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Pervaporation methodology for improving alcohol-free beer through aroma recovering

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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.

Keywords

Membranes, Pervaporation, Beer, De-alcoholization, Aroma recovery

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 et al., 2009). Membrane-based processes include reverse osmosis (Labanda et al., 2009; López et al,. 2005; 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., 1996; 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 M. 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 M. 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):

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

$D_{i,m}$ 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:

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

Equation (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):

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

Where a_i, ϕ_i and v_i are the activity, the volume fraction and the molar volume of de i-th 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, χwould be:

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

Were R is the gas constant, T the absolute temperature, and, δ_I and δ_p are the Hildebrand solubility parameter of the i-th 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:

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

As the Flory-Higgins 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, Equation (4) is substituted by:

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

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

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

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

we can obtain S_i^{mass} as required by equation (2). X_i is the molar fraction of the i-th 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
- Strictly, it only applies to non-polar molecules
- It only accounts for combinatorial entropy

Fortunately there are semiempirical correlations in literature that allow an easy calculation of solubility if the Hildebrand parameters are known (Reddy et al., 1996).

$$S_i^{mass} = \frac{B}{\left(\delta_i - \delta_p\right)^2} = \frac{B}{\left(\delta_i^d - \delta_p^d\right)^2 + \left(\delta_i^p - \delta_p^p\right)^2 + \left(\delta_i^h - \delta_p^h\right)^2} \quad (8)$$

B can be calculated for one of the permeants in the polymer with known S_i^{mass}.

The diffusivity of the i-th component can be evaluated by:

$$D_{i,m} = RTA_D e^{B_D/V_f} \quad (9)$$

A_D is a constant accounting for the shape and size of the i-th component. B_D denotes a constant related to the size of the polymeric jumping unit (the free volume necessary in order to allow jumping of the solute), y V_f the free volume of the polymer (Frisch and Stern, 1983).

The mass concentration enrichment factor for the i-component can be defined as:

$$\beta_i = \frac{c_i^{permeate}}{c_i^{feed}} \quad (10)$$

Where $c_i^{permeate}$ is the mass concentration of i in the permeate, and c_i^{feed} in the feed.

The pervaporation selectivity for a pair of components i and j, $\alpha_{i,j}$, corresponds to the ratio of their enrichment factors:

$$\alpha_{i,j} = \frac{\beta_i}{\beta_j} \quad (11)$$

For diluted solutions and for very low downstream pressures (Cuusler, 1997):

$$\alpha_{i,j} = \frac{P_i H_i}{P_j H_j} \quad (12)$$

H_i and H_j are the Henry's constants for the i and j components.

Equation (12) can be written according to Equations (2), (8) and (9) as:

$$\alpha_{i,j} = \frac{\left(\delta_j - \delta_p\right)^2 A_{D,i} H_i}{\left(\delta_i - \delta_p\right)^2 A_{D,j} H_j} \quad (13)$$

if the constant B of Equation (8) and E_D and V_f of Equation (9) are supposed to depend only on the polymer.

A_D must decrease for molecules of larger sizes and thus can be assumed to be inversely proportional to the area of the surface of the molecule:

$$A_{D,i} = \frac{k}{A_i} \quad (14)$$

Because k should depend only on the polymer:

$$\alpha_{i,j} = \frac{\left(\delta_j - \delta_p\right)^2 A_j H_i}{\left(\delta_i - \delta_p\right)^2 A_i H_j} \quad (15)$$

Equation (15) predicts selectivities that could be compared with the experimental ones as obtained from Equation (11).

2. Materials and methods

2.1 Materials

- *Membrane:* The membrane used in the work was a hydrophobic membrane commercialized by Pervatech, (Enter, The Netherlands) with a support of PET (polyethylene), an intermediate Ultrafiltration membrane of polyimide and a thin layer of PDMS (poly-di-methyl-siloxane) (tg=130ºC) with hydrophobic/organophilic characteristics which allow a high flow of organic compounds. The thickness of the PDMS active layer is 1 μm (Van Hecke et al., 2012).

- *Beer:* We used four different types of beer, even though all of them are lager beers. A Special beer having 13.10% extract Original Gravity, OG, with 5.5% Alcohol By Volume, ABV, and a Reserve beer, 15.05% extract OG and 6.5% ABV. On the other hand we used a low-alcohol beer (less than 1% ABV) which comes from the Special beer and an alcohol-free beer (less than 0.1% ABV) which comes from the Reserve beer.

- *Reagents:* We have used four reagents to make the synthetic solution for the initial experiments: ethanol (96.0%), isobutyl alcohol (99.0%), ethyl acetate (99.5%) and isoamyl acetate (98.0%), all of them from Sigma-Aldrich.

Pervaporation system: The experimental device is described in Figure 1. The membrane is in a flat sheet cell which provides a membrane active area A = $6.6 \cdot 10^{-3}$ m^2. A pump extracts the solution or beer to pervaporate from the thermostated feed tank. This fluid circulates tangentially on the membrane in order to limit the effects of concentration-polarization. Downstream, after the membrane cell, a vacuum pump reduces the pressure down to 1 mbar. The permeate condensates in liquid nitrogen cold traps.

Gas chromatography (GC) conditions: The GC system consisted of an Agilent Technologies Chromatograph 7890 A. The injection volume was 1 µl. A Nucleosil column C 18 (250 × 4.6 mm, 5 µm) was used and the carrier gas was He 34.62 cm/s 16.057psi (35°C).

2.2 Methods

Two liters of a synthetic aqueous solution of ethanol (5.0 % v/v) was prepared with three aroma compounds (isobutyl alcohol, 12.67 ppm; ethyl acetate, 16.18 ppm and isoamyl acetate, 1.38 ppm). These concentrations are quite similar to those of a typical commercial beer (Catarino et al., 2009). Although, as will be apparent below, the beers we used here have higher concentrations of these species, the separation properties depend only slightly on concentration. Actually we performed experiments with concentrations close to 100-fold those used here without relevant changes in separation. These aroma compounds were selected because of their wide range of boiling points, one close to ethanol (78.4 °C at 1 atm.) and the rest much higher (Table 1). They are also very relevant aroma compounds to define the overall aroma of beer (Catarino et al., 2009).

This solution was filtered in order to test the membrane and the process to establish optimal conditions for pervaporation and to apply them to beer samples. Each experiment took six hours at least. Samples of permeate were taken at intervals of two hours. These samples were taken in cold tramps (Figure 1) where, by using liquid nitrogen, the permeate condensed. Gas Chromatography (GC) was the technique used to analyze the samples. GC was performed at 25ºC.

$3 \cdot 10^{-5}$ m^3/s was the flow of recirculation through the feed recirculation loop (retentate side). Pressures were 94.7 kPa in the retentate side and 0.1 kPa in the downstream side. Temperatures over 25ºC would accelerate pervaporation, but they would also enhance

evaporation in the feed and could cause denaturation of beer. Lower temperatures would slow down the process.

In preliminary tests, the synthetic solution was pervaporated at different feed pressures without any significant variation of flux. This would discard convective fluxes. Also measurements at 80 ºC were performed with fluxes nearly 4 times those at 25ºC. This seems to confirm that there is no convection and the solution-diffusion model should be appropriate as used in common literature (Baudot et al., 1999; Borjesson et al., 1996;Dobrak et al., 2010) for this polymer.

The flow rate used corresponds to a tangential speed of 1 m/s which allows considering concentration polarization as negligible. The feed pressure is only slightly over the atmospheric pressure and is determined by the recirculation flow rate, while the downstream pressure gives a high enough gradient of concentration through the membrane.

Once optimum conditions for the experiment were reached, beer samples were pervaporated. The duration of the tests was equal to those of the preview tests (6 hours), for the Special Beer. In the case of Reserve Beer, each experiment took 8 hours due to its more aromatic character. Samples of permeate were taken every two hours. Samples of feed, retentate and permeate were taken to analyze their content of aroma compounds using GC.

We incorporated the recovered permeate into low-alcohol and alcohol-free beers to enrich their flavor. The permeated solution is added into a non-alcoholic beer volume equal to the volume of regular beer used to recover these aromas by pervaporation.

After enrichment, we checked by sensory evaluation if the enriched beers were preferred to original non-alcohol beers. Sensory analysis of the beer samples was conducted in the sensory analysis room of the Department of Agricultural and Forest Engineering (Food Technology Area, University of Valladolid). The panel was composed of 10 assessors who had been trained according to the Standard ISO 8586-1:1993 (ISO 8586-1, 1993). The panel evaluated different beers with a wide variety of sensory characteristics as external appearance, smell or olfactory-gustatory sensations. After their training, the panel realized two tests, firstly the enriched sample had to be distinguished from non-enriched samples, and, after this, they had to decide which sample they preferred. The samples were presented to the tasters in glass cups and in single cabins.

3. Results and Discussion

In Figure 2 the time evolution of the permeate for both the special and reserve beers and the synthetic solutions are shown. The average fluxes for the two beers are shown as well.

For both the beers, the flux is more or less stable. For the Special beer, there is a higher flux at the initial steps of the process probably due to its lower content of substances hindering the transport of aromas. In fact, this beer has a lower free dry matter content than the Reserve beer, as mentioned in section 2.1. The average and final flux are higher for the Reserve beer, which has a larger concentration of volatile compounds than the Special beer.

The synthetic solution has similar flux evolution than the special beer possibly because they have similar alcohol contents. Fluxes are slightly lower for the synthetic solution and they decrease after the initial increase because its aroma contents are a lower and the decrease of concentration is significant. A slower decay at long times appears also for the special beer probably due to similar reasons.

The consecutive average concentrations for the feed and permeate are shown in Figure 3. The ethanol concentration in the permeate is quite similar for each beer along time. This seems logic because the feed concentration of ethanol is constant for each beer. The average concentration of ethanol in the permeate for the special beer is 3.9±0.8 g/L and 4.3±0.2 g/L for the reserve beer. These data correspond to a very similar enrichment factor of ethanol in both the beers and the synthetic solution; $\beta_{Ethanol}$=9.9±0.5. If the variation of ethanol in the beers is evaluated we obtain 0.11% ABV for the special beer and 0.19% ABV for the reserve one.

Generally, recovery of compounds increases in Reserve beer because, as mentioned, Reserve beer is usually more aromatic than Special beer. It is important to appreciate in this figure how the recovered concentration of ethyl acetate decreases in each time slot for both beers. The same holds true for isoamyl acetate. This is due to the decrease of the content of these compounds in the feed with time.

From data in Figures 2 and 3, the flux for each aroma can be evaluated as shown in Figure 4. The flux of ethanol is almost constant and higher for the reserve beer as could be expected due to its initial higher alcohol content. The alcohol flux is some orders of magnitude higher than the corresponding flux for the aromas again due to their much slower concentration in the feed. The highest flux corresponds to ethyl acetate for both beers. Initially for all the aromas, and especially for ethyl acetate, there is a strong increase in flux followed by a significant decrease and stabilization. In all cases flux is correlated with the initial concentration of the aroma.

To avoid the influence of initial concentration, the mass concentration enrichment factor for each component has been evaluated according to Equation (10). As can be seen in Figure 5, the two most abundant aromas have actually a clear initial over-flux followed by a clear stabilization. Ethyl acetate has the highest enrichment factor, while the other two aromas have much lower enrichment factors and are quite similar for a long period of time in both beers.

To understand why enrichment is obtained the membrane-solute interaction has to be taken into account. In our case the appropriate membrane must be hydrophobic in order to prevent the passage of water, the main component of beer by far. The membrane selected showed an ethanol/water selectivity over 15 for aqueous 5 % ethanol solution.

This strong hydrophobicity will hinder the transport of other polar species such as ethanol against other less polar substances such as those responsible for the aroma in beer. This is interesting in order to selectively retard the passage of ethanol. The compounds passed through the membrane could then be incorporated into non-alcohol beer without requiring ulterior separations to avoid an undesired increase of alcohol content.

A relevant parameter to quantify the membrane-solute interactions is the partition coefficient K_r. It is the ratio of concentrations of each species in non-polar and polar phases. Given that this coefficient has a wide range of variation, a logarithmic scale is conventionally used, log K_r

(sometimes it is called log P, here we preferred to use log K_r to avoid possible confusions with permeability). It was previously suggested (Blanco et al., en el 2007) that log K_r is correlated with the molecular surface (Table 1) and with the affinity of this surface to each species. The values obtained for log K_r are shown in Table 1. The compound with a higher log K_r would dissolve better in the organic phase and thus would pervaporate better. As shown in Figure 6 the order for log K_r is the same as that based on the solubility parameters. As expected, the polar solubility coefficient was particularly well correlated with log K_r .

As mentioned in the theory section, the flux of the flavor substances depends on the feed concentration and their interaction with the membrane that determines their solubility (Equation (8)) and diffusivity (Equation (9)) according to Equation (15). The selectivity can also be evaluated from their mass concentration enrichment factors and Equation (11).

In Figure 7, the experimental selectivity (Equation (11)) is shown in relation to that of ethanol in the synthetic solution and in the three beers studied compared to the theoretical selectivity according to Equation (15).

Figure 7 shows the experimental tendency is in accordance with the theoretical one. Of course the accordance is far from being accurate as should be if the points in this figure were on the plotted bisecting line. Note there are many factors that have not been taken into account in Equation (15), among them, for example, the interaction solute-solute which would be very different in the three solutions studied. Hence, a perfect accordance could not be expected. In any case, there can be no doubt that such a study can be useful to design and predict performances in order to adopt an appropriate pervaporation procedure because the trend is correctly predicted.

The membrane clearly shows a higher selectivity for ethyl acetate over ethanol. The same is true for isoamyl acetate to a lower extent. Nevertheless its presence in the permeate is low (Figure 3) due to its low concentration in the feed. In the figure it can be seen that both the esters show a decreasing concentration in the permeate while isobutyl alcohol gives an almost constant concentration. Which is due to its low solubility.

It is worth noting that the differences in $\delta_j - \delta_p$ between isobutyl alcohol and ethyl acetate or isoamil acetate show that it could be less transported due to the contribution of hydrogen bonds to solubility (see δ_i^h in Table 1).

Except for the special beer, isobutyl alcohol, exhibits a selectivity below 1. This means that a significant recovering of this aroma would imply an appreciable passage of alcohol to the permeate. Fortunately this is not too important because of its low impact on the flavor of beer and sensations in mouth (also true for other high molecular weight alcohols) (García et al. 1994).

After adding the aroma compounds recovered by pervaporation from the alcoholic beers into the original low-alcohol and alcohol-free original beers, they were analyzed by Gas Chromatography (GC). Table 2 shows how the concentration of aroma compounds generally increased in both reduced alcohol beers after aroma addition. In the case of isoamyl acetate, its concentration in the beers (with or without alcohol) was so low that addition could not be detected by GC. The increase in the alcohol content of the beers after addition of aromas was also negligible. This corresponds to the loss of pervaporated beers that was already mentioned

394 to be 0.11 % for the special beer and 0.19% ABV for the reserve one. These small increases in
395 the alcohol degree keeps the enriched beers between the law requirements mentioned in the
396 introduction.

397 We can also see in Table 2 how the increase in the concentration of aroma compounds is
398 important in both beers. For instance, isobutyl alcohol in alcohol-free beer increases 16.33% in
399 the enriched beer, and ethyl acetate in low-alcohol beer increases 35.72% due to the
400 enrichment of this beer.

401 The increase of aroma compounds in enriched beers, shown in Table 2, has a high impact on
402 the sensorial properties of beers. Sensory evaluation was performed in two tests as mentioned
403 above, informing of a certain improvement in aroma. The preference test, showed that, 90% of
404 tasters preferred enriched low-alcohol beer instead of low-alcohol beer and 80% of tasters
405 preferred enriched alcohol-free beer instead of alcohol-free beer. These results can be
406 interpreted as a relevant improvement in quality of non-alcohol beers due to the addition of
407 the aroma compounds recovered by pervaporation. As can be seen in Table 2, the percentages
408 of the selected aroma compounds in the enriched beers are still far below those in the special
409 and reserve beers, further additions would increase even more the taste of the enriched beers
410 although the percentages reached clearly improve their flavour.
411
412 **4. Conclusions**
413
414 We have demonstrated that pervaporation can be used to recover aroma compounds in beer.
415 The addition of these aroma compounds to more or less de-alcoholized beer enriches their
416 flavor. This increases their appreciation and could be used to meet the quality standards
417 required by the market.

418 The relevance of the polymer of the membrane has been highlighted here. Note that according
419 to Equation (15) a polymer will transmit almost perfectly a species if their solubility parameters
420 coincide. A wise tuning of the polymer (or polymers) with the adequate solubility parameter
421 would allow us to obtain very selective membranes for a given (or several) volatile
422 components. In particular it is clear that similar feed concentrations are recovered to different
423 extents due to their different solubilities.

424 The theoretical approximate calculation of relative selectivities from solubility parameters can
425 help in the design of the process and the selection of the membrane in order to comply with
426 specific separation requirements. A good selection of the membrane material could be the key
427 to reaching higher productivities for aroma recovery in beer and other pervaporation
428 processes.

429

430 ***5. Acknowledgements***
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432 Financial support from Junta de Castilla y León (VA332A12-2) and from “Ministerio de Ciencia e
433 Innovación (MCINN)” (CTQ2009-07666, CTQ2012-31076 and MAT2011-25513) is gratefully
434 acknowledged.

435 The authors would like to express their gratitude to Hijos de Rivera S. A. for supplying the
436 beers used in this study.

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Figure and table captions

Figure 1.- Pervaporation Diagram.

Figure 2.- Time evolution of flux during pervaporation for the two beers studied and the synthetic solution. Each point corresponds to an average of no less than three experiments.

Figure 3.- Concentrations of aroma compounds in Special and Reserve beers before and after permeation.

Figure 4.- Flux versus time for ethanol and the three aromas studied: (a) Special beer and (b) Reserve beer.

Figure 5.- Mass concentration enrichment factor for each component versus time for the three aromas studied: (a) Special beer and (b) Reserve beer.

Figure 6.- The different contributions to the solubility parameters as a function of log K_r.

Figure 7.- Experimental (Eq. (11)) selectivity versus the theoretical (Eq. (15)) selectivity referred to ethanol for the two beers and the synthetic solution. The best linear fit and the corresponding 95% confidence interval are shown too.

Table 1.- Parameters of ethanol and aroma compounds. Solubility constants are taken from the handbook of Brandrup and Immergut (Brandrup and Immergut, 1989).The Henry constants are taken from the thesis of Schäffer (Schäffer, 2002). Areas are calculated from Blanco (Blanco, 2007) and Log Kr from Řezáč (Řezáč, 2009). The rest of constants are also taken from the Handbook of Chemistry and general literature.

Table 2.-Concentration for the aroma compounds studied in original and enriched beer.

610

	Ethyl acetate	Isobutyl alcohol	Isoamyl acetate	Ethanol
Boiling point (°C at 1 atm)	77.0	107.89	141.85	78.4
Area ($Å^2$)	114.47	105.07	195.62	70.71
MW (g/mol)	88.11	74.122	130.18	46.07
Log K_r	0.98	0.89	2.09	0.1
H_i (kPa)	630.8	597.7	3030.2	23.9
δ_i ($Mpa^{1/2}$)	18.1	22.2	17.1	26.5
δ_i^d ($Mpa^{1/2}$)	15.8	15.8	15.3	15.8
δ_i^p ($Mpa^{1/2}$)	5.3	5.7	3.1	8.8
δ_i^h ($Mpa^{1/2}$)	7.2	14.5	7.0	19.4
$\delta_i - \delta_p$ ($Mpa^{1/2}$)	5.8	11.3	4.0	17.1

611

612

613 Table 1.- Parameters of ethanol and aroma compounds. Solubility constants are taken from
614 the handbook of Brandrup and Immergut (Brandrup and Immergut, 1989).The Henry constants
615 are taken from the thesis of Schäffer (Schäffer, 2002). Areas are calculated from Blanco
616 (Blanco, 2007) and Log Kr from Řezáč (Řezáč, 2009). The rest of constants are also taken from
617 the Handbook of Chemistry and general literature.

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622

	Ethylacetate	Isobutyl alcohol	Isoamyl acetate
	Concentration (ppm)		
Special	30.66	23.72	1.25
Alcohol-free	5.23	0.49	1.88
Enriched Alcohol-free	5.48	0.57	-
Reserve	24.23	27.92	2.23
Low-alcohol	9.49	2.88	3.31
Enriched Low-alcohol	12.88	6.70	1.15

623

624 Table 2.-Concentration for the aroma compounds studied in original and enriched beer.

625

Figure

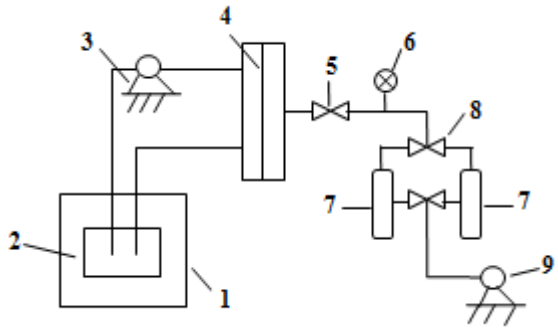


Figure 1.

Figure

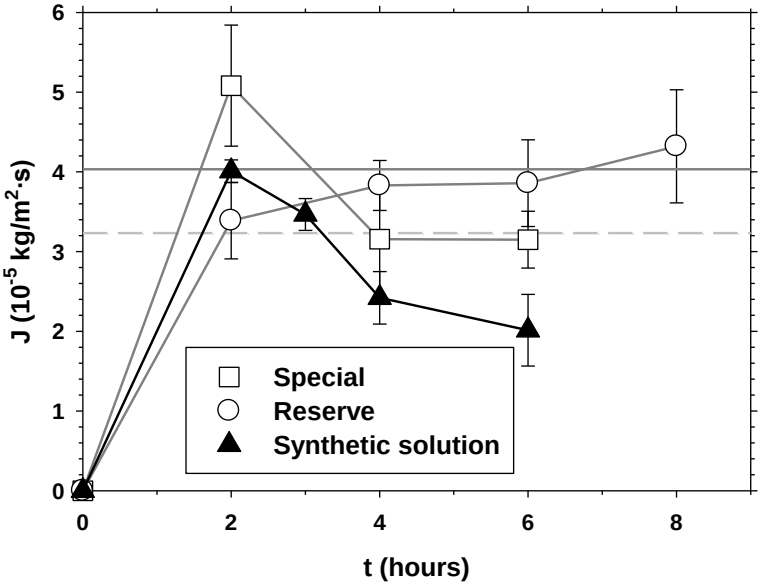
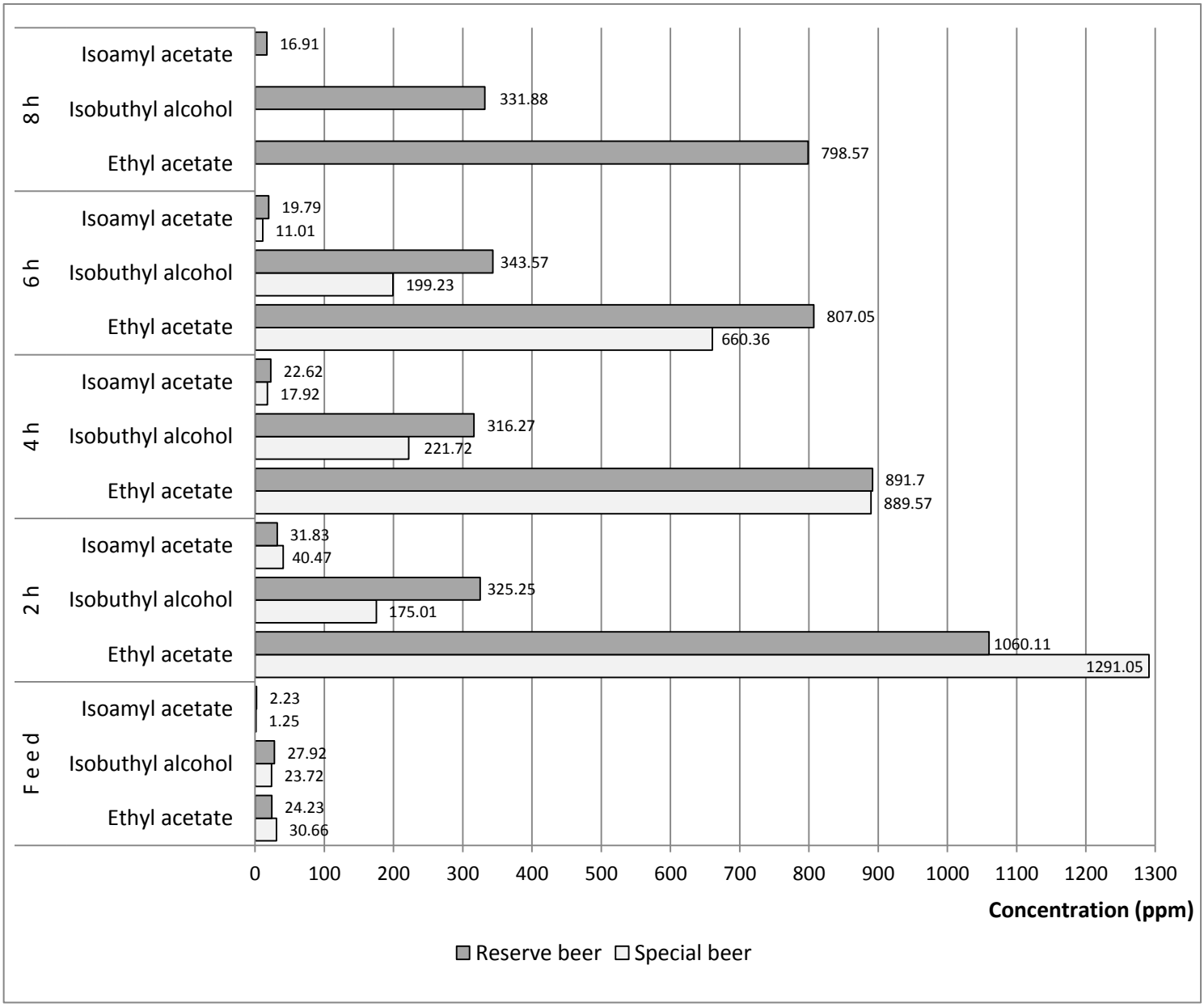


Figure 2

Figure


8 h
Isoamyl acetate
Isobuthyl alcohol
Ethyl acetate
6 h
Isoamyl acetate
Isobuthyl alcohol
Ethyl acetate
4 h
Isoamyl acetate
Isobuthyl alcohol
Ethyl acetate
2 h
Isoamyl acetate
Isobuthyl alcohol
Ethyl acetate
Feed
Isoamyl acetate
Isobuthyl alcohol
Ethyl acetate
16.91
331.88
798.57
19.79
11.01
343.57
199.23
807.05
660.36
22.62
17.92
316.27
221.72
891.7
889.57
31.83
40.47
325.25
175.01
1060.11
1291.05
2.23
1.25
27.92
23.72
24.23
30.66
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
Concentration (ppm)
Reserve beer
Special beer

Figure

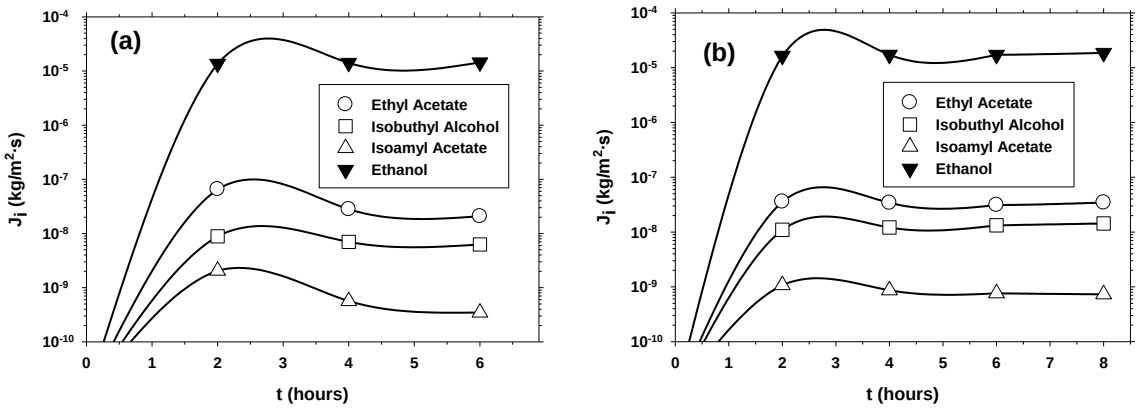


Figure 4

Figure

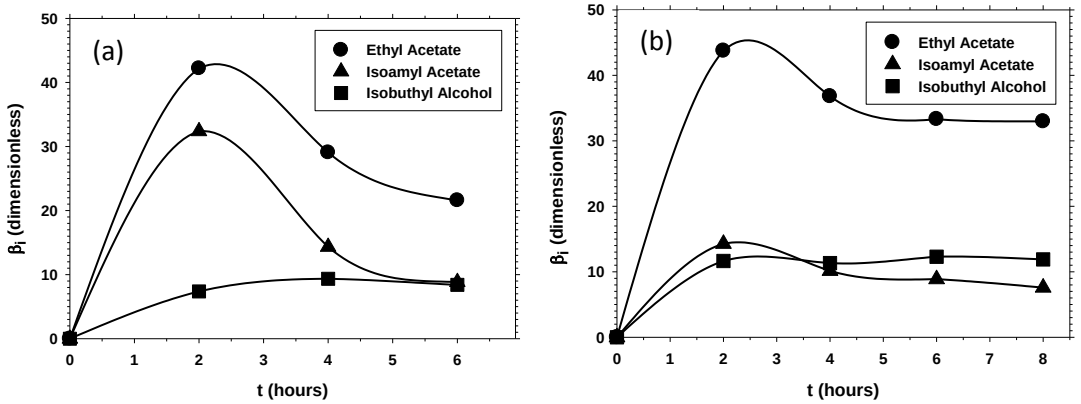


Figure 5

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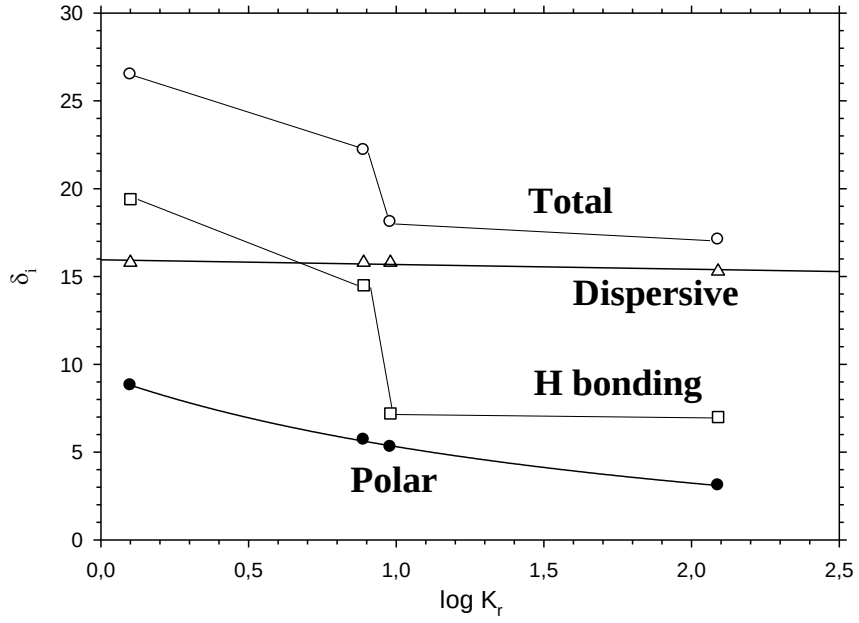

Figure 6

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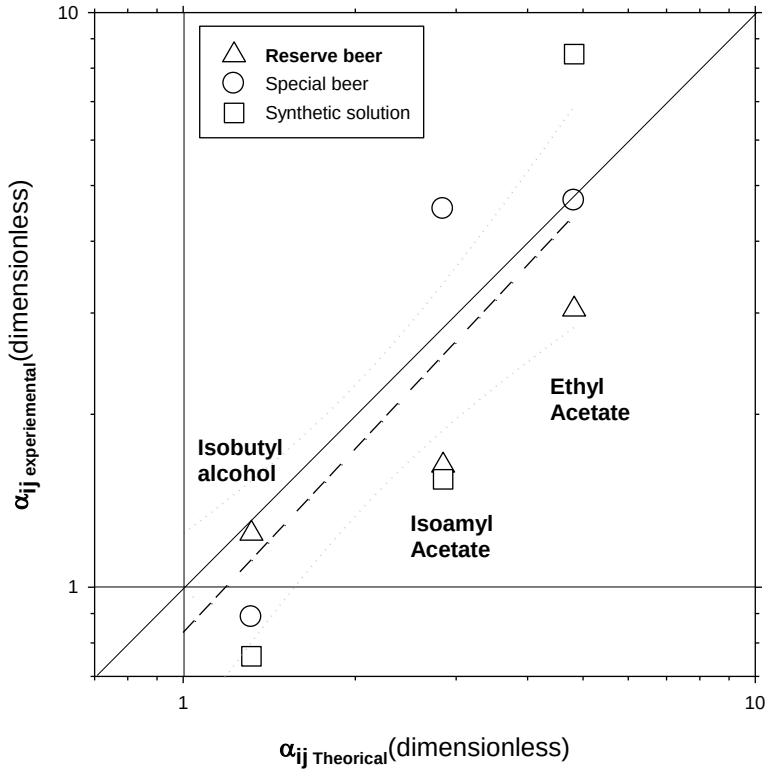

Figure 7