Pervaporation methodology for improving alcohol-free beer quality through aroma recovery

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ABSTRACT

Two different beers, a Special beer (5.5% ABV) and a Reserve beer (6.5% ABV) were pervaporated in order to recover aromas to be added to a low-alcohol beer (less than 1% ABV) and an alcohol-free beer (less than 0.1% ABV) to improve their sensory quality. Sensory analysis confirmed that this was accomplished.

Through the pervaporation process, three flavor constituents of beer (isobutyl alcohol, ethyl acetate and isoamyl acetate) were analyzed in detail. Selectivities were roughly predicted by an easy model based on the Hildebrand solubility parameters for the polymer and the species in the solution. According to the model, a polymer will transmit a species almost perfectly if their solubility parameters coincide.

This model helps to calculate the relative selectivities from solubility parameters and can provide guidance when choosing the membrane for specific separation requirements in food processing or other separation problems where pervaporation can be of great help.

1. Introduction

Beer is obtained by the brewing and fermentation of starch (mainly derived from malted barley) germinated in water in the presence of yeast. It is a traditional beverage and closely linked to the Mediterranean culture (Olaniran et al., 2011). Recent studies have demonstrated that a moderate consumption of beer produces beneficial effects on health (Nascentes et al., 2005).

Non-alcohol beer is a beer with very low or no alcohol content. Depending on legal regulations in different countries, the required alcohol by volume (ABV) maximum thresholds are diverse. In most of the EU countries beers with low alcohol content are divided into alcohol free beers, less than or equal to 0.5% ABV, and low-alcohol beers with no more than 1.2% ABV. However, in the United States alcohol-free beer means that there is no alcohol present, while 0.5% ABV corresponds to the upper limit of so-called non-alcoholic beer or "near-beer" (Brányik et al., 2012).

The market of non-alcoholic brews has improved over the last five to ten years, mainly because new driving/drinking rules, a healthier lifestyle and religious reasons. However, alcohol-free and low-alcohol beers markedly differ in taste and flavor from regular beer. This stems from a lack of flavor due to the elimination of ethanol and other alcohols, some favorable compounds are missing

because ethanol operates as a solvent and the risk of non-alcohol beer contamination with spoilage microorganisms increases as a result of the lack of ethanol (Blanco et al., 2013). Therefore, it becomes important to bring the flavor of non-alcoholic beverages into line with that of their typical alcoholic counterparts. Despite recent developments, there still seems to be a gap in the market waiting to be filled.

Habitual non-alcoholic brews, such as beer or wine, are produced by arresting fermentation. During fermentation, yeasts produce by-products, such as higher alcohols and esters, making a great contribution to the aroma and taste of the brew. If the fermentation is interrupted, the flavor of the non-alcoholic brew does not improve unto the typical flavor of the alcoholic brews (Kunze, 1999). There are other processes for producing non-alcoholic beverages, by restricting the ethanol fermentation, such as the use of special or immobilized yeasts as well as the use of low sugar raw materials (Lewis and Young, 1995; Pickering, 2000).

Alternatively, non-alcoholic beverages can be produced by removing the ethanol from a completely fermented beverage. The most common separation techniques for beverage dealcoholization are heat treatment or membrane-based processes (Catarino et al., 2007). Heat treatment processes include evaporation and distillation or vapor stripping, in both cases under vacuum conditions (Gómez-Plaza et al., 1999; Belisario-Sanchez et al., 2009). Membrane-based processes include reverse osmosis (Labanda et al., 2009; López et al., 2002; Pilipovik and Riverol, 2005),

nanofiltration (Verhoef et al., 2008), dialysis (Petkovska et al., 1997; Leskosek et al., 1997) and pervaporation (Takacs et al., 2007).

Pervaporation is a process used to separate one or more compounds in a liquid using semipermeable membranes in which the permeate exits as vapor in the low pressure permeate side where there is vacuum, while the material retained remains as liquid (Feng and Huang, 1997; Kimmerle and Gudernatsch, 1991). Permeate which is in vapor phase is then condensed and would be reintroduced into de final product. The retentate keeps other components and may be used by other process or recycled for further separation.

Pervaporation is one of the most effective membrane processes for aroma recovery in beverages. Pervaporation membranes are very selective for several chemical groups important in the aroma profiles of beverages (Shepherd et al., 2002; Sampranpiboon et al., 2000; Baudot et al., 1999; Dobrak et al., 2010). During the last years, pervaporation has been successfully applied for recovering aroma compounds from fruit juices (Figoli et al., 2009; Raisi and Aroujalian, 2011; Pereira et al., 2002; Karlsson and Tragardh, 1997; Borjesson et al., 1996) for subsequent addition to the same juice, after concentration by evaporation (Karlsson and Tragardh, 1996; She and Hwang, 2006; García et al., 2008). Pervaporation has been also applied, over the last few years, for ethanol removal (Verhoef et al., 2008; Takacs et al., 2007) and aroma recovery from alcoholic beverages (Karlsson et al., 1995; Brazinha and Crespo, 2009). It has also been used in wine dealcoholization (Catarino and Mendes, 2011a). This method has been used too in the process of developing non-alcohol beer (Kimmerle and Gudernatsch, 1991).

Catarino tried to extract and analyze seven aromatic compounds characterizing the profile of a beer by pervaporation (Catarino et al., 2009). The compounds analyzed were four alcohols (ethanol, propanol, isobutanol and isoamyl alcohol), two esters (ethyl acetate and isoamyl acetate) and an aldehyde (acetaldehyde). The ratio alcohol/ester increases with increasing temperature and decreases with the feed rate and pressure (Catarino et al., 2009).

In 2010 Catarino produced non-alcohol beer extracting firstly the aromas by pervaporation using POMS/PEI type membranes and then proceeding to dealcoholization by spinning cone column distillation (SCC); the extracted aroma was reincorporated and subsequently both the quality of the aroma and productivity of the process were assessed (Catarino and Mendes, 2011b).

Pervaporation represents an alternative to the conventional separation processes, such as, steam distillation, liquid solvent extraction and vacuum distillation. Their energy consumption is normally lower and there is no need of chemical additives. Besides, they can be operated at low temperatures, which is essential when sensitive aroma compounds are intended to be separated (Pereira et al., 2005; Bluemke and Schrader, 2001; Raisi et al., 2008).

The aim of this work was to develop a non-alcoholic beer recovering flavors from regular beers by pervaporation and incorporating them later to non-alcoholic beer.

1.1. Theory

The flux of matter of an i-species through a pervaporation membrane can be described by a solution-diffusion model (Lonsdale et al., 1965):

$$J_i = \frac{D_{i,m} S_i^{mass}}{\Delta x} \frac{\rho_{polymer}}{M_{polymer}} w_{i,feed} \qquad (1)$$

$D_{i,m}$ is the diffusion coefficient of the i-component in the membrane, S_i^{mass} accounts for the solubility in terms of its mass fraction in the polymer (for a polymeric membrane). $M_{polymer}$ and $\rho_{polymer}$ are the molar mass and density of the polymer. Δx is the thickness of the membrane and $w_{i,feed}$ is the mass fraction of the i-th component in the feed solution. The multiplication of the diffusion coefficient and the solubility gives the permeability:

$$P_i = D_{i,m} S_i^{mass} \qquad (2)$$

Eq. (1) can be obtained from Fick's first law, by assuming small concentration gradients through the membrane, diluted solutions and a negligible partial pressure of all components in the permeate side (downstream). In terms of these relationships the key factors to estimate the flux are its diffusivity and solubility for a given membrane.

According to the Flory–Huggins theory, the activity of the solvent can be evaluated by (Prausnitz et al., 1999):

$$\ln a_i = \ln \phi_i + \left(1 + \frac{v_i}{v_p}\right)\phi_p + \chi_i \phi_p^2 \qquad (3)$$

where a_i, ϕ_i and v_i are the activity, the volume fraction and the molar volume of de ith species respectively. χ is the Flory Huggins interaction parameter, and it depends on the intermolecular forces between the polymer chain and the solvent.

According to the Scatchard–Hildebrand model, χ would be:

$$\chi_i = \frac{v_i}{RT}(\delta_i - \delta_p)^2 \qquad (4)$$

where R is the gas constant, T the absolute temperature, and, δ_i and δ_p are the Hildebrand solubility parameter of the ith component and of the polymer respectively. The Hildebrand solubility parameters, δ, can be evaluated (Niemistö et al., 2013) from the Hansen dispersion parameter, δ^d, the Hansen polarity parameter, δ^p, and the Hansen hydrogen-bonding parameter, δ^h, as:

$$(\delta_i - \delta_p)^2 \equiv \Delta\delta^2 = (\Delta\delta^d)^2 + (\Delta\delta^p)^2 + (\Delta\delta^h)^2$$
$$= (\delta_i^d - \delta_p^d)^2 + (\delta_i^p - \delta_p^p)^2 + (\delta_i^h - \delta_p^h)^2 \qquad (5)$$

As the Flory–Huggins interaction parameter goes to zero, there is an increasing affinity within the polymer and the component of the solution with higher solubility and permeability will result through the membrane.

Frequently, Eq. (4) is substituted by:

$$\chi_i = \alpha \frac{v_i}{RT}\left[\left(\delta_i^d - \delta_p^d\right)^2 + \frac{1}{4}\left(\delta_i^p - \delta_p^p\right)^2 + \frac{1}{4}\left(\delta_i^h - \delta_p^h\right)^2\right] \qquad (6)$$

with $\alpha = 0.6$ as obtained by fitting to a big number of polymers (Lindvig et al., 2002).

From Eqs. (3), (4), (6) if the Hansen solubility parameters are to be used, the activity in the polymer can be evaluated. Of course from activity by:

$$a_i = \gamma_i X_i = \Omega_i S_i^{mass} \Rightarrow S_i^{mass} = \frac{a_i}{\Omega_i} \qquad (7)$$

we can obtain S_i^{mass} as required by Eq. (2). X_i is the molar fraction of the ith component in the polymer, γ_i is the activity coefficient based on mole fractions while Ω_i is based on mass fractions. This would lead to approximate results and needs a quite complete knowledge of the thermodynamics of the polymer solution system including Ω_i, ϕ_i, ϕ_p, v_i and v_p.

These are some of the limitations of the Flory–Huggins theory:

- It is based on a lattice model that uses various approximations in the "counting" process.
- It ignores "free volume".
- It assumes random mixing of chains when calculating the entropy and segments in calculating the enthalpy.