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Sustainable Low-Alcohol Beer Production by Combination of Membrane Osmotic Distillation and Pervaporation

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Membrane osmotic distillation (OD) is applied in this work for the partial dealcoholization of beer (5.2 v/v% alcohol content) to diminish its ethanol content by around 50% giving rise to a low alcohol beer. A compromise is sought between the low alcoholic degree achieved and beer sensory properties. Moreover, the feasibility of the membrane OD process intensification is studied thanks to its combination with membrane pervaporation (PV). Two successive PV stages, one hydrophobic and the other hydrophilic, allow the production of recycled water (with less than 0.5 wt% ethanol) for the membrane OD operation and bioethanol (99% ethanol) as valuable byproduct.

1. Introduction

Beer is one of the most important alcoholic beverages in the world with an annual production of almost 2000 million hectoliters per year,[1] being also the most consumed alcoholic beverage in Western society.[2] Currently, beer industry is betting on a series of innovative products such as alcohol-free beer and different carbohydrate composition beers[3] in response to the current social trend for a healthier life. Gluten-free beer is also a way to extend beer consumption to people excluded, in principle, for health reasons.[4] Nonalcoholic beer has recently grown in interest due to the fact that it allows beer consumption when the consumer plans to drive a vehicle,[5] or is following some medical advice when suffering from a certain illness.[3] In addition, nonalcoholic beer could be a way to expand the beer market to Islamic countries, where alcohol consumption is prohibited by law.

Nonalcoholic beer seeks to maintain the intrinsic healthy and organoleptic properties of beer, without the adverse effects of ethanol. However, the "normal beer" sensory characteristics are not easily being obtained in dealcoholized beers since they are negatively affected by the dealcoholization process. For instance, the reduction of ethanol by enzymatic activity generates a sweet taste in beer, while those processes (e.g., evaporation or distillation) that require an increment in temperature produce less intense products with a reminiscent caramel flavor.[6,7]

To avoid a thermal damage of the organoleptic and nutritional characteristics of the final product, the use of membranes for beer dealcoholization (mainly through nanofiltration and reverse osmosis processes) has increased along the last years.[8–11] Membranes can diminish the ethanol content in alcoholic beverages operating at room temperature. Nonetheless, these techniques demand a relatively high energy consumption to achieve the required pressure (the driving force), raising the total cost of the process. Moreover, this pressure also affects the rest of components different from ethanol to a greater or lesser extent, with the produced beer, poor in body and aroma, being still far from meeting the preferences of consumers.[7]

Contrarily, latest membrane technologies are able to work at low pressure and ambient temperature,[12] reducing the required energy consumption and the impact over the product compared to most of membrane and nonmembrane based technologies. In this context, membrane osmotic distillation (OD) has already been used in wine and beer dealcoholization.[13–19] Unfortunately, the sensory properties of beers dealcoholized by OD do not fully satisfy consumer preferences.[20]

In membrane OD, the feed (beer in this case) is separated by the membrane to a solution with low content in the component of interest (ethanol). Ethanol partial pressure gradient between both membrane sides acts as the driving force instead of using

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a total pressure difference (which remains null). Moreover, the role played by the volume ratio between feed and stripping streams establishes the limit of dealcoholization grade and aromas losses. While a total dealcoholization of wine by OD reported a huge loss of volatile compounds of up to 98%,[16,21] lower degrees of dealcoholization (until −5 v/v%) made possible to obtain wines with sensory characteristics closer to those of the parent wines.[14,22] A similar behavior can be expected for a beer subjected to partial dealcoholization by membrane OD, potentially showcasing this technique as an effective tool to carry out beer partial dealcoholization with a higher preservation of volatile compounds at a certain dealcoholization degree (2–3 v/v%).[23] Beer aroma and taste are less related to those components that undergo the highest losses, namely certain alcohols and esters, than in wine.[18] In these conditions, the beer quality, and thus its sensory features, can be related with parameters such as ethanol content, pH, antioxidant activity, total carbohydrates, bitterness and color, typically controlled in the brewing industry.

Beer with a lower ethanol concentration is a very common world tendency, being nowadays very consumed in the U.S. market,[24] although its success has not been replicated in Europe, where this beer has been attributed similar defects to those associated with full dealcoholized beer. However, without requiring a total dealcoholization, low-alcohol beer production by OD would make possible to achieve a trade-off between the decrease of the alcoholic degree and the loss of beer properties, being a healthier beverage with aroma and body profiles similar to those of a regular beer. From an energy consumption point of view, two streams are generated after the OD: dealcoholized (or partial dealcoholized) beer and an extracting stream, basically water with a low ethanol content and which could be considered a waste. However, recent studies have reported a novel intensified process based on the combination of membrane OD with pervaporation (PV, a membrane operation for the separation of liquid mixtures by selective evaporation through, typically, a dense film) to recover the ethanol present in the OD waste (ODW).[25] This intensified process allows the reuse of the water stream and revalorizes the removed ethanol from wine as bioethanol. In order words, the combined process reduces the total energy demand by OD facilitating its potential industrial application. **Figure 1** shows the schematic representation of the OD-PV process combination.

In this work, membrane OD is proposed for the partial dealcoholization of beer in order to reduce its ethanol content by around 50%, aiming at achieving a compromise between a low alcoholic degree and key beer properties, related to its sensory behavior, such as pH, antioxidant activity, total carbohydrates, bitterness and color. Moreover, the feasibility of the membrane OD process intensification by combination with PV was studied in the context of low-alcohol beer production.

2. Experimental Section

2.1. Materials

Beer submitted to dealcoholization in this work was kindly provided by La Zaragozana S.A. (Zaragoza, Spain): Ambar Especial, a Lager beer with an alcoholic content of 5.2 v/v% whose main quality parameters are in **Table 1**.

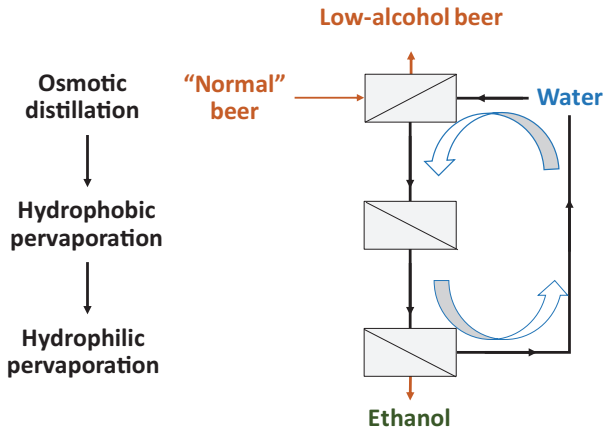

Figure 1. Intensified process (OD-PV combination) scheme for beer dealcoholization with membranes.

Table 1. Quality parameters measured in this work for beer Ambar Especial.

Beer quality parameter	Value
Ethanol concentration [v/v%]	5.3
pH [–]	4.2
Antioxidant activity [μM Ga]	301
Total carbohydrates [g·100 mL^{-1}]	4.7
Bitterness (IBU)	24
Color (EBC)	12.3

A hydrophobic porous polypropylene (PP) membrane module supplied by 3M with an effective membrane area of 0.18 m^2 (MM – 1 × 5.5 × 50 Liqui-Cel) was used in this work. The 3M membrane module was equipped with 2300 hollow fibers (HF) with a nominal pore size of 0.03 μm, an effective membrane length of 14 cm, and internal and external diameters of 220 μm and 300 μm, respectively. Regarding PV membranes, tubular zeolite membranes (25 cm^2 of membrane area; 1.2/0.86 cm of outer/inner diameters) were placed in a homemade stainless steel permeation module equipped in the PV setup. Hydrophobic (HFB) silicalite-1 (SIL, with the MFI-type structure) and hydrophilic (HFL) mordenite (MOR, with the MOR-type structure) membranes were applied to carry out the combined HFB-HFL PV on the OD stripping stream. Preparation and physicochemical characterization of the zeolite membranes were previously reported elsewhere.[26–28]

2.2. Experimental Setup

OD experiments were carried out by duplicate in a lab scale plant equipped with the above described PP membrane modules. In each dealcoholization trial, 200 mL of beer (V_f) was fed to the shell side of the membrane module, while a certain volume (in the 200–400 mL range) of deionized water (V_s, stripping stream) was fed to the tube side in a counter-current configuration to enhance the ethanol extraction.[29] Feed or retentate (Q_f) and stripping or permeate (Q_s) flows were continuously recirculated to the beer and the water tanks thanks to two peristaltic pumps (Dinko,

Table 2. Operating conditions for membrane OD at room temperature (11 °C), V_f = 200 mL and Qs = 39 mL min^{-1}.

Condition	Q_f [mL min^{-1}]	V_s [mL]	Ethanol flux [L m^{-2} h^{-1}]	Ratio $V_s \cdot V_f^{-1}$ [–]	$[EtOH]_s$ [a)] [v/v%]	$t_{1/2}$ [b)] [min]
C1	20	400	0.039	2	1.4	50
C2	74	400	0.043	2	1.4	45
C3	74	200	0.031	1	2.6	90[c)]
C4	74	300	0.031	1.5	2.0	60

Note: Beer partial dealcoholization performances under each experimental condition are also included. [a)] $[EtOH]_s$, ethanol concentration in the stripping volume; [b)] $t_{1/2}$, time to reduce from 5.2 to 2.5 v/v%; [c)] Under the operating conditions, it was not possible to achieve the value of 2.5 v/v%, see also Figure 2.

model 1.9735.15). Pressure (1 atm) and temperature (11 °C) in the system were monitored and controlled by pressure indicators and a chiller bath circulator (Julabo, CORIO-201F), respectively. An inert atmosphere inside the dealcoholization module, vessels and pipes was achieved before each dealcoholization trial forcing nitrogen gas to flow at 100 cm^3 (STP) min^{-1} through the experimental system during 2 h. After each experiment, a cleaning protocol ensured that the OD plant and the membrane module were in suitable conditions. Briefly, several cycles with pressurized deionized water and compressed air were applied to clean the OD system and the membrane modules were subjected to additional cleaning with 0.5 wt% NaOH water solution at 60 °C.

Table 2 shows the conditions corresponding to the partial dealcoholization trials carried out in this work. The effect of feed flow was evaluated in trials C1 and C2, while the influence of the volume ratio between feed and stripping streams was studied in trials C2–C4. It is worth mentioning that beers were previously decarbonated by a slight aging under inner atmosphere during 4 h. Quality parameters from original and decarbonated beer were comparable (Figure S1, Supporting Information).

The stripping stream from the beer partial dealcoholization by membrane OD was treated in an ethanol recovery station that basically consists of two PV membrane modules equipped with membranes SIL (hydrophobic separation, HFB) and MOR (hydrophilic separation, HFL). HFB-HFL combined PV setup fed both membrane modules with a flow of 15 mL min^{-1}, achieving a permeate vacuum pressure of 4 mbar thanks to a vacuum pump (Pfeiffer MPV-040-2). See our previous publication for this PV applied to wine membrane ODW for further details.[30] It is worth mentioning that 100 mL of the stripping stream from beer dealcoholization (i.e., beer ODW) was fed in each PV trial for an easier comparison of its performance with those previously obtained with wine ODW in our just cited work.

2.3. Beer Analysis

During OD and PV experiments, aliquots of all streams leaving the membrane modules were taken at constant time intervals in order to analyze their ethanol concentration and the other quality parameters related to the sensory properties of beer. Regarding the ethanol analysis, 20 µL of methanol (HPLC grade, Scharlau) was added to 1 mL of sample as internal standard. This mixture (0.5 µL) was injected in a gas chromatograph 7820A (Agilent Technologies) equipped with a PORAPAK Q80/100 column, 2 m × 1.8 in. × 2 mm and a flame ionization detector. The injector worked in splitless mode with a 1:100 ratio at 250 °C. Helium was used as carrier gas at a constant flow of 1 mL min^{-1} and the temperature in the oven was fixed at 200 °C. From the ethanol concentration and stripping weight, membrane fluxes at fixed time intervals were calculated with the following equation

$$J_{Exp}(t) = \frac{\Delta W}{A_e \cdot \Delta t} \quad (1)$$

where ΔW is the variation of the ethanol mass for an interval of time, Δt, and A_e corresponds to the effective membrane area. The performance of membrane PV was expressed as a function of PV flux and separation factor, two parameters that often behave in the opposite way, and pervaporation separation index (PSI), obtained as a product of PV permeation flux and separation factor, to achieve a deeper knowledge about membrane PV performance.[31]

pH was measured with Thermo Scientific pH-meter Orion Star A2011. A UV–vis spectrophotometer (Jasco V-670) was used to obtain several parameters in order to characterize the beer. These parameters are: color (EBC units, European Brewing Convention), bitterness (IBU, International Bitterness Units), total carbohydrates (g·100 mL^{-1}) and antioxidant activity. Beer color was evaluated according to the standard method (EBC, 2008), measuring directly the sample absorbance at a wavelength of 430 nm (Abs_{430}). It is calculated with the following equation

$$Color_{EBC} = 25 \cdot Abs_{430} \quad (2)$$

EBC method 9.8 was followed to obtain the bitterness extracting the bitter substances from beer, mainly iso-α-acids.[32] The following procedure was applied: 10 mL of beer, 1 mL of HCl 3M (ACS reagent, Sigma Aldrich), 20 mL of isooctane (>99%; Carlo Erba), and 50 µL of 1-octanol (>99%; Sigma-Aldrich) were added into a 50 mL centrifuge tube. The mix was vortexed (Ibx V05 series) at 60% for 15 min. The resulting emulsion was centrifuged at 1900 rpm for 5 min at room temperature, generating two phases. The upper phase (organic solution) was collected and analyzed by UV spectrometry at a wavelength of 275 nm (Abs_{275}) using 50 µL 1-octanol/20 mL isooctane as a blank. Bitterness was calculated in IBU as follows

$$Bitterness\ (IBU) = 50 \cdot Abs_{275} \quad (3)$$

To measure the total carbohydrate concentration, the phenol-sulfuric acid method was applied.[33] Briefly, a certain amount of beer was diluted by a factor of 1:1000 and 2 mL of this was mixed with 1 mL of 5 v/v% phenol (90%; Sigma Aldrich) in water. After that, 5 mL of sulfuric acid (>95%; Scharlau) was added to the previous resulting mixture. A standard solution was prepared following the same procedure using a solution of dextrose (2 v/v% in deionized water) instead of beer, while 2 mL of deionized water was mixed with the same phenol/sulfuric acid ratio used for the samples. All solutions were vortexed for 10 min (until a homogenous aspect was observed) and analyzed by UV spectrometry at a wavelength of 490 nm. The total carbohydrate concentration in

the sample was expressed in g·100 mL^{-1} applying the following equation

$$Total\ carbohydrates = \frac{0.9 \cdot \left(Abs_{sample} - Abs_{blank}\right) \cdot 2}{\left(Abs_{standard} - Abs_{blank}\right)} \quad (4)$$

The antioxidant activity in beer was evaluated following the DPPH method previously used by Tafulo et al.[34] Shortly, a solution (0.19 × 10^{-3} M) of DPPH, 2,2-diphenyl-1-picrylhydrazyl (pure, Sigma Aldrich), was prepared in a sodium acetate hydroalcoholic solution (50 v/v% ethanol) 0.1 M. A certain amount of beer (200 µL) was diluted 15 times with the DPPH solution. After 10 min, the DPPH radical reaction was measured at a wavelength of 525 nm, expressed as Ga equivalent concentration (µM). Finally, the total solids present in the different solutions were quantified by the weight difference method, measuring weights before and after overnight total evaporation of each solution at 100 °C.

3. Results and Discussion

To link the behavior of several quality parameters of beer with its composition, the beer was diluted with deionized water producing several diluted beers. The spectrophotometric analysis used to obtain the values of the quality parameters of all of the diluted beers showed, as expected, a linear correlation with the dilution grade (Figure S1, Supporting Information). Meanwhile, several studies have reported that some of these parameters (pH, antioxidant activity, total carbohydrates, bitterness, and color) maintained at acceptable values with a minor loss of volatile components close to 90%.[35,36] This suggests that the concentration of these volatile compounds has not a major influence on the typical beer quality parameters evaluated here, within the interval suggested.

3.1. Beer Ethanol Removal by Membrane OD

Once the analysis of quality parameters was validated with sample dilutions (Figure S1, Supporting Information), 200 mL of Lager beer was submitted to partial dealcoholization by OD under different experimental conditions (Table 2) until achieving a low-alcohol beer with a 2.5 v/v% alcohol content. The stripping/feed volume ratio ($V_s \cdot V_f^{-1}$) is critical, determining the maximum amount of each component that migrates from the beer to the stripping stream through the membrane. In fact, the dealcoholization degree and eventual volatile components loss are strongly dependent on the volume ratio used. With the objective of a reduction of the alcoholic degree until 2.5 v/v%, i.e., around 50% regarding the initial amount of ethanol, three trials were carried out under the same feed flow (Q_f = 74 mL min^{-1}) and different $V_s \cdot V_f^{-1}$ ratios. Condition C3: the minimum that allows the removal of the ethanol objective, $V_s \cdot V_f^{-1} = 1$; condition C2: twice that in C3, $V_s \cdot V_f^{-1} = 2$: and condition C4: an intermediate ratio, $V_s \cdot V_f^{-1} = 1.5$. As shown in Table 2, the higher the defined volume ratio, the lower the experimental time required to produce the low-alcohol beer, as a consequence of the higher ethanol flux achieved.

The effect of the feed flow (Q_f) was evaluated with the comparison of trials C1 and C2, using Q_f of 20 and 74 mL min^{-1}, respectively. In agreement with the previous results for wine dealcoholization using the same experimental system,[17] the ethanol flux increased from 0.039 to 0.043 L m^2 h^{-1} and, in consequence, the time for ≈50% dealcoholization decreased from 50 to 45 min (**Figure 2** and Table 2). The ethanol fluxes obtained here are in line with those previously reported for beer dealcoholization: an ethanol flux of 0.04 L m^2 h^{-1} was obtained by Liguori et al.[15] working at 10 °C with a $V_s \cdot V_f^{-1}$ ratio of 2, while 0.028 L m^2 h^{-1} was achieved by De Francesco et al. with higher volume ratio feed/stripping streams ratio = 1/6) and dealcoholization degree (a reduction around 90% in the alcohol degree).[35] Nevertheless, in general, all these ethanol fluxes, including the ones obtained here, are minor than those obtained when partially dealcoholizing wine with the same type of PP membranes (0.10–0.12 L m^2 h^{-1}).[17] The difference is probably due to the presence of traces of dissolved CO_2 in beer, which may clog the membrane pores, thus hindering the passage of ethanol through them. Another contribution may be the higher amount of dissolved solids in the beer, potentially contributing to the membrane fouling. Figure 2 shows the variation of the ethanol content in the feed and stripping streams as a function of time under the different experimental conditions shown in Table 2 (runs C1–C4).

Under C3 conditions (see Figure 2), the partial dealcoholized beer only achieved an alcoholic degree of 2.7 v/v% when reaching the steady state after about 45 min (2.6 v/v% at 90 min) due to the limitation of the stripping volume with the lowest value tested of 200 mL (Table 1). In any event, this value is not far from the target of 2.5 v/v% but with a considerable saving of water as compared to the other conditions. A slightly dilution, an allowed practice in the brewing industry,[37] of the beer obtained under these conditions could help to achieve the target of dealcoholization. Comparing C2 and C4, a higher volume ratio (2 vs 1.5) allowed to obtain the low-alcohol beer in a faster way (45 and 60 min, respectively). However, this time reduction implied the use of a higher amount of stripping volume (water needed in C4 was reduced by 25%), consequently increasing the consumption of water and ODW generation. Moreover, ethanol recovery from this ODW would require a less energy demand as ethanol concentration in this stream increases (from 1.4 to 2.0 v/v%, see Table 2). With this in mind, the optimum condition corresponds to C4, achieving the dealcoholization degree target in a reasonable time and generating an ODW stream with a higher ethanol concentration. Furthermore, the overall volume of ODW generated was reduced by 25%, facilitating the recovery process.

3.2. Quality Parameters of Low-Alcohol Beer

To study the influence of the experimental conditions on the quality of the obtained product, five parameters and their dependence on the dealcoholization degree were evaluated. It is worth mentioning that the values obtained from C3 conditions were not included here due to the fact that the alcohol removal target was not achieved. It is evident that the values of quality parameters should raise due to the removal of ethanol during OD, i.e., increasing in a 2.5% after a reduction of 50% in the alcohol degree. Table S1 (Supporting Information) summarizes all previous reports used here for an accurate comparison with the performance achieved in this work.

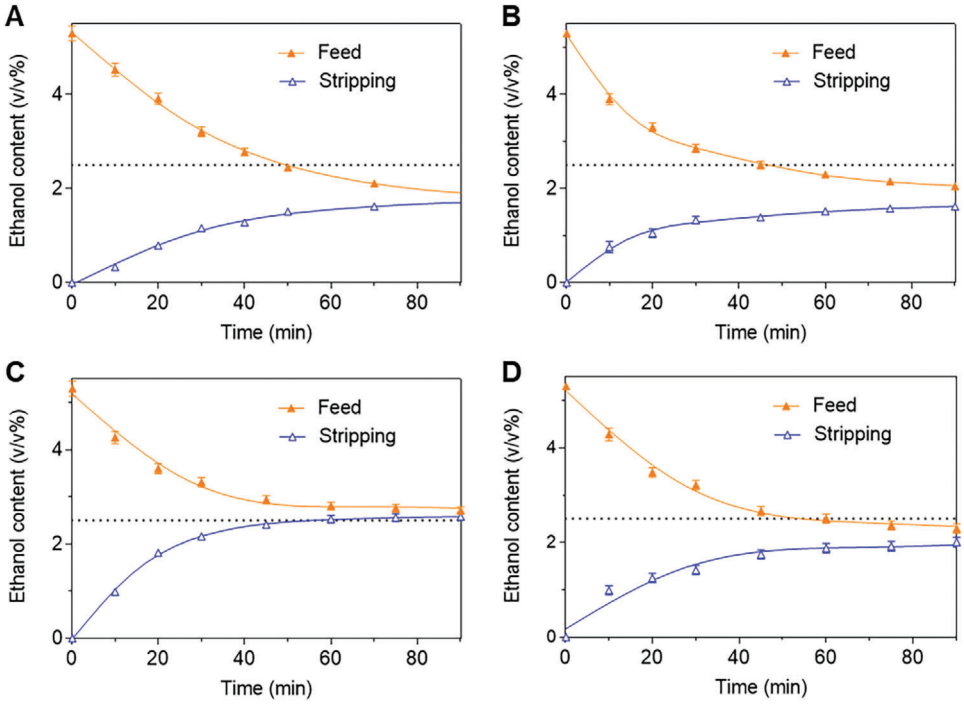

Figure 2. Ethanol content as a function of the time corresponding to a beer feed with 5.2 v/v% of ethanol. Experimental conditions for (A)–(D) correspond to C1–C4 in Table 2. Represented data are the mean values with the corresponding standard deviations. The curves are only guides to the eye. Dashed horizontal lines indicate the target for the degree of dealcoholization, 2.5 v/v%.

3.2.1. pH and Antioxidant Activity

The pH analysis of beer allows the estimation of the presence of acids playing in turn an important role in the beer resistance to microbial contamination.[38] These acids are organic ones such as acetic, pyruvic, lactic or succinic acids.[39] However, as **Table 3** shows, there is no correlation between the pH, the dealcoholization degree (when comparing C0 with the rest of conditions) and the different dealcoholization conditions applied. The slight changes observed were independent of the mentioned conditions and can be related to the presence of traces of dissolved CO_2 in beer. The absence of correlation indicates a nonsignificant impact of OD on the acid composition, which is in agreement with previous reports.[15,35,40] Carboxylic acids are in general more polar than alcohols, what limits their transport through the hydrophobic PP membrane; therefore, their composition remains unaltered. This hypothesis is in accordance with recent studies reporting that the acid composition in beer was not significantly altered by the OD dealcoholization, except for acetic acid.[41] Interestingly, this exception has also been found in several wine dealcoholization studies, where the loss of acetic acid was explained by its high volatility as compared to those of other polar compounds.[16,21]

Table 3. Quality parameters without correlation with the dealcoholization degree.

Condition	C0	C1	C2	C4
Alcoholic degree [v/v%]	5.2	2.5	2.7	2.5
pH value	4.19 ± 0.01	4.20 ± 0.01	4.19 ± 0.00	4.19 ± 0.01
Antioxidant activity [μM Ga]	301 ± 8	292 ± 15	296 ± 19	287 ± 5

Concerning beer antioxidant activity, this has been typically evaluated by the measurement of the scavenging capacity of free radical DPPH. This assessment is based on the changes observed in the stable radical DPPH by the electron donating ability of the sample.[42] As can be seen with Tables 2 and 3, the antioxidant activity decreases with the time required by each condition to reach the same dealcoholization degree, from 296 to 287 × 10^{-6} M Ga for C1–C4 conditions, being 301 × 10^{-6} M Ga in the starting beer (C0). A strong relation between beer antioxidant activity and the presence of polyphenols generated from the Maillard reaction (e.g., the chemical reaction between reducing saccharides and amino acids) has been previously stablished.[43,44] In this sense, the change in the antioxidant activity of beer can be explained by the higher oxidation degree of polyphenols as a consequence of the handling of the beer samples and the exposure time to the dealcoholization conditions,[45] even if the necessary precautions were taken into consideration during the treatment of beer (e.g., purging the system with N_2 to remove the air, as done here).

3.2.2. Total Carbohydrates

As depicted in **Figure 3**A, the concentration of total carbohydrates shows, for all the experimental conditions eptudied, a nonlinear increase as a function of the percentage of ethanol removal.

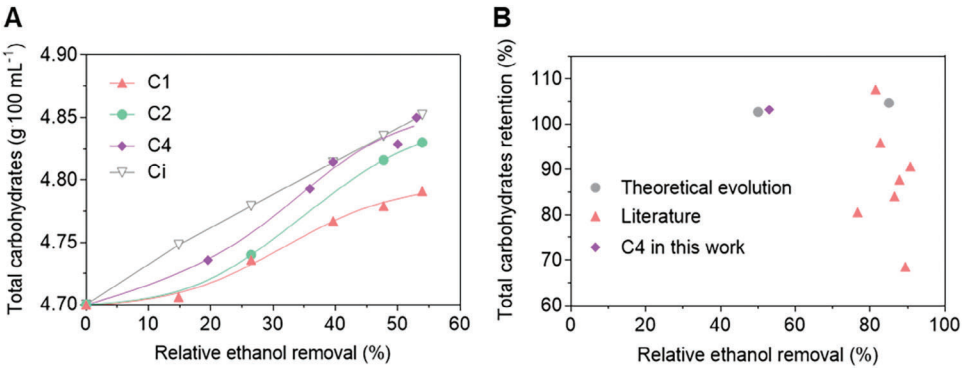

Figure 3. Total carbohydrates in beer as a function of the relative ethanol removal. A) Evolution of total carbohydrates from starting beer (4.70 mg L^{-1}) under C1, C2, and C4 conditions. The "theoretical values" (Ci) correspond to the concentration increase due to the removal of ethanol (see Figure S1, Supporting Information). B) Relative total carbohydrates retention in dealcoholized beers obtained from different studies (Figure S1, Supporting Information). The lines are only guides to the eye.

The results suggest that for C4 conditions total carbohydrates could be close to the expected maximum values, not being recommended a higher dealcoholization degree for the remaining conditions (C1 and C2) where the losses of carbohydrates were slightly greater. C1 conditions (at the lowest feed flow of 20 mL min^{-1}) diverges more from the theoretical values (Ci), suggesting some component retention by the membrane due to the low surface velocity.

Comparing the values of total carbohydrates obtained from each condition with each other and with the values (Ci) obtained from the concentration increase due to the removal of ethanol, the low-alcohol beers obtained when applying C1 (4.79 g·100 mL^{-1}) and C2 (4.83 g·100 mL^{-1}) conditions present a less amount of carbohydrates, while C4 and Ci are equal (≈4.85 g·100 mL^{-1}), at the same ≈50% dealcoholization. The evolution of carbohydrates below the expectation (the straight line corresponding to Ci) can be due to their retention by the membrane, since they are quite hydrophilic and larger in size than ethanol. Together with ethanol, carbohydrates are the main source of calorific energy in beer, thus being relevant in the nutritional value of the product. Even if the carbohydrate composition is complex, two main chemical families of carbohydrates can be found in beer: fermentable sugars (25%), such as maltotriose or maltose, and dextrins (75%), a nonfermentable sugar coming from the hydrolysis of starch.[46,47] The first ones are directly related with the sweetness of beer and contribute to the beer body on mouthfeel. Meanwhile, dextrins have also a great contribution to the beer taste and body. Therefore, the similar values of total carbohydrates displayed by C4 light and original beer suggest that the beer obtained would present the body that consumers demand in a nonalcohol beer. To contextualize the results obtained here, Figure 3B compares the percentage of total carbohydrate left in the partially dealcoholized beer as a function of the percentage of ethanol removal under C4 conditions (see Table 2) with analogous values taken from recent literature (see Table S1, Supporting Information). As can be seen, the total carbohydrates left in this work were close to the expected theoretical values, while most of the non-alcoholic beers reported in literature have a total carbohydrate retention clearly lower than the theoretical value, thus demonstrating the higher efficiency of our approach.

3.2.3. Bitterness

As can be seen in **Figure** 4A, bitterness parameter was much more affected than total carbohydrates under all the experimental conditions studied. The worst result was obtained when running the OD with the lower feed flow (i.e., C1 condition at 20 mL min^{-1} feed flow, which would favor component retention by the membrane as suggested when discussing the evolution of carbohydrates). This dealcoholization condition produced bitterness values far below those of the original beer (Ci value, corresponding to the concentration correction as said above) and of the other obtained under C2 and C4 conditions. In fact, these two conditions produced low-alcohol beers with bitterness values higher than that of the original one (24 IBU), although the bitterness tended to decrease as the dealcoholization degree approached the target in both cases.

Iso-α-acids, polar compounds, are responsible for the beer bitterness[48] contributing to the beer bitter taste by around 80%.[49] Thus, a good control of bitterness value (C2 and C4 conditions) is consistent with the permanence of such compounds in the beer upon its partial dealcoholization. Besides, iso-α-acids contribute to the microbiological stability of beer[50,51] and have a favorable health effect on beer consumers.[52,53] Therefore, bitterness can be considered as a positive indicator of the beer quality. However, iso-α-acids are presented in beer in both isomeric form with a trans/cis ratio about 0.4,[54] showing these a different contribution to the positive effects.[48] The trans α-acid exhibits the best properties in both aspects.[55] In addition, as shown in Figure 4B, as a consequence of the ethanol removal, non-alcoholic beers previously reported show a lower retention capacity of compounds responsible for bitterness than the expected theoretical value. Even if under C4 conditions both the theoretical values and the experimental almost coincide, the general trend (lower bitterness) can be explained by isomer conversion from the trans to the more stable cis during the dealcoholization process, decreasing the absorbance value of bitterness, in agreement with previous reports. This conversion is also supported by the less solubility in water of the trans isomer, which in turns favors the cis isomer formation.[56]

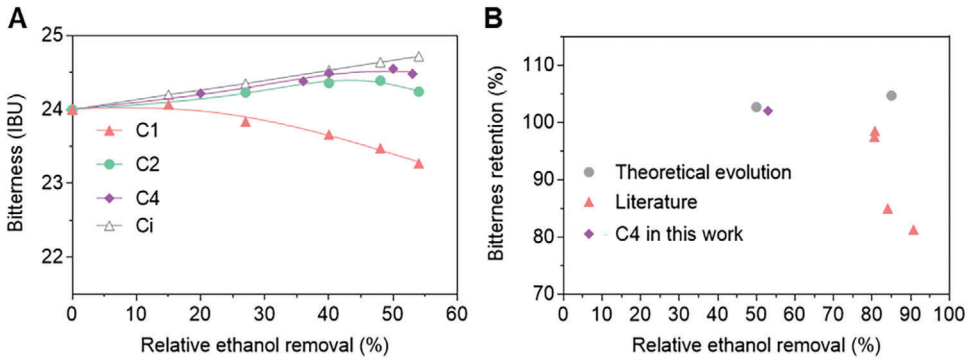

Figure 4. Bitterness (IBU) in beer as a function of relative ethanol removal. A) Evolution of bitterness from feed beer (with 24.0 IBU) under C1, C2, and C4 conditions. The "theoretical values" (Ci) correspond to the concentration increase due to the removal of ethanol (see Figure S1, Supporting Information). B) Relative bitterness value retention for dealcoholized beers obtained from different studies (Figure S1, Supporting Information). The lines are only guides to the eye.

3.2.4. Color

The beer color is mainly attributed to melanoidins, nitrogen-containing polymers formed from the Maillard reaction over the brewing.[57] Melanoidins constitute a very heterogeneous group of compounds with antioxidant capacity,[58] but only a few of them have been isolated. One of them is perlolyrine, [59] whose boiling temperature is around 534 °C, expecting that its loss during the dealcoholization should not be significant (OD is based on vapor phase separation). **Figure** 5A shows a continuous and linear color increase as a function of the removal of ethanol under all experimental conditions.

The color increases are consistent with the retention of melanoidins, explaining the enhancement of the antioxidant activity of the low-alcohol beers obtained, discussed above. Alternatively, the increase was not only due to the Maillard reaction products. In this sense, several studies have concluded that the oxidative degradation of some polyphenols is responsible for the color increment observed during beer storage.[58] Unfortunately, the major issue is that this oxidative degradation not only affects the color intensity but also the correlation with chill haze formation (i.e., the precipitation of beer polyphenols and proteins[60]) reported by several authors, leading to a decline in the beer stability properties.[61] In any event, since the relative changes in color are small, the increment observed here is closer to the predicted value, as shown in Figure 5B. On the contrary, those beers with a lower ethanol amount (≈90% of ethanol removal) presented in Figure 5B exhibited, in general, a higher color increment than the predicted one. This can be explain by the sharper oxidation of polyphenols with a less amount of ethanol in beer.[62]

3.3. OD Waste Water Valorization via PV Process

The suitability of the combined HFB-HFL PV as an ethanol recovery station was tested here feeding the PV setup (Figure 1) with the ODW generated in experiment C4. **Table** 4 compares the PV performance achieved with the same membranes (silicalite-1-SIL as hydrophobic-HFB and mordenite-MOR as hydrophilic-HFL membranes) applied in our previous work to treat wine ODW.[30] As a first result, changing the feed from the wine residue to the beer residue did not affect the essential PV performance giving rise to similar ethanol/water (36–39, with the HFB membrane) and water/ethanol (≈6500–6900, with the HFL membrane) separation factors. This allowed a good intensification by coupling both OD and PV processes and reducing the ethanol concentration in the ODW in the hydrophobic step until 0.5 wt%, which would allow its reuse as stripping stream, as demonstrated for wine.[30] Meanwhile, the HFL step produced an ethanol concentration over 99% (i.e., producing bioethanol). These results

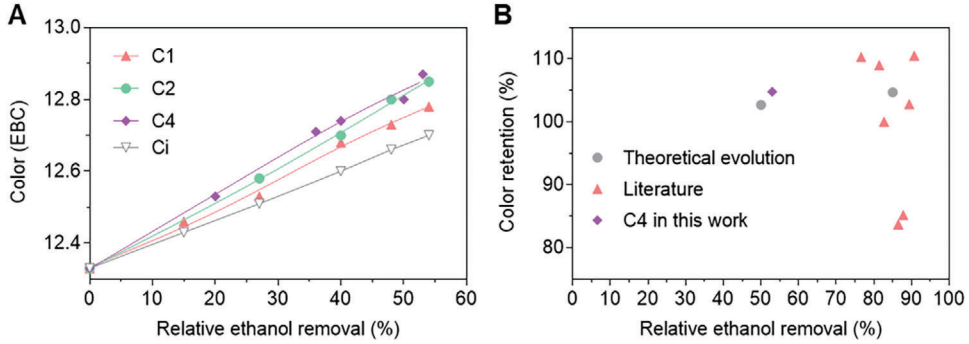

Figure 5. Color in beer as a function of relative ethanol removal. A) Evolution of color from feed beer (with 12.3 EBC) under C1, C2, and C4 conditions. Theoretical values (Ci) correspond to the concentration increases due to the removal of ethanol. B) Relative total color value retention in partial and total dealcoholized beers obtained from different studies (Figure S1, Supporting Information). The lines are only guides to the eye.

Table 4. Comparison of hydrophobic (HFB)–hydrophilic (HFL) PV performance with beer and red wine OD waste.

Feed	Separación	Ethanol content [wt%]		Time [min]	$\alpha_{ethanol/water}$ (HFB) $\alpha_{water/ethanol}$ (HFL)	PV total flux [kg m^{-2} h^{-1}]	PSI[a)]
		Initial (feed)	Final (retentate)				
Beer ODW	HFB	2.0	0.5	280	39	0.47	18
	HFL	23	>99	75	6524	1.4	8090
Wine ODW	HFB	5.3	0.4	550	36	0.72	26
	HFL	36	>99	300	6919	1.2	8303

[a)] PSI (pervaporation separation index) calculated as PV total flux multiplied by ($\alpha_{ethanol/water}-1$).

agree with previous works in which ethanol–water mixtures were separated by combining hydrophobic and hydrophilic PV processes,[30,63,64] generating permeate streams with more than 80 wt% ethanol (hydrophobic PV) and more than 99 wt% water (hydrophobic PV), respectively.

The PV water flux reduction in the HFB PV when treating beer ODW as compared to wine ODW (see Table 4) obtained can be linked to a higher organic matter amount present in the beer waste water than in the wine one (transferred from the corresponding parent alcoholic products to the stripping streams during OD). This contribution has been corroborated by quantifying the total suspended solids present in both beer and wine waste waters: 170 mg L^{-1} (25 200 mg L^{-1} in parent beer) and 85 mg L^{-1}, respectively.

Finally, the HFB-HFL PV in combination with the OD allowed obtaining the target product (i.e., low-alcohol beer) with a negligible water consumption per liter of beer produced, revalorizing 85% of the removed ethanol as bioethanol. However, the main challenge was observed in the hydrophilic step as a consequence of the reduced alcohol content of the OD stripping stream that led to obtain a HFB PV permeate with a lower ethanol concentration as compared to that obtained from wine (23% and 36%, respectively, see Table 4). Interestingly, this difference only seemed to increase the experimental time required (in relation with the total amount feeding) without a pernicious influence over the PV total flux or separation factor. This suggests that the organic matter present in the waste water would have been mainly retained in the HFB PV retentate.

The HFB-HFL PV in combination with the OD allowed obtaining the target product (i.e., low-alcohol beer) with a negligible water consumption per liter of beer produced. The total mass balance led in turn to the estimation of a recovery of 98% of the streaming stream with around 0.5 wt% ethanol, while 85% of the removed ethanol was recovered as bioethanol (with >99 wt% purity). **Figure 6** depicts a scheme of the HFB-HFL PV process where concentrations and quantities of each stream are included.

Finally, it is worth mentioning that, even if the application presented here is new, the membranes used for it have good industrial application perspective with recent up scaling[65] and life cycle analysis[66] studied of PP membranes for dealcoholization, application of hydrophilic membranes for solvent dehydration[67] and promising application of silicalite-1 membranes for hydrophobic application.[68]

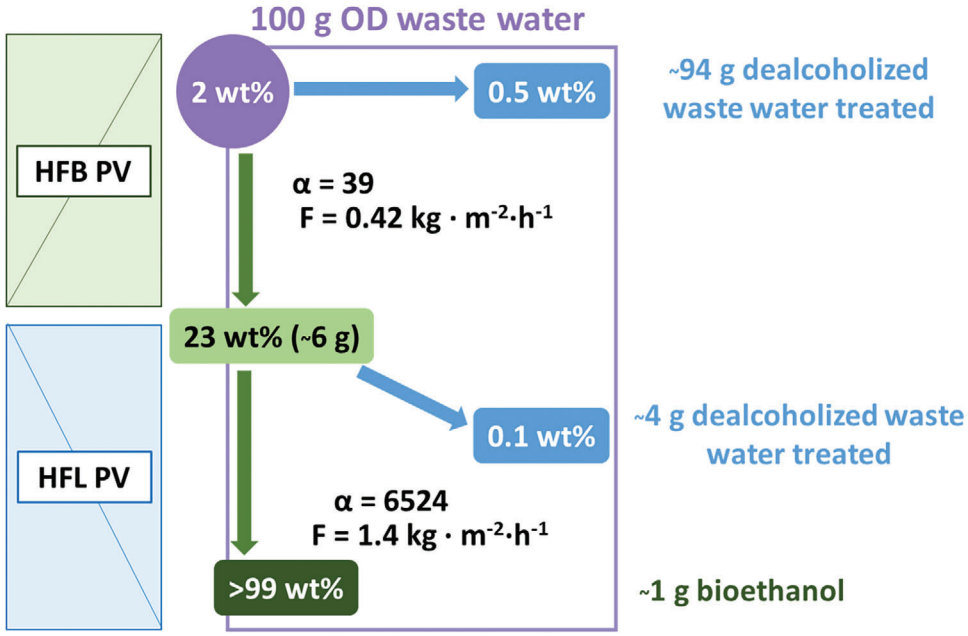

Figure 6. General of the HFB-HFL PV coupling.

4. Conclusions

Membrane osmotic distillation has been demonstrated as a feasible technology for beer partial dealcoholization using a polypropylene hollow fiber membrane module. A low-alcohol beer, with 2.5 v/v% of ethanol, was produced by feeding the dealcoholization plant with a Lager type beer with an ethanol degree of 5.2 v/v%. The viability of the approach was adequately assessed though the analysis of several quality parameters typically considered by the brewing industry such as pH, antioxidant activity, total carbohydrates, bitterness, and color. These parameters resulted to be a useful tool to set up those soft operation conditions to achieve a better preservation of the beer quality and sensorial properties.

Furthermore, silicalite-1 and mordenite being suitable zeolites to constitute robust pervaporation membranes, the combination of hydrophobic pervaporation with a silicalite-1 membrane, to concentrate in ethanol the membrane OD waste water, and subsequently hydrophilic pervaporation with a mordenite membrane, to dehydrate the ethanol, allowed a good process intensification producing water with a 0.5 wt% ethanol (susceptible of being reused as a stripping agent) and 99% bioethanol. All together, the membrane OD working at low temperature, preserving the beer properties upon its partial dealcoholization, and the combined pervaporation, clearly adding value to a waste, constitute a sustainable approach to the production of low-alcohol beer.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

beer, membrane osmotic distillation, pervaporation, polypropylene, zeolite

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