane CA995PE shows the lowest ethanol rejection, while NF97 membrane shows the highest one. Membranes NF99 HF, NF99 and YMHLS1905 show similar ethanol rejection. The order of values is quite different from Table 6.2 because this table considers the concentration of the accumulated permeate after 150 min of operation. In fact, for high flux membranes, the addition of diafiltration water was performed batch-wise two or three times during the 150 min of operation in order to maintain the concentration of non-permeable species constant in the feed tank and then the osmotic pressure.

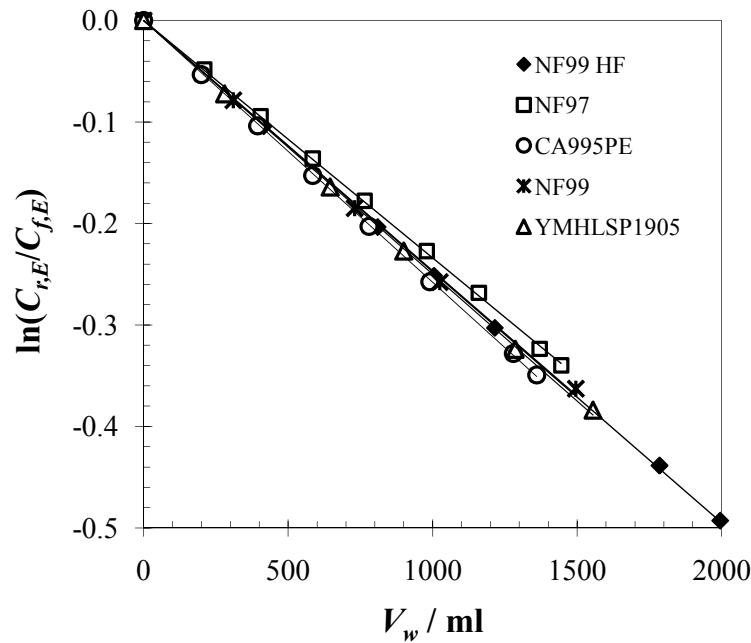


Figure 6.3. Ratio between the ethanol concentration in the retentate and original feed as a function of the volume of added water (dots – experimental values; lines – model, Eq. (6.8)).

Figure 6.4 shows the ethanol concentration on the retentate as a function of permeation time. Since the membranes show similar ethanol rejection, one can say that the slope is mostly related to the membrane flux. Thus, membranes NF99 HF, NF99 and YMHLS1905 show higher permeate fluxes while membranes CA995PE and NF97 show lower fluxes. These results are consistent with the ones presented in Table 6.2. Membranes

NF99 HF, NF99 and YMHLSP1905 show a more equilibrate behaviour between permeation and ethanol rejection.

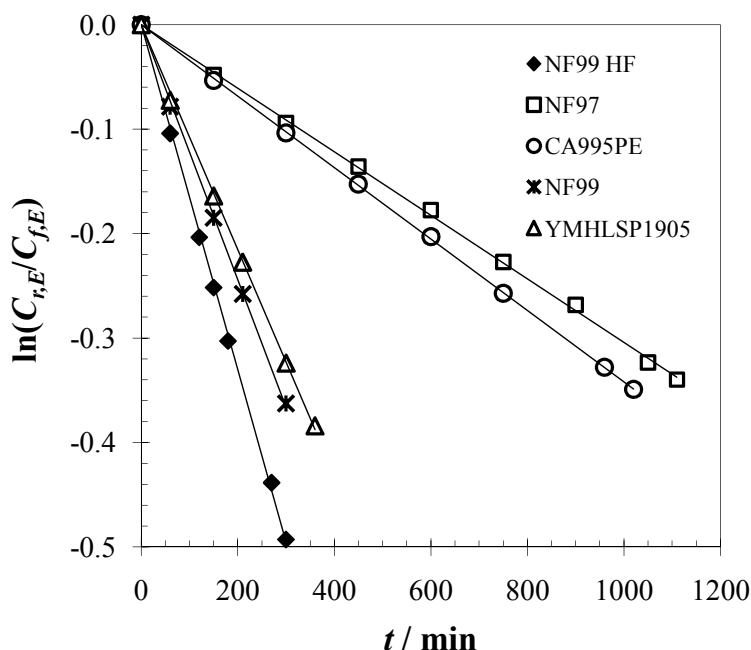


Figure 6.4. Ratio between the ethanol concentration in the retentate and original feed as a function of permeation time (dots – experimental values; lines – model of Eq. (6.6)).

6.4.2. Aroma compounds rejection

Besides the permeate flux and ethanol rejection, the membranes were evaluated concerning their rejection to wine aroma compounds. Table 6.3 shows the concentration of aroma compounds on the permeate as a function of the permeation time and the permeate volume. For low flux membranes, NF97 and CA995PE, it was collected only one sample, after 150 minutes, while for high flux membranes, there were collected two or three samples. For these membranes, the concentration of aroma compounds shows insignificant variations with the permeation time. For comparing the aroma rejection of the membranes one can use the values obtained for $t=150$ min. As a result, the rejection of aroma compounds can be compared for all membranes at instant 150 min. Experiments performed with the same membrane indicate a good reproducibility of results, except for NF99 HF flux, as referred before.

Table 6.3. Cumulative concentration of aroma compounds on the permeate as a function of the permeation time and permeate volume.

Membrane	<i>t</i> (min)	<i>V_p</i> (ml)	<i>C_{p,E}</i> (vol.%)	<i>C_{p,Ac}</i> (mg·L ⁻¹)	<i>C_{p,Pr}</i> (mg·L ⁻¹)	<i>C_{p,iB}</i> (mg·L ⁻¹)	<i>C_{p,AA}</i> (mg·L ⁻¹)	<i>C_{p,EA}</i> (mg·L ⁻¹)	<i>C_{p,iAA}</i> (mg·L ⁻¹)
NF99 HF – 1	60	415	11.30	1.06	25.71	29.17	155.62	54.29	0.32
	120	810	10.79	1.04	24.06	27.02	144.24	52.00	0.32
	150	1005	10.51	1.03	23.49	26.28	140.29	50.51	0.31
NF99 HF – 2	60	355	11.58	1.14	25.90	28.95	153.29	56.09	0.37
	120	680	11.12	1.16	24.78	27.40	144.76	54.56	0.36
	150	835	10.87	1.15	24.11	26.62	140.47	53.31	0.35
NF97	60	-	-	-	-	-	-	-	-
	120	-	-	-	-	-	-	-	-
	150	210	10.86	0.43	20.33	10.81	50.06	46.86	0.08
CA995PE	60	-	-	-	-	-	-	-	-
	120	-	-	-	-	-	-	-	-
	150	200	11.64	2.13	27.58	42.86	247.31	58.84	0.48
NF99 – 1	60	310	11.20	1.60	23.15	24.26	123.61	52.35	0.22
	120	-	-	-	-	-	-	-	-
	150	730	10.90	1.62	22.93	23.72	120.89	51.00	0.23
NF99 – 2	60	275	11.38	1.67	23.88	25.00	126.52	55.06	0.26
	120	-	-	-	-	-	-	-	-
	150	685	10.95	1.73	23.36	24.38	123.60	53.78	0.27
YMHLSP1905 – 1	60	280	11.56	2.24	25.96	31.69	172.12	57.80	0.36
	120	-	-	-	-	-	-	-	-
	150	645	11.19	2.30	25.29	30.54	165.52	56.38	0.37
YMHLSP1905 – 2	60	245	11.48	2.39	25.89	30.99	166.31	57.55	0.40
	120	-	-	-	-	-	-	-	-
	150	585	11.14	2.48	25.75	30.39	163.96	56.94	0.39

Figure 6.5 shows the rejection of aroma compounds for each membrane read after 150 min of operation. Membrane NF97 shows the highest rejection for all compounds, followed, in general, by membranes NF99, NF99 HF, YMHLS1905 and CA995PE. Concerning the overall aroma compounds rejection, membrane NF97 exhibits the best behaviour, above 70 %, which allows producing dealcoholized wine with higher aroma content, while membrane CA995PE shows the lowest overall aroma compounds rejection, below 10 %. These results are in agreement with the ones obtained for ethanol rejection. On the other hand, other authors reported that polyamide membranes show higher rejections to aroma compounds than cellulose acetate membranes [14]. It can be seen that the aroma compounds rejection of the membranes decreases according to the following order: acetaldehyde > isoamyl acetate > amyl alcohols, isobutanol > propanol, ethyl acetate; except for membrane CA995PE that shows lower rejection for isobutanol and amyl alcohols. On the other hand, all membranes show higher rejection to aroma compounds than to ethanol, which is advantageous for the dealcoholization process, allowing the production of low alcohol wine with a minimal aroma loss. The rejection increases with the molecular weight of the compounds, except for acetaldehyde and ethyl acetate. For these two compounds, the mass transport should be controlled by the affinity to the membranes.

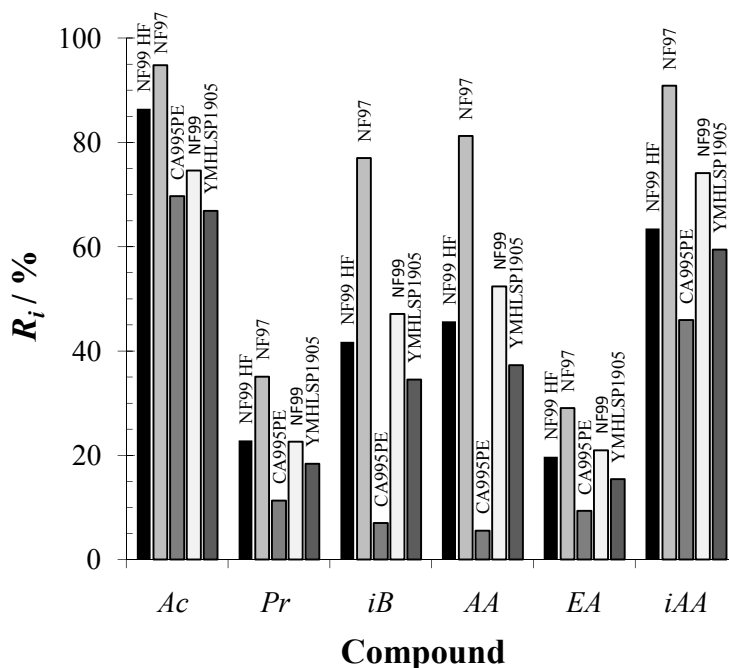


Figure 6.5. Aroma compounds rejection for each membrane.

6.4.3. Product characterization

After membranes characterization in terms of permeate flux, ethanol and aroma compounds rejection, it was analysed the physicochemical and organoleptic properties of the dealcoholized wine samples. The membranes were used to produce single step dealcoholized wine samples with an ethanol content of ca 7 – 8 vol.% (cf. Table 6.4). Because samples were collected and analysed off-line, the final ethanol concentration varies a little from sample to sample. Membranes with higher flux (membranes NF99, NF99 HF and YMHLSP1905) were used for producing reconstituted wine samples based on deep dealcoholized samples (ca. 5 vol.%) and subsequent blending with fresh original wine to obtain 7 vol.% of ethanol. Table 6.4 shows the original wine and dealcoholized wine properties for each membrane and for both methods. Regarding the residual sugar (*RS*) concentration, all samples show slightly lower values than the original wine; NF97 and NF99 samples show the highest values. Comparing the acidity of wine samples, the tartaric acid (*TA*) content decreased for the dealcoholized samples produced by each membrane (being the NF97 the less permeable to the acids) although all samples show similar pH. Concerning the composition of volatile aroma compounds, the membrane that produced the wine with general higher concentration (closer to the original wine) was membrane NF97 and the membrane that originated, in general, the lowest concentration was membrane CA995PE. These results are in agreement with the aroma compounds rejection determined before (see Figure 6.5); the higher the rejection, the higher the concentration of the aroma compounds in the dealcoholized wine. The results of the reconstituted wines are close to the correspondent single step dealcoholized wines. For all samples, it was observed an increase in the acetaldehyde concentration. This increase should be related to the wine oxidation during the ethanol removal process since this effect was more significant in experiments with higher dealcoholization time (NF97, CA995PE and removal of ethanol down to ca. 5 vol.%).

Table 6.4. Characterization of wine samples before and after dealcoholization for each membrane and method.

Membrane	Residual				pH	$C_{r,Ac}$ (mg·L ⁻¹)	$C_{r,Pr}$ (mg·L ⁻¹)	$C_{r,iB}$ (mg·L ⁻¹)	$C_{r,AA}$ (mg·L ⁻¹)	$C_{r,EA}$ (mg·L ⁻¹)	$C_{r,iAA}$ (mg·L ⁻¹)
	$C_{r,E}$ (vol.%)	Sugar (wt.%)	$C_{r,TA}$ (g·L ⁻¹)								
Original wine	11.9	2.7	5.3		3.6	7	31	46	261	65	0.9
NF99 HF – 1	7.2	2.4	4.3		3.6	12	20	36	209	41	0.6
NF99 HF – 2	7.0	2.5	4.4		3.6	10	20	35	206	39	0.6
NF97	8.5	2.6	4.9		3.6	14	24	43	251	47	0.6
CA995PE	8.4	2.4	4.4		3.6	14	22	35	199	46	0.5
NF99 – 1	8.3	2.5	4.4		3.6	8	22	38	222	46	0.7
NF99 – 2	7.0	2.5	4.1		3.7	10	20	35	212	39	0.6
YMHLS1905 – 1	8.2	2.5	4.4		3.6	9	22	36	212	45	0.6
YMHLS1905 – 2	7.0	2.4	4.2		3.6	11	19	33	194	39	0.6

1 – single step dealcoholized wine samples; 2 – reconstituted wine samples

Once the quality of wine depends on the balance between the ethanol content, acidity, aroma and taste, the dealcoholized samples were submitted to a sensorial analysis (SA) performed by a trained panel of tasters. The wine samples were evaluated according to their colour, aroma, taste, body, acidity, astringency, and compared to the original wine. Tasters were asked to sort the wine samples according to their overall preference, taking into account the above-mentioned wine characteristics. Figure 6.6a shows the analytical and sensorial analyses of the original wine and single step dealcoholized wine samples. Membrane NF97 produced the wine sample with the closest aroma profile to the original wine. Despite this, the sample originated the worst sensorial analysis; tasters mentioned unbalanced aroma profile. Membrane CA995PE produced the wine sample with the poorest aroma profile and a poor sensorial analysis; tasters referred a diluted sensation. The membranes with better results on sensorial analysis were YMHLSP1905 and NF99. Membrane NF99 HF produced wine samples with good aroma profile, good equilibrium between ethanol, aroma and taste, close to the original wine. However, these samples have a high astringency that can be easily corrected or improved. According to sensorial analysis, membranes YMHLSP1905, NF99 and NF99 HF showed the best results, exhibiting an aroma and taste profiles close to the original wine; moreover, these membranes are also the most permeable ones (cf. Table 6.2).

Figure 6.6b shows the analytical and sensorial analyses of the original and reconstituted wine samples. Membranes NF99 and NF99 HF show a similar performance when used for producing single step dealcoholized wine samples or reconstituted wine samples, while YMHLSP1905 membrane present a better performance for producing reconstituted wine samples (better SA results). It seems that blending dealcoholized wine with fresh original wine can improve some aroma and taste sensations of the reconstituted wine. However, reconstituted wine is more time consuming to produce and other aroma sensations, like oxidation notes, can appear after a long dealcoholization time.

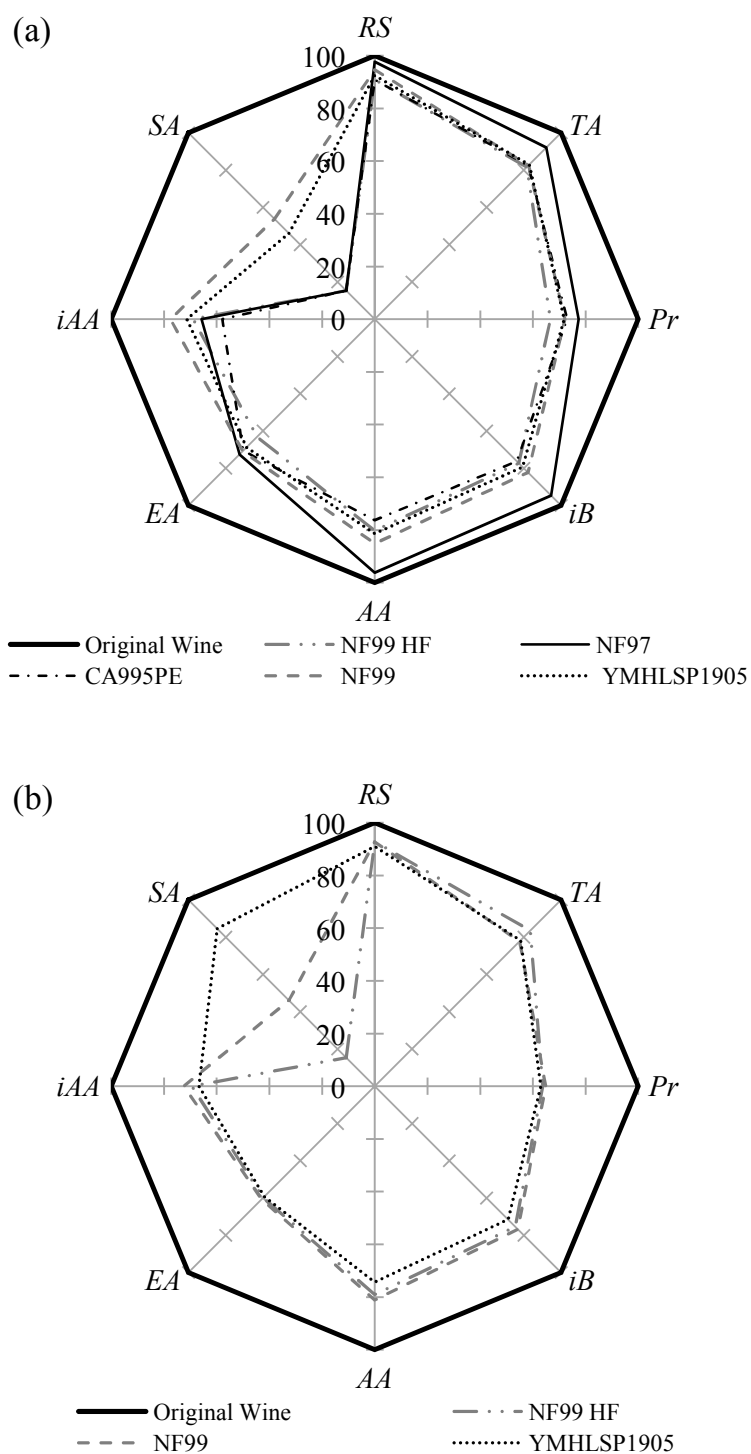


Figure 6.6. Analytical and sensorial analyses of dealcoholized wine samples and the original wine: (a) single step dealcoholization method; (b) reconstituted wine samples.

6.4.4. Aroma compounds recovery

Nanofiltration membranes (YMHLSP1905, NF99 and NF99 HF) showed to be very effective for removing alcohol from wine, originating low ethanol wine samples with good aroma profile, close to the original wine. Nevertheless, it is possible to improve the aroma and taste profiles by adding aroma compounds previously extracted from the original wine.

Pervaporation proved to be an effective process for recovering aroma compounds that are lost during beverages processing such as dealcoholization or concentration [23,24,26,27]. In the present study the aroma compounds were extracted using a composite POMS/PEI membrane operated at temperature 12 °C, and permeate pressure of 1.0 mbar; the permeate stream was condensed using a liquid nitrogen trap. These conditions were selected based on the previous study made with beer, as described in Chapter IV (section 4.3.3). It was added 0.3 vol.% of extracted aroma to dealcoholized wine samples. Table 6.5 shows the concentration of ethanol and aroma compounds of dealcoholized wine samples obtained after aroma correction. These wine samples show higher concentration of aroma compounds, especially esters, compared to the uncorrected dealcoholized samples; as reported before, POMS/PEI membranes are more selective to esters than to higher alcohols (cf. sections 2.3.1 and 4.3.2). On the other hand, the addition of extracted aroma did not significantly increase the ethanol content of the dealcoholized samples, due to the high selectivity of the pervaporation membrane to the aroma compounds compared to ethanol. In general, the perception of the tasters of the wine samples was that of a beverage with an aroma and taste typical of a natural wine.

Table 6.5. Characterization of wine samples before dealcoholization and after dealcoholization with incorporation of pervaporated aroma.

Membrane	$C_{r,E}$ (vol.%)	$C_{r,Ac}$ (mg·L ⁻¹)	$C_{r,Pr}$ (mg·L ⁻¹)	$C_{r,iB}$ (mg·L ⁻¹)	$C_{r,AA}$ (mg·L ⁻¹)	$C_{r,EA}$ (mg·L ⁻¹)	$C_{r,iAA}$ (mg·L ⁻¹)
Original wine	11.9	7	31	46	261	65	0.9
NF99 HF – 1	7.3	12	21	37	222	55	0.8
NF99 HF – 2	7.1	10	20	36	219	53	0.8
NF97	8.6	14	24	45	264	62	0.8
CA995PE	8.6	14	23	37	212	60	0.7
NF99 – 1	8.4	9	23	39	235	60	0.9
NF99 – 2	7.1	10	20	37	224	54	0.9
YMHLS1905 – 1	8.3	9	23	38	225	59	0.9
YMHLS1905 – 2	7.1	11	20	35	207	53	0.8

1 – single step dealcoholized wine samples; 2 – reconstituted wine samples

Figure 6.7 shows the analytical and sensorial analyses of the wine dealcoholized samples, after addition of aroma recovered by pervaporation. The addition of the extracted aroma compounds partially corrects the profile of the dealcoholized sample towards the original wine sample. It can be concluded that pervaporation coupled to nanofiltration is a good approach for obtaining high quality low alcohol wines.

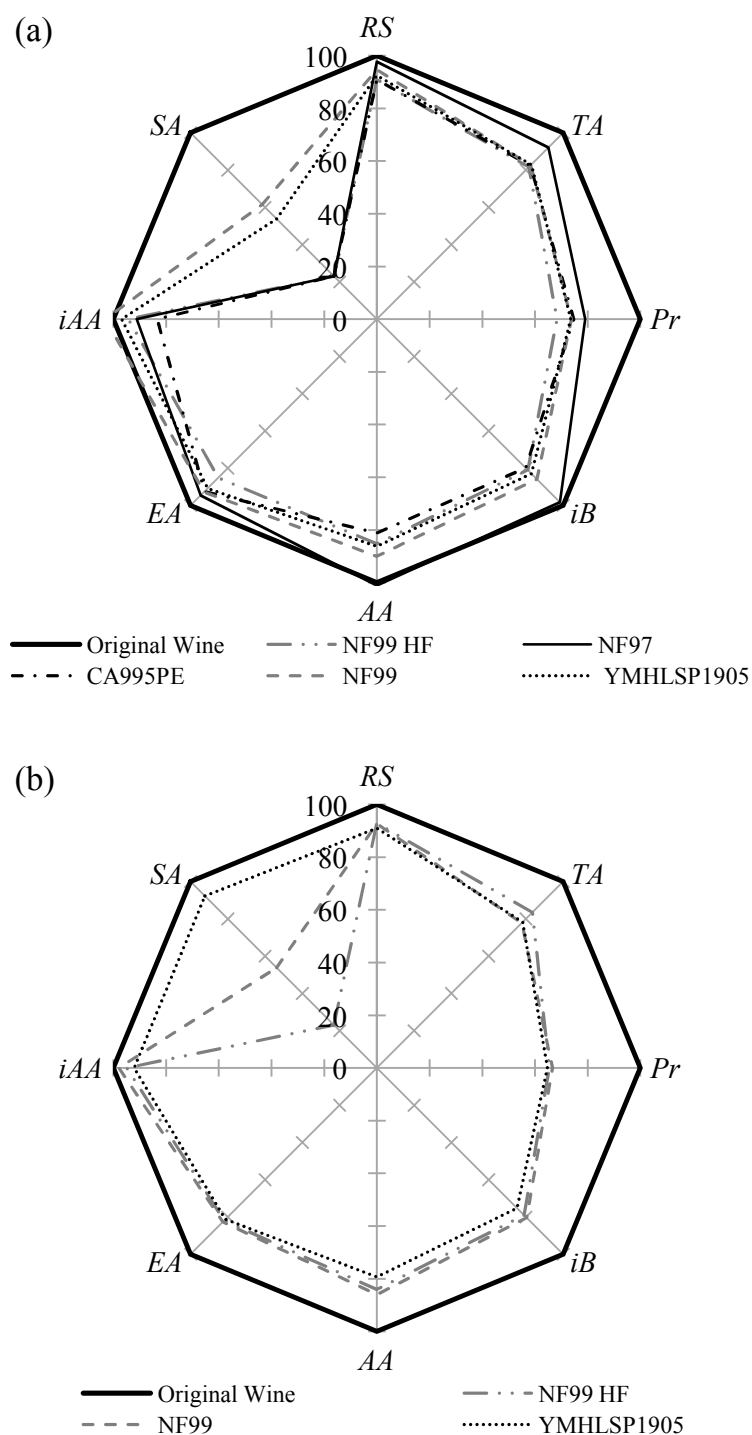


Figure 6.7. Analytical and sensorial analyses of original wine and aroma enriched samples:
(a) single step dealcoholization method; (b) reconstituted wine samples.

6.5. Conclusions

In this chapter, a combination between two membrane processes was investigated for producing a high quality low alcohol wine from a standard alcoholic wine (ca. 12 vol.% of ethanol). Various membranes of reverse osmosis and nanofiltration (CA995PE, NF99 HF, NF99, NF97 from Alfa Laval and YMHLSP1905 from Osmonics) were used for removing the ethanol, by diafiltration. In the first approach, all membranes were used for removing the ethanol from ca. 12 vol.% to ca. 7 – 8 vol.% (single step dealcoholization). Then, the most promising membranes (NF99 HF, NF99 and YMHLSP1905) were used for dealcoholizing the original wine down to ca. 5 vol.%. The resulting dealcoholized wine samples were then blended with the original wine to produce reconstituted wine samples. Finally, it was added 0.3 vol.% of an aroma extract obtained by pervaporation of the original wine to the wine samples produced by the two methods, single step dealcoholization and reconstituted method, improving the aroma and taste profile of these samples.

The performance of the dealcoholization membranes was evaluated taking into account the membrane flux, ethanol rejection, aroma compounds rejection and organoleptic properties of the resulted dealcoholized wine samples. Reverse osmosis membrane, CA995PE, showed the lowest ethanol rejection, which is good for the dealcoholization process, but also showed the lowest permeate flux. Nanofiltration membrane NF97 showed low flux as well as high ethanol rejection, making this membrane also unsuitable for this application. On the other hand, membranes NF99 HF, NF99 and YMHLSP1905 showed high fluxes and acceptable ethanol rejection. Concerning aroma compounds (higher alcohols and esters), membrane NF97 showed the highest rejection. The aroma rejection coefficients decrease following the order NF99, NF99 HF, YMHLSP1905 and CA995PE. Membrane NF97 produced dealcoholized wine samples with residual sugar content, acidity and volatile aroma compounds closer to the original wine. However, these wine samples failed on the sensorial analysis due to unbalanced aroma and taste. Membrane CA995PE presented the worst results concerning aroma compounds content and sensorial analysis. Membranes YMHLSP1905 and NF99 produced the dealcoholized wine samples with the most equilibrated analytical aroma profile and sensorial analysis. Membrane NF99 HF produced wines with good aroma profile, well balanced, but failed in the sensorial analysis because of the high astringency. In addition,

membranes YMHLSP1905, NF99 and NF99 HF showed similar performances when employed for producing wine samples by the two methods.

Finally, it was studied the extraction of aroma compounds from the original wine by pervaporation. The aroma compounds were extracted using a composite POMS/PEI membrane and the extract added (0.3 vol.%) to the dealcoholized wine samples. It was observed that the volatile aroma compounds concentration, especially the esters, increased in the corrected dealcoholized wine samples without significantly increasing the ethanol concentration. On the other hand, the incorporation of the extracted aroma compounds originated dealcoholized wine samples with a sensorial perception closer to that of a natural alcoholic wine.

Concerning all indicators, it was concluded that nanofiltration membranes YMHLSP1905, NF99 and NF99 HF are the most effective for producing low alcohol wine. In addition, the incorporation of aroma compounds obtained by pervaporation of the original wine into the dealcoholized samples originates a high quality low alcohol wine.

6.6. List of symbols

C	concentration (vol.%, wt.% or $\text{mg}\cdot\text{L}^{-1}$)
J	flux ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
k_A	solvent permeance ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{bar}^{-1}$)
P	pressure (bar)
Q	flowrate ($\text{L}\cdot\text{min}^{-1}$)
R	rejection or retention coefficient (%)
RS	residual sugar (wt.%)
SA	sensorial analysis (–)
t	time (s or min)
TA	tartaric acid ($\text{g}\cdot\text{L}^{-1}$)
V	volume (L or ml)

Greek letters

Δ	absolute difference (–)
π	osmotic pressure (bar)

Subscripts

A	solvent
AA	amyl alcohols
Ac	acetaldehyde
E	ethanol
EA	ethyl acetate
f	feed
iAA	isoamyl acetate
iB	isobutanol
p	permeate
Pr	propanol
r	retentate
w	water

6.7. References

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Chapter VII

7. General conclusions and future work

7.1. Main conclusions

The research work developed during the present thesis aimed mainly the study of an innovative technology for producing non-alcoholic beer (ethanol content less than 0.5 vol.%) with an aroma profile similar to the typical alcoholic beers. As the usual method for producing non-alcoholic beer – interrupting the fermentation – leads to a restriction on the reduction of wort carbonyl compounds (aldehydes) and a consequent decrease on the formation of important beer aroma species, it was challenged to use separation processes for achieving the proposed main goal. This approach considers the production of the non-alcoholic beer using physical separation processes applied to a completely fermented beer (ethanol content around 5.5 vol.%). During this thesis it was studied the performance of reverse osmosis and vacuum distillation (spinning cone column) on the ethanol removal from beer. Reverse osmosis operating in diafiltration mode uses an ethanol permeable membrane (and thus ethanol is removed through the permeate side), while the SCC distillation uses a stripping medium (water vapour) that removes the ethanol from the original beer. The mutual disadvantage of these dealcoholization processes is the loss of important aroma compounds. For overcoming the loss of aroma compounds, it was proposed to recover them by pervaporation before beer being submitted to dealcoholization and adding them to the dealcoholized beer. The core of this thesis was the study of pervaporation extraction of beer aroma compounds, such as higher alcohols and esters, and designing the industrial plant now installed in the company (Unicer). The process developed proved to produce a very successful beer with a balanced aroma profile, similar to the original one.

Beer dealcoholization

During the development of this thesis, two ethanol removal processes were studied. Reverse osmosis operating in diafiltration mode is effective for achieving an ethanol content on the dealcoholized beer below 0.5 vol.%. Besides, beer is treated at room temperature or even lower, which is suitable for protecting heat sensitive compounds. It was concluded that acetate cellulose (CA) RO membrane is the most efficient for removing ethanol from beer due to its higher permeate flux and lower ethanol rejection. Main operating conditions, such as feed pressure, feed temperature and feed flowrate, affect directly the permeate flux and RO membranes rejection. It was observed that permeate flux increases with the feed pressure. The CA membrane rejection to ethanol and higher alcohols also increases as the feed pressure increases, while the rejection to esters decreases. Permeate flux increases with feed temperature while membrane rejection decreases. Feed flowrate has a positive effect on the permeate flux while it has a marginal effect on aroma compounds rejection (minimal concentration polarization). As a result, high feed pressures, low feed temperatures and high feed flowrates should be used for ethanol removal from beer and assuring a good rejection of important aroma compounds.

Despite the good effectiveness of reverse osmosis for removing ethanol from beer, this process proved to be unfeasible for industrial dealcoholization of beer for very low values of ethanol, lower of 0.45 vol.%. This disadvantage is related to the diafiltration operation mode, which leads to a significant increasing water consumption as ethanol is being removed.

Heat treatment processes are highly effective for dealcoholizing beer to ethanol contents down to 0.05 vol.%. However, high temperatures can damage beer aroma compounds. During this work, it was studied the use of a spinning cone column for dealcoholizing beer once it has advantages over typical distillation columns. The contact time in SCC is low and the working temperatures are moderate due to the applied vacuum. These characteristics minimize the thermal impact on the beer compounds. The distillation is carried out under high turbulent flows with high contact area between beer and vapour, resulting in an increased ethanol removal. SCC distillation was successfully applied for dealcoholizing beer at industrial level, producing beer with less than 0.05 vol.%.

Both separation processes lead to a loss of important beer aroma compounds such as higher alcohols and esters. SCC distillation has, however, a more severe impact on aroma compounds loss.

Recovery of beer aroma compounds

It was studied the use of pervaporation for extracting aroma compounds from a fresh and clarified alcoholic beer. This study comprised the research laboratory work as well as the definition of the operating and design conditions needed for building the industrial plant.

In a first phase of the project, several pervaporation membranes made of PDMS (polydimethylsiloxane) and POMS (polyoctylmethylsiloxane) were tested and compared. PDMS membranes showed higher permeate flux while POMS membranes showed higher selectivity towards aroma compounds over ethanol. Thus, the POMS membranes permeate can be easily added to the dealcoholized beer for improving the aroma profile, without increasing the ethanol content significantly. The thinner POMS membrane supported in PEI (polyetherimide), ca. 1 μm thick, exhibited the best results concerning the aroma compounds selectivity and permeance. After a preliminary study for assessing the effect of the feed temperature, feed pressure, feed velocity and permeate pressure on the aroma extraction, it was concluded that the feed pressure did not affect significantly the pervaporation performance while the other operating parameters play a significant role.

The surface response methodology (RSM) with central composite design (CCD) was then used to design the experiments needed to be performed for modelling the effect of feed temperature, feed velocity and permeate pressure on the pervaporation flux and selectivity. It was concluded that the second order polynomial fitting models represent well the experimental results inside the operating range. These models, concerning pervaporation flux and selectivity, were also used to interpolate the influence of operating conditions on the process responses. Generally, the feed temperature and permeate pressure affect the permeate flux and higher alcohols selectivity in the same direction, while the esters selectivity is affected reversely. Feed velocity has a higher positive influence on esters selectivity, more than for higher alcohols. It was also concluded that POMS membranes are more selective towards esters, which enhances the effect of concentration polarization. After the esters, acetaldehyde is the compound more permeable, followed by higher alcohols and finally by ethanol. RSM was also used for optimizing the operating conditions, considering a trade-off between all the controlled responses. It can be referred that RSM is very effective on predicting the effect of operating factors on the process responses. It is possible namely to tune the permeate aroma profile playing with the operating conditions.

Industrial combined process

After the selection of the most effective membrane and determining the role of the operating variables for extracting aroma compounds from beer, it was designed and assembled an industrial pervaporation plant. This unit was designed to be integrated in the industrial production of non-alcoholic beer at Unicer (Leça do Balio, Portugal). It was observed at lab scale that the extracted aroma from the original beer is more appealing than the aroma extracted from SCC dealcoholization side streams. Thus, the industrial production of non-alcoholic beer considered the pervaporation of beer before this being submitted to dealcoholization. The correction of aroma profile of the dealcoholized beer is obtained adding a fraction (ca. 5 – 10 vol.%) of fresh original beer and extracted aroma compounds from the pervaporation plant (ca. 0.3 vol.%), resulting an improved non-alcoholic beer with less than 0.5 vol.% of ethanol.

The industrial pervaporation plant comprises four envelope membrane modules of POMS/PEI (40 m²) and the permeate pressure range is between 1 mbar and 8 mbar. It uses two sets of condensers with two condensers each. The condensation temperature ranges between -75 °C and -85 °C. Several experiments for optimizing the aroma compounds extraction from the beer were performed in the industrial pervaporation plant. The optimized operation mode considers the operation in batch-wise, using the four condensers in two lines of two condensers each, for a more efficient aroma collection. The permeate is produced semi-continuously following aroma extraction and aroma defrosting stages. The best operating conditions were found to be 25 °C of feed temperature and 500 L·h⁻¹ of feed flowrate (stage cut of ca. 1.1 %).

The laboratory and industrial units originate close but different aroma profiles being the lab extract more concentrated. These differences are mainly related to the presence of dissolved carbon dioxide in the industrial unit feed and the under dimensioned industrial condensers. As a result of the less effective condensation in the industrial plant, the vacuum pressure is not as low as desired and a significant fraction of lighter aroma compounds is lost.

During the industrial production of aroma extract, it was observed a decreasing permeate flux and aroma concentration over the 8 months of operation. In order to understand the membrane ageing process it was studied this effect at laboratory level. From this study, it was concluded that membranes should be kept wet all the time. On the other hand, it was studied several cleaning solutions to clean the pervaporation membranes.

New perspectives of application

It was considered to apply the know-how obtained for beer dealcoholization and beer aroma recovery to other beverages. As a result, it was considered removing ethanol from wine from ca. 12 vol.% down to around 7 – 8 vol.%. Dealcoholization by nanofiltration or reverse osmosis (more gentle for wine than heat treatments) and pre-recovery of aroma compounds by pervaporation were used. Nanofiltration membranes made of polyamide were compared to reverse osmosis membranes made of cellulose acetate. It was found that nanofiltration membranes were more effective for alcohol removal, due to their higher ethanol flux and high rejection to important wine flavour compounds. The addition of pervaporated wine aroma to the dealcoholized wine increased the sensorial perception of the original alcoholic wine.

7.2. Future work

A research work is always an endless process, aiming the continuous improving of the results. During this thesis it was studied the effectiveness of separation processes for producing non-alcoholic beer from a regular alcoholic beer. This work was mainly focused in pervaporation and its performance towards the recovery of aroma compounds lost during the dealcoholization process. However, for getting a better understanding of pervaporation and improving the industrial process, some tasks are suggested:

- i) improve the condensing system of the pervaporation industrial plant, by redesigning the condensers for allowing the complete condensation of aroma compounds, increasing the volume of the aroma collected and improving the aroma profile and also allowing a continuous production of aroma;
- ii) study the effect of carbon dioxide removal from the feed beer on the aroma compounds extraction;
- iii) optimize the cleaning process of industrial membranes for restoring their original properties and preventing future membrane fouling;
- iv) use a beer model solution to study the elementary phenomena of pervaporation, namely sorption studies should be accomplished for predicting the behaviour of aroma compounds at the membrane surface; it would be important to obtain the activity coefficients of aroma compounds for determining the driving force of permeation; the mass transfer

coefficients on the feed boundary layer and membrane should be studied and the transport of aroma compounds from the beer bulk to the permeate modelled;

- v) development and validation of phenomenological models to optimize the pervaporation process both at laboratory and industrial scale;
- vi) based on the previous theoretical knowledge, search, modify and evaluate new selective pervaporation membranes;
- vii) implement the developed methodology to new beverages and namely to wine, since the aroma profile of the pervaporated wine extract needs to be optimized for improving the sensorial quality of the dealcoholized wine. Also, concerning wine dealcoholization, this work only studied the most promising nanofiltration membranes. Nevertheless, it is necessary to study the effect of the critical operating conditions, such as feed temperature, feed pressure and feed flowrate, on the ethanol removal from wine and on the membrane retention of wine aroma compounds.

Appendix A

A. Process for enriching the aroma profile of a dealcoholized beverage

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(54) Title: PROCESS FOR ENRICHING THE AROMA PROFILE OF A DEALCOHOLIZED BEVERAGE

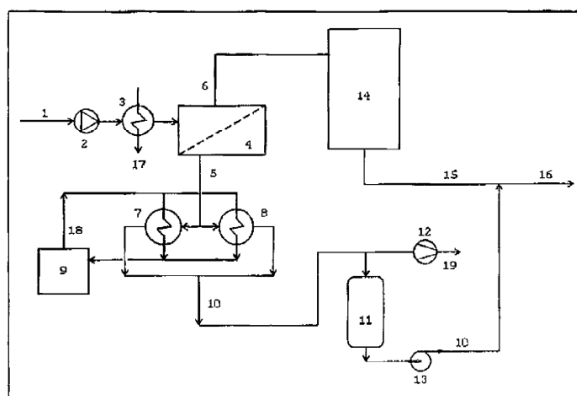


Fig.1

(57) Abstract: The present invention concerns a process for enriching the aroma profile of beverages, especially beer and wine, by means of extraction, using pervaporation, of aromas from the original beverage and subsequent addition of the extracted aromas to the beverage, after total or partial dealcoholization. The original beverage (1) is fed to the membrane separation module (4) wherein the permeate side (5) is under vacuum, provided by a vacuum pump (12). The feed contacts with the membrane surface and the aromas are selectively permeated to the permeate side of the membrane, where they suffer evaporation. The vapor permeate stream (5) is condensed (10) at an appropriate temperature, which can be cryogenic. After the aroma extraction, the beverage (6) is fed to a dealcoholization unit (14) for obtaining a non-alcoholic drink (15), however depleted in aroma compounds. Finally, the extracted aromas (10) are added to the dealcoholized beverage, thus an aroma enriched product (16) being obtained without considerably increasing its alcohol content.

Description

PROCESS FOR ENRICHING THE AROMA PROFILE OF A DEALCOHOLIZED BEVERAGE

Background of the Invention

- [1] The present invention concerns the extraction/recovery of aroma compounds from an alcoholic beverage, such as beer or wine, for the subsequent addition to a beverage lacking on these compounds, and makes use of the pervaporation technology. Nowadays, pervaporation showed to be a highly promising process in the food industry for separating aroma compounds. It is a highly selective membrane separation process [1]. Moreover, this process can be operated at low temperatures, in contrast with other processes such as distillation. This characteristic of pervaporation is an advantage when the objective is the separation of thermosensitive compounds^[1-4], such as some aroma compounds of alcoholic beverages obtained by fermentation.

Prior Art

- [2] The aroma recovery from juices or fermented beverages, such as wine or beer, is an increasingly important operation concerning the food processing industry. The aroma of beverages, such as juice, beer or wine, consists of a large group of volatile organic compounds (VOCs), which are responsible for the odor and taste of the beverage, and whose concentration levels are low, usually at the ppm level^[1-4]. These aroma compounds can belong to different chemical functional groups, such as alcohols, esters, aldehydes, lactones, carboxylic acids, phenols, ethers, etc.^[2,3]. Each group of aroma compounds is responsible for a typical odor and taste. Esters, for example, confer to the drink a sweet and fruity flavor, while aldehydes are associated to the freshness (immaturity) of the beverage. On the other hand, alcohols, which are the major group of aroma compounds in fermented drinks, such as beer and wine, where ethanol is the dominant one, provide an alcoholic, fruity and immature flavor^[5].
- [3] During the past years it has been observed a significant increase in the low alcohol beverages market. This trend is due mainly to health and civil responsibility reasons. However, some of the non-alcoholic drinks available in the market have a limited acceptability by the consumers due to their lack in aroma compounds. In fact, products obtained by means of interrupted fermentation do not have the typical aroma profile of the alcoholic beverages. On the other hand, some dealcoholization processes submit the product to drastic conditions that might lead to the loss of the original aroma, which is the greatest contribution for its quality, and consequently for its acceptance by the consumers^[4]. The beverage processing, especially if carried out at high temperatures, can considerably modify the aroma composition. This modification can be

due to physical losses and/or chemical reactions that change the original aroma compounds^(1,2,6,7). As a consequence, the sensorial quality of the product can drastically differ from that of the initial beverage. So, the success of the dealcoholized beverages depends on the ability to reproduce the original aroma profile.

- [4] To overcome the modification of the sensorial profile of the beverages, it can be considered to recover the aroma compounds lost during the drinks processing for lowering the alcohol content, or to extract these aroma compounds before the dealcoholization heat-based process, and adding them subsequently to the final product. Presently, there are available several effective processes for this application, the membrane processes such as pervaporation being the most attractive. Besides its high selectivity, pervaporation can be carried out at low temperatures, which is suitable for the treatment of thermosensitive aromas⁽¹⁻⁴⁾. Moreover, pervaporation is a physical separation process, thus being favored by the international food legislation, having a low energetic consumption and not requiring any additives such as in solvent extraction^(3,4,8,9). Besides these advantages, it is a process that allows the extraction/recovery of the original aromas, which have an important commercial value due to the natural, non synthetic, nature of the aroma compounds.
- [5] Pervaporation technology has been improved tremendously during the past decade, especially for dehydration applications, although being a process finding application in the separation of thermosensitive compounds, mixtures with azeotropes and isomers mixtures^(10,11). In summary the applications of pervaporation can be divided in three main groups: a) dehydration of organic-aqueous mixtures; b) removal of organic compounds from aqueous solutions; c) separation of organic solvent mixtures. The first major industrial application of pervaporation was the dehydration of solvents, being still the most important application⁽¹¹⁾. For these applications hydrophilic membranes are required. The employment of pervaporation for removing organic compounds from aqueous solutions is also carried out at industrial level, but in minor extent⁽¹⁰⁾, since it was developed more recently. This application requires the use of hydrophobic membranes. Lately, pervaporation has been largely used in chemical and petrochemical industries for the separation of organic mixtures⁽¹¹⁾.
- [6] Nowadays, one can observe an increase trend in the use of pervaporation for recovering aroma compounds in food applications, especially in the recovery and enrichment of aromas such as in fruit juices. The heat treatment processes of juices, such as pasteurization and mainly the conventional processes for juice concentration such as evaporation, cause the loss of the original aromas and as a result the loss of quality of the processed products^(1,6,7). Besides the use of pervaporation in the fruit juice industry, its use has also been reported for aroma recovery from fermented beverages, such as beer or wine^(4,12), due to the aroma loss that occurs during heat treatments of these

beverages and even in dealcoholization processes.

- [7] Despite the numerous scientific publications referring the pervaporation use in the aroma recovery from alcoholic beverages, there are no references reporting the use of pervaporation as disclosed in the present invention. The core of the present invention concerns obtaining an aroma concentrate to be added to an aroma-depleted beverage, e.g. a partially or totally dealcoholized beer, in order to obtain a beer with an aroma-enriched profile and for example similar to the original beer. This operation mode differs from the ones previously disclosed.
- [8] US 4,792,402 (December, 1988) discloses a process for concentrating alcoholic drinks, by means of dehydration using reverse osmosis, in order to reduce the transport costs due to the large contribution of water content in the beverages. This document corresponds to EP 0116462 of August 1984, which was also worldwide disclosed in August 1984 WO 84/03102. In this process, the original beer is submitted to reverse osmosis, where the membrane is permeable to water and might be partially or totally permeable to ethanol and aroma compounds. The retentate from the reverse osmosis - the concentrated beverage - can or not be recycled to the feeding tank, according to the operation mode - batch or continuous, respectively. In order to not significantly change the beverage aroma profile, the permeate stream from the reverse osmosis, which is mostly water, is led to a distillation unit (under vacuum) for separating ethanol and the aroma compounds. The distillation column can consists of a typical column or a packed column, comprising a vapor stripping bottom section and a rectification top section, wherein the permeate stream is fed at the intersection of the sections. The permeate flows down through the stripping section. At the bottom it boils and the vapor flows up through the stripping section absorbing ethanol and aromas from the descending permeate. Next, the vapor containing alcohol and aromas continues flowing up, through the rectification section, where the fractional distillation takes place. The said vapor leaves the column with a little amount of water and, after condensation, is added to the concentrated beverage. The beverage can finally be reconstituted with deaerated water up to the desired concentration (amount of ethanol and density). This process differs from the one reported in the present invention, mainly because patent US 4,792,402 employs distillation for recovering aroma compounds, while in the present invention a pervaporation process is employed. The main target of US 4,792,402 patent is the concentration of alcoholic beverages by water removal, to make their transport easier, whereas the present invention targets the aroma enrichment of a dealcoholized beverage.
- [9] US 5,030,356 (July, 1991) describes a process for recovering organic compounds from liquid streams. This method combines two separation processes: pervaporation and decantation. A continuation in part of that patent - US 5,169,533 - was submitted

in December 1992. Later, in November 1993, a new patent was submitted - US 5,266,206 - as a continuation in part of the previous one. The process reported in these patents concerns the separation and recovery of organic compounds from industrial liquid effluents. The choice of the operation mode depends on the nature of the feeding stream. If the feed is an aqueous solution with a small organic concentration, forming a single-phase solution, it is advantageous to use pervaporation first. In this embodiment, the permeate stream from the pervaporation unit contains an organic concentration above the water solubility and then forms two phases which are separated (after condensation) in a decanter. The aqueous phase, typically saturated in organic(s) compound(s), is recycled back to the pervaporation unit. When the feed stream comprises two phases, it is first fed to the decanter, for separating the phases, the aqueous phase being fed to the pervaporation system. The leaving permeate stream forms two phases and is recycled back to the decanter. In both embodiments two streams are formed: an aqueous stream with residual concentration of organic compounds and a high-purity concentrated organic stream that might be recovered and reused. In this invention, the solutions that are intended to be treated can be industrial effluents or wastewater from food or beverage processing, containing aromas, essences or other organic compounds. This process is especially useful to treat streams from evaporators, used for concentrating fruit juices (such as apple juice), which have aroma compounds that contribute to the juice flavor and taste. After the treatment, the organic phase, whose aroma concentration is very high, can be added to the juice or, on the other hand, it can be used in the aroma and fragrances industries. This process differs from the one herein disclosed, mainly because the objective of patent US 5,266,206 is the recovery of organic compounds (e.g. aromas) from an industrial aqueous effluent, while the present invention consists on the extraction of aroma compounds from a main stream for adding them back to the same stream, after dealcoholization. On the other hand, in patent US 5,266,206 an aqueous and an organic streams are formed, which does not occur in the present invention.

- [10] US 5,263,409 (November, 1993) discloses a membrane separation process for removing bitter agents from citrus juice, without significantly changing the amount of important nutritional compounds. The method consists of the separation through two membrane contactor modules, where the compounds are transferred between streams by means of selective membranes. In the first module, the bitter agents permeate a semi permeable membrane, from the juice to an extractor fluid (e.g. organic fluid). This enriched fluid is fed to a second membrane contactor, wherein the bitter agents permeate a second membrane and are hydrolyzed (from carboxylic acids to esters) by a second fluid, which flows in the opposite side of the membrane. This stream becomes depleted in these compounds and is recycled to the first module to flow along the

permeate side. The bitter removal is carried out up to the desired level, the important nutritional elements (such as the ascorbic acid) being kept in the citrus juice once the first membrane is impermeable to these compounds. This process (US 5,263,409) is different from the present invention since two membrane contactors are used for extracting and removing undesirable compounds (bitter agents).

- [11] US 5,308,631 (May, 1994) discloses a process for producing non-alcoholic beer and concentrated beer aroma by means of adsorption with hydrophobic adsorbents and subsequent distillation of the extracted phase. This document corresponds to EP 0486345 of October 1991. The process is based on co-adsorption of ethanol and aroma compounds in hydrophobic adsorbents, such as zeolites. As a result, an aqueous eluant and an adsorbed phase are formed. The second part of the process consists on separating the aqueous phase from the adsorbent, saturated with alcohol and flavors. In order to recover the later, desorption is required. After desorption, the desorbed phase is fed to a distillation unit where it is fractionated into a highly alcoholic stream and a concentrated aroma stream. Finally, the non-alcoholic beer is reconstituted by mixing the dealcoholized eluant with the aromatic extract and then pressurized with gaseous carbon dioxide. This process (US 5,308,631) differs from the one described in the present invention mainly because it uses an adsorption process for extracting aromas followed by distillation for producing a low alcohol aqueous phase and an aroma concentrate for adding to the dealcoholized beer.
- [12] US 5,385,647 (January 1995) discloses a process for producing a non-alcoholic beer by means of dealcoholization by pervaporation of a regular alcoholic beer. In this process, the pressure that is applied to the vacuum side of the membrane and the condenser temperature allow the selective permeation of ethanol over the aroma compounds. On the other hand, when the recovery of aroma compounds is required, a second condenser, working under extremex conditions (lower condensation temperature), is placed in series with the first one. In this embodiment of the invention the permeate from the second condenser is added to the retentate stream in order to overcome the loss of aroma compounds during the dealcoholization. This process (US 5,385,647) is different from the one disclosed in the present invention since it targets the dealcoholization of beer, instead of the aroma extraction for subsequent addition to the beer after dealcoholization.
- [13] US 5,817,359 (October, 1998) discloses a process based on membrane separation (perstraction with controlled absorption) for removing ethanol from fermented beverages. In this process the alcoholic brew contacts with the hydrophobic membrane surface. In the downstream side of the membrane a strip solution flows, in order to extract ethanol (and some aroma compounds) from the feed, resulting in an alcoholized strip solution and in a non-alcoholic product. In general, the strip solution consists of

deaerated water and preferentially carbon dioxide saturated water, in order to avoid its transfer through the membrane and the consequent decarbonation of the beverage. In following dealcoholizations, at least a fraction of the dealcoholized beverage and/or a fraction of the strip solution obtained in the previous dealcoholization (since both streams contain aroma compounds) could be used as strip solution. Accordingly, the concentration of aroma compounds (excluding ethanol) in the strip solution side is kept high, minimizing the permeation through the membrane, since the driving force between both sides of the membrane is reduced. As a consequence, the aroma loss during this process is minimized. This process (US 5,817,359) differs from the one reported in the present invention mainly because it uses a membrane contactor (dialysis) for dealcoholizing beverages, while in the present invention a pervaporation process, for extracting aromas and subsequent addition to the dealcoholized beverage, is proposed.

- [14] US 6,162,360 (December, 2000) discloses a membrane separation process that uses dialysis for transferring the aroma compounds from a regular alcoholic beer to a commercial non-alcoholic beer. In July 2002 a new patent (US 6,419,829) was filed as a continuation in part of the previous one. In this process the hydrophobic membrane, which might be a solid or liquid membrane, is placed between the feed solution and the stream that is intended to enrich (the pick-up fluid). In this case the feed stream corresponds to the solution from which the aroma compounds are extracted, such as a regular alcoholic beer available in the market. The pick-up fluid consists of a commercial non-alcoholic beer (e.g. produced by distillation or dialysis) with low or no aroma concentration. Hence, the aroma compounds permeate selectively the membrane, according to the concentrations profile, towards the beverage which is intended to improve. The separation process is carried out until the equilibrium within the aroma compounds concentration is achieved in both sides of the membrane. At the end of the process both beverages show the same aroma profile except for ethanol, whose membrane permeability is lower than for other aroma compounds, and consequently this profile is slightly less concentrated than the original beer profile. According to this invention, the feed solution can also be a beer containing undesirable compounds (such as ethanol, for instance), which can be extracted for a permeate such as water or carbon dioxide, in which the aromas are absorbed or solubilized, resulting in a beverage comprising the desirable aroma and depleted or exempt from undesirable aroma. So being, enriched drinks can be obtained, either by increasing the content in desirable aromas or by decreasing their undesirable contents, selecting for each case appropriated feeding streams and permeate pick-up fluids. This process (US 6,419,829) diverges from the one described in the present invention, mainly because it employs a membrane contactor for dialysis of aroma compounds from an alcoholic and

aroma-enriched beer into a non-alcoholic beer and thus depleted in aroma flavors, while the present invention proposes pervaporation for extracting aromas from the original alcoholic beer and its subsequent reincorporation in the same beer, after the dealcoholization process.

- [15] US 6,287,618 (September, 2001) discloses a process for producing a concentrated citrus aroma and also citrus aromas and fragrances, using for this purpose an evaporation unit working under vacuum and distillation using a spinning cone column supplied by Flavourtech (US 4,995,945). This unit is mainly used for the dealcoholization of drinks and aroma extraction. The process herein disclosed is used for producing a citrus aroma concentrate whose composition is suitable for being used as raw-material in the production of aromas and fragrances. The method for producing the concentrated aroma consists of concentrating up to 100 to 150 times the original juice, by continuous evaporation under vacuum. Next, a filtration step is carried out to separate the floating essential oil, which contains the aroma compounds, from the recovered solution. The remaining recovered solution of concentrated citrus is led to a spinning cone column in order to separate the aroma or flavor compounds. Finally, these compounds can be added to juices or desserts. This process (US 6,287,618) is different from the present invention since it considers the aroma concentration of fruit juices by means of vacuum evaporation and vacuum distillation (using a spinning cone column).
- [16] US 6,518,050 (February, 2003) discloses a process for producing aroma compounds from by-products of the fermented brews distillation, such as wine, and extracting the respective aroma by means of pervaporation. The PCT application of this patent was submitted on October 1999 - WO 99/54432. Wine distillation yields by-products which contain many essential nutrients for growing microorganisms, such as yeasts, without ethanol or aromas, once these compounds are removed through the distillate. Microorganisms can produce compounds like aromas or fragrances based on wine distillation by-products as substrates and optimized growing conditions. Some available separation processes, such as pervaporation, might be used for extracting the valuable products from the culture medium. This process (US 6,518,050) differs from the one disclosed in the present invention because it employs pervaporation in a completely distinct context, in particular the aroma extraction from one certain substrate, without having to reestablish the aroma balance of such substrate after dealcoholization. In the present invention, the pervaporation process is used for extracting aroma compounds from a main process stream (e.g. beer), which should be submitted to dealcoholization with consequent loss of its aroma profile and, after dealcoholization, the extracted aroma compounds are reincorporated in the dealcoholized beer.
- [17] US 6,755,975 (June, 2004) discloses a process for separating mixtures containing

water and organic compounds, using pervaporation and dephlegmation (reflux condensation) of the permeate, in order to improve the selectivity towards the more desirable compounds. In this invention, the feed solution (containing the compound to be extracted) goes to the pervaporation module. The membranes in this unit can be hydrophilic or hydrophobic, depending on the nature of the compounds to be removed. The permeate solution from the pervaporation step is sent, in the vapor phase, to the dephlegmator for partial condensation. The structure of that unit (such as packed columns) should be able to provide heat and mass transfer between the rising flowing vapor and sliding flowing condensate. By this way the overhead vapor product is enriched in the more volatile compound and the bottom condensate product is richer in the less volatile compound, depending on the desired separation. This method of partially condensing the permeate stream increases the separation of the most desired compounds. This process can be applied to the food industry, for processing beverages, such as juices, wine or beer; during extraction of aromas; or even in the ethanol continuous removal from the fermentation reactors, for avoiding the yeast inhibition due to high contents of ethanol in the fermentation broth. This process (US 6,755,975) is distinct from the present invention since it employs pervaporation coupled to dephlegmation, while the present invention proposes pervaporation for extracting aroma compounds from a main stream that should be submitted to a dealcoholization process, and hence to an aroma profile loss. On the other hand, in the present invention, the extracted aromas are reincorporated in the original beverage after dealcoholization.

- [18] PT 102976 (June, 2004) discloses a process for reducing the ethanol content of beverages by means of nanofiltration, with subsequent alcohol removal from the permeate by distillation and its addition to the beverage to be treated, its corresponding PCT application having been filed in December 2004 - WO 2004/113489. The disclosed process employs nanofiltration membranes for total or partial removal of ethanol from beverages. The resulting permeate (which is mainly water, ethanol and some salts) is sent to a distillation unit for ethanol removal. The bottom product (without ethanol) is added back to the nanofiltration beverage in order to keep its organoleptic characteristics. This process (PT 102976) differs from the one disclosed in the present invention mainly because it uses nanofiltration for wine dealcoholization and distillation for recovering the aroma compounds of the nanofiltration permeate stream. In contrast, the present invention proposes pervaporation for extracting aromas and subsequent addition to the original beverage, after dealcoholization.

Brief Description of the Invention

- [19] The present invention discloses a process for complete or partial recovery of the original aroma profile of a beverage, submitted to a total or partial ethanol removal. This disclosed process employs the pervaporation technology for extracting the desired

aroma compounds from the original beverage, which are added to the resulting beverage after dealcoholization, and thus depleted at the sensorial level.

- [20] In the mentioned process, the original alcoholic beverage (such as beer or wine, for instance) whose aroma compounds are intended to be extracted, is fed to the membrane separation module of the pervaporation unit. At the membrane module, a feed fraction selectively permeates through the membrane (aroma compounds) and evaporates when leaving the membrane at the permeate side, which is maintained under vacuum. The permeated aromas are collected after condensation in a heat exchanger. The condensation temperature should be low enough in order to avoid the loss of the most volatile aroma compounds, therefore should be lower than -80°C and could be cryogenic (-196°C). On the other hand, the permeate pressure should also be low enough to allow a high permeate flux and a selective permeation of the heaviest compounds. The permeate pressure should be between 100 Pa and 10 kPa, according to the application. The feed fraction that does not permeate the membrane (the retentate) leaves the membrane module and consists of a solution slightly depleted in the original aroma compounds. The retentate stream from the pervaporation unit could be recycled in order to extract therefrom the remaining aroma compounds, or instead it might be sent to a dealcoholization system in order to obtain the dealcoholized beverage to which it is intended to add the concentrated aroma.

- [21] The aroma profile of the extracted compounds can be adjusted by tuning the operation and design conditions of the process. These conditions comprise the membrane thickness and composition, which affect mainly the permeate flux and the aroma compounds permselectivity, respectively; the feed temperature, once it influences the membrane permeability towards different aroma compounds and the driving force of chemical species through the membrane, as a consequence of their evaporation ratio after permeation (because the vapor pressure in the permeate side is also affected); the feed flow rate, which should be high enough in order to minimize the concentration polarization; and the vacuum pressure that is applied at the permeate side, which affects the selectivity and the permeate flux, although the effect of the permeate pressure on the aroma selectivity shows different behaviors according to the compounds' volatility - the permeation selectivity towards the more volatile aroma compounds increases with the permeate pressure increase (less vacuum), while it decreases in the case of the heaviest compounds. Concerning the membrane flux and in the absence of permanent dissolved gases, the permeate flow rate depends mainly on the feed temperature and on the permeate pressure, increasing with the first operating variable and decreasing with the second one. On the other hand, the retentate pressure has a slight influence on the membrane flux and selectivity. In the presence of dissolved permanent gases, such as carbon dioxide, the temperature increase leads to a

higher amount of gas desorption. Consequently, the pressure on the permeate side might increase due to head losses and/or limitations of the vacuum pump. The condensation temperature is also a critical factor on the process and hence it should be carefully selected, once it should allow the total or partial condensation of the most desired aroma compounds.

[22] In general one can say that:

a) the membrane should be as thin as possible for increasing the productivity, but not too thin in order to avoid the deterioration of the selectivity due to swelling and in order to keep the mechanical strength;

b) the feed temperature should be as high as allowed by the beverage sensitivity, since it leads to a productivity increase due to the exponential increase of the membrane flux with temperature; on the other hand, it should be as low as possible in order to balance the selectivity towards the most desired compounds, such as high-alcohols and esters, against ethanol, taken that in POMS (polyoctylmethylsiloxane) membranes supported in PEI (polyetherimide), a temperature increase leads to an increase of high-alcohols concentration on the permeate side compared to ethanol and, consequently, high-alcohols selectivity increases with temperature; on the other hand, in the esters concentration a decrease in the permeate concentration is observed, as well as a selectivity decrease, as temperature rises;

c) the feed flow rate should be high enough in order to guarantee a turbulent flow regime over the membrane surface for minimizing the concentration polarization;

d) the permeate pressure should be as low as possible, in order to increase the productivity, but not too low, in order to reduce the vacuum costs; on the other hand, the lower the permeate pressure the higher amounts of heavy compounds (such as amyl-alcohols) will be recovered. According to this, the condensers should have little head loss in order to keep the permeate side of the membrane modules at sufficiently low pressure, driven by the vacuum pump. The vacuum ducts, mainly the ones from the modules until the condensers (where the volume flow rate is very high) should be designed in order to keep the head loss very small;

e) the condensation temperature should be as low as possible to maximize the aromas condensation and to reduce the vacuum costs, but not too low because of the cooling costs; on the other hand, the lower the condensation temperature, the higher the concentration of light aromas on the final product.

[23] Finally, it was observed that composite membranes made of POMS (polyoctylmethylsiloxane) supported in PEI (polyetherimide) show good selectivity and permeability towards the key beer aroma compounds.

[24] Hence, according to the proposed in the present invent, the aroma compounds, such as high-alcohols and esters, which have the highest contribution to the aroma profile of

fermented alcoholic beverages, can be selectively permeated through a hydrophobic membrane using a pervaporation process. As a result, a high concentrated permeate of aroma compounds is obtained, whose ratio towards the origin beverage might be of tens, in the case of high-alcohols, or hundreds, in the case of esters. The permeate can be added to the dealcoholized beverage, thus depleted from aroma compounds, in order to improve its sensorial quality, without significantly increasing its ethanol content. The aroma concentrate volume that is needed to be added to the beverage represents a small fraction of the total volume.

Brief Description of the Drawings

- [25] The present invention discloses a process for obtaining an aroma concentrate by means of pervaporation of a beverage with regular ethanol content. This concentrated aroma is intended to be added to an aroma-depleted profile beverage, such as a dealcoholized beer, in order to produce a non-alcoholic beer (ethanol content less than 0.5 %v/v) with good organoleptic characteristics.
- [26] Figure 1 represents a flow diagram of an industrial pervaporation unit for extracting beer aroma compounds and a dealcoholization unit, which can also include a treatment step of the dealcoholized beverage, whose aroma content is compensated with a permeate stream from the pervaporation unit. The set-up comprises a feed stream or original beverage connection (1); a feeding pump (2); a feed heat exchanger (3); a set of pervaporation membrane modules (4); a connection of the permeate vapor stream, from the modules (5); a connection of the feed fraction that does not permeate de membrane - the retentate (6); two condensers sets (7 and 8); a circulator (9); a connection of the condensed permeate (10); a tank for collecting the permeate in liquid state (11); a vacuum pump (12); a dosing pump (13); a dealcoholization system (14), which can include a final treatment system; a dealcoholized drink stream connection (15); a final product stream connection (16); a heat water connection (17); a cooling fluid connection (18), and a vacuum pump vent (19) through which the non-condensable compounds are vented.

Detailed Description of the Invention

- [27] The present invention discloses a process for producing non-alcoholic or low-alcoholic beverages, such as beer or wine, with an enriched aroma profile, which might be similar or not to the original alcoholic beverage profile.
- [28] Therefore, it is assumed that an original beverage, whose alcohol concentration is above the target value, is submitted to a process for total or partial removal of its ethanol content. This alcohol removal process causes the loss of a more or less important fraction of the beverage aroma compounds.
- [29] The present invention also describes a process for the complete or partial recovery of

the aroma profile of the original beverage.

- [30] This process is based on the pervaporation of the original beverage, aiming at extracting aroma compounds and the subsequent addition to the dealcoholized drink.

- [31] 1. Extraction of the aroma compounds.

The original alcoholic beverage is sent to the membrane separation module of the pervaporation unit, where it tangentially contacts with the selective membrane surface.

- [32] The membranes used in this application are composite membranes, where the selective film has a thickness between 0.1 and 2 μm , and where the selective layer can be made of polydimethylsiloxane (PDMS) or polyoctylmethylsiloxane supported in polyetherimide (POMS/PEI).

- [33] According to the targeted aroma profile for the permeate, the original beverage can be heated from 5 to 40 °C, before the membrane pervaporation module inlet. The permeate side is kept under vacuum, being the pressure in this side preferentially in the range between 100 Pa and 10 kPa.

- [34] In the pervaporation process described, the original beverage is usually fed to the membrane modules at atmospheric pressure or at a slightly higher pressure, such as 0.4 MPa absolute.

- [35] 2. Permeate recovery.

The permeated aroma compounds leave the membrane in the vapor phase and are collected, after condensation, in a system of heat exchangers set in parallel that operate alternate to each other to allow the semi-continuous collection of the aroma permeates.

- [36] In the condenser system, a pair number of heat exchangers working in alternated mode are used. One set of condensers is used for condensing the volatile compounds of the permeate stream during half of the cycle, while the other set of condensers is cut from the vacuum and heated, up to a temperature which is high enough to allow defrosting and collecting the volatile condensates.

- [37] The condensation temperature should be lower than -80 °C and could be cryogenic (-196 °C). In this case, a couple of two condensers, working at extremex conditions, should be placed in series with the previous condenser system, in order to allow the condensation of the more volatile fraction of the original beverage aroma profile.

- [38] 3. Recovery of the non-permeable feed fraction.

The non-permeated feed fraction (retentate) leaves the membrane module and consists of a slightly depleted solution on the extracted aromas.

- [39] The recycling of a retentate fraction can be important in order to increase the flow velocity of the liquid stream over the membrane surface, allowing a negligible concentration polarization. Under these conditions, the retentate stream can be used as a second feed solution in order to recover its remaining aroma compounds.

- [40] On the other hand, the retentate flow from the pervaporation unit is directed to a

dealcoholization set-up in order to produce the respective dealcoholized beverage and to which the aroma concentrate is to be added.

[41] 4. Dealcoholization of the beverage.

Depending on the embodiment of the present invention, the original beverage, from which the aroma compounds are extracted by means of pervaporation, can be fed to a dealcoholization unit.

[42] The alcohol removal process can be provided by means of countercurrent flow contact between the beverage and steam under vacuum or by means of reverse osmosis. During beverage processing, alcohol is continuously removed through the vapor phase, a non-alcoholic drink or a low-alcoholic drink being obtained, depending on the targeted requirements for the final product.

[43] During the dealcoholization process most of the compounds which are essential to the beverage aroma/flavor balance are usually lost. In these conditions the addition of aroma compounds is required.

[44] 5. Enrichment of the beverage in aromas.

The permeate stream from the pervaporation unit is an aqueous solution enriched in the aroma compounds of the original alcoholic beverage. After condensation and defrosting provided by the condenser system, operating in alternated mode, the permeate solution is collected in an intermediate tank before its addition to the dealcoholized beverage, at the end of the process. The aroma extract is added directly to the dealcoholized beverage stream through a dosing pump that feeds the exact quantity of permeate which is needed to enrich the beverage.

[45] This aroma quantity represents a small fraction of the beverage total volume, and is selected according to the aroma profile that is intended, and according to the requirements of ethanol limits that are allowed by the legislation for the final beverage.

[46] **Example 1**

Extraction of aroma compounds from a regular alcohol content beer using a lab pervaporation unit

The original beer (alcohol content around 5.5 % v/v), stored in the feeding tank, is sent to a membrane module, with an effective membrane area of 107.46 cm². The membranes used are flat POMS composites with a thickness of about 1.5 µm, supported in a porous layer of PEI. The feed stream is pumped by means of a centrifugal pump. Before entering in the membrane module, the feed stream is fractioned and a portion thereof is recycled back to the feeding reservoir, through a plate heat exchanger (effective area of 20 dm²). The other feed fraction is directed to the membrane module and the aroma compounds selectively permeate through the membrane, wherein the driving force results from the sub-atmospheric pressure by means of a vacuum pump with a nominal minimum vacuum pressure of 0.2 Pa and a

maximum water vapor flow rate of 0.22 kg·h⁻¹.

- [47] The permeate leaves the membrane in the vapor phase and is condensed in a cold-trap, immersed in liquid nitrogen. The cold-trap consists of two concentric cylinders made of stainless steel, specifically designed for this application, the cold-trap being placed in an isolated dewar flask filled with liquid nitrogen, at -196 °C (in order to allow the complete condensation of the aroma compounds, even the most volatile ones). The cold-trap connects with the membrane module and with the vacuum pump downstream by means of stainless steel flexible tubes. All these tubes are attached by clamp type connectors for easier disconnection and permeate collection. The aromas are collected from the cold-trap after defrost, which can be carried out by immersing it in glycol-water mixture at about 0 °C, in order to avoid the loss of the most volatile aroma compounds. After defrosting, the aromas are collected in glass flasks.
- [48] The fraction of the beer that is fed into the module, and which does not permeate the membrane, leaves the module through the retentate exit and is also recycled back into the feeding tank, through the plate heat exchanger. The retentate flow rate is measured using a rotameter and is controlled by needle valves.
- [49] The feed pressure is read using a manometer, placed at the module's inlet, and is regulated by needle valves. This feed arrangement allows independently adjusting the feed/retentate flow rate and the pressure of the first stream.
- [50] The permeate flow rate is gravimetrically measured after the predetermined permeation time has finished. The downstream pressure (permeate side) is monitored by a pressure sensor/transmitter and is adjusted by tuning a diaphragm valve.
- [51] Feed temperature was maintained at ca. 5 °C and the absolute pressure at about 0.4 MPa. The permeate pressure was kept at about 100 Pa. This lab set-up allows the production of an aroma concentrate such that, when added to a dealcoholized beer (0.0 % v/v of ethanol), produced by a spinning cone distillation column, allows obtaining a final beer with less than 0.05% v/v of ethanol (so-called 0.0 % alcohol beer) and with an aroma-enriched profile. The added amount of concentrated aroma was about 0.4 % and the final beer presented an aroma composition similar to the original one, mainly in esters composition, whose profile is totally recovered. Moreover, a sensorial analysis to the product, made by a restrict group of tasters, recognized a good aroma profile and taste, similar to the original beer.

[52] **Example 2**

Industrial production of a non-alcoholic beer from an alcoholic beer with reincorporation of original aroma compounds

The original beer (1), from which it is intended to extract the aroma compounds, is a concentrated beer with about 6 % v/v alcohol content and with a residual carbon dioxide content (around 3.8 g·l⁻¹). The beer is fed into the membrane module (4), with

an effective area of 40 m² of composite POMS supported in PEI membrane. The transfer of the original beer to the module is made by a centrifugal pump (2) at an absolute pressure of 0.25 MPa, in order to keep a maximum pressure drop of 0.2 MPa between the feed and retentate sides of the module. The feed flow rate is 20 hl·h⁻¹. Before entering the separation module, the beer might be heated from 5 to 40 °C, in order to increase the membrane productivity and to improve the selectivity towards the most desired compounds. In order to warm the beer stream and keep it at a stable temperature, water can be used in constant circulation inside the heat exchanger (3) (Figure 1).

- [53] On the permeate side of the membrane module, pressure is kept under atmospheric pressure (100 Pa to 10 kPa) by means of a rotary vane vacuum pump (12). The vacuum allows the mass transfer of the aroma compounds from the feed to the permeate side and subsequent evaporation of the same in this side of the membrane. The permeate stream in vapor phase (5), containing high concentrations of aroma compounds, is fed into the first set of condensers (7). A circulator machine (9) supplies a cooling fluid (18), at -80 °C, to the condensers, for condensing the permeate. The above-mentioned system of condensers (7) operates in an alternated mode with the second set of condensers (8), in order to allow the semi-continuous recovery of aromas. A second condenser system, working at extremen temperature conditions, can be placed in series on the permeate line, in order to guarantee the complete condensation of the aromas which did not condense on the previous condensers (7 and 8). A cryogenic fluid, such as liquid nitrogen at -196 °C, might be used on the last condenser. The non-condensable compounds, such as carbon dioxide, are expelled through the vacuum pump vent (19).
- [54] Once condensed, the permeate stream (10) is stored in a tank (11). The permeate discharge is carried out by means of a dosing pump (13), which sets the aroma compounds flow rate (about 8 l·h⁻¹) that is needed to be added to the final beer.
- [55] The feed fraction (6) that does not permeate the membrane - retentate - corresponds to a slightly depleted beer in aromas. This stream is fed into the dealcoholization unit (14) wherein a beer with an alcohol content of less than 0.5 % or even less than 0.05 % by volume is obtained.
- [56] At the end of the process, the permeate from the pervaporation unit is added, after condensation (10), to the dealcoholized beer (15), once during the ethanol removal process most of the volatile aroma compounds are lost together with ethanol. So being, a non-alcoholic beer (16) is obtained, which mostly preserves the flavor profile from the original beer.
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Claims

- [1] Process to obtain beverages with an enriched/balanced aroma profile, comprising aroma extraction, by means of aroma pervaporation from the original beverage and subsequent addition of the aroma extract to the totally or partially dealcoholized beverage.
- [2] Process, according to claim 1, comprising the following steps:
- a) Obtaining a beverage stream from the storage tank, where the original beverage is present, and feeding it into the pervaporation unit;
 - b) Establishing the feed temperature to the pervaporation membranes modules, by means of a heat exchanger;
 - c) Fractionating the feed stream at the pervaporation membrane modules;
 - d) Recycling part of the fractioned feed stream (retentate) to the storage tank where a portion of the original beverage is still present;
 - e) Feeding the remaining fraction of the retentate, that has not been recycled to the storage tank, into the dealcoholization unit;
 - f) Condensing the permeate vapor that left the membrane module;
 - g) Adding the aroma extract to the dealcoholized beverage.
- [3] Process, according to claim 1, comprising the following steps:
- a) Establishing a feed stream from the storage tank, where the original beer is present, into the pervaporation unit;
 - b) Establishing the feed temperature to the pervaporation membranes modules, by means of a heat exchanger;
 - c) Fractionating the feed stream at the pervaporation membrane modules;
 - d) Feeding the whole retentate current into the dealcoholization unit, without any recycling of the retentate current, which leaves the membrane modules of the pervaporation unit;
 - e) Condensing the vapor permeate that left the membrane module;
 - f) Adding the aroma extract to the dealcoholized beverage.
- [4] Process, according to claims 2 and 3, characterized in that the beverage is preferably alcoholic, not exclusively being beer or wine.
- [5] Process, according to claims 2 and 3, characterized in that the permeation is carried out through composite polydimethylsiloxane (PDMS) membranes, comprising a selective film of 0.1 to 2 μm , or through a composite polyoctylmethylsiloxane (POMS) membranes with a 0.1 to 2 μm thick selective film.
- [6] Process, according to claims 2 and 3, characterized in that the permeation is carried out through composite polyoctylmethylsiloxane/polyetherimide

- (POMS/PEI) membranes, comprising a selective film of 0.1 to 2 μm .
- [7] Process, according to claims 2 and 3, characterized in that the condensation takes place at a temperature between 77 K and 193 K, the permeate pressure is set between 100 Pa and 10 kPa, the operation temperature at the membrane module being variable between 278 K to 313 K.
- [8] Process, according to claims 2 and 3, characterized in that the addition of the aromas to the dealcoholized beverage is carried out directly, by means of a dosing pump, which flow rate is in agreement with the desired aroma profile and the highest ethanol content that is admissible for the produced non-alcoholic beverage.

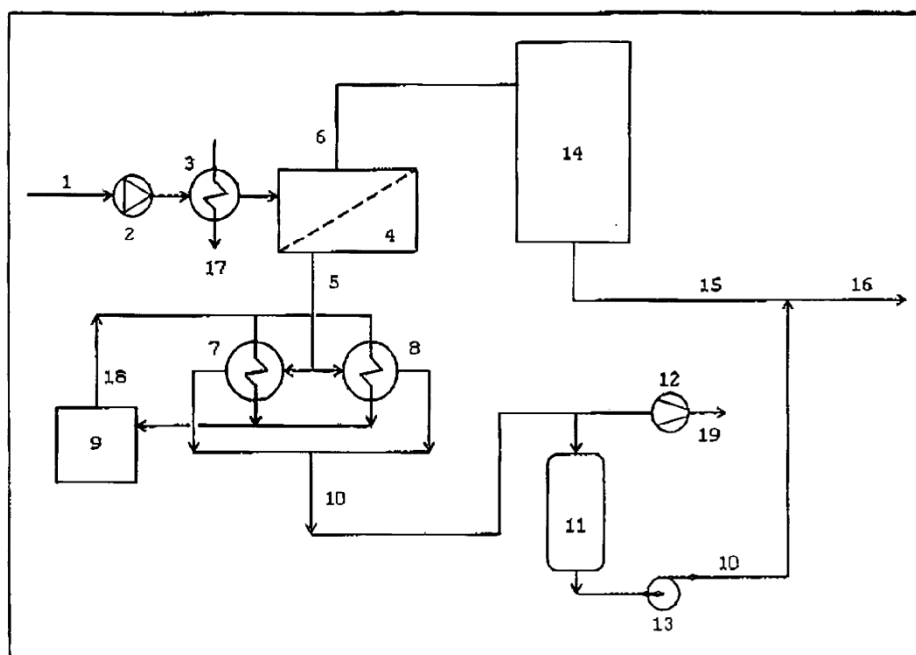


Figure 1