

Investigation of Osmotic Distillation Technique for Beer Dealcoholization

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A growing demand for low-alcohol drinks, due to health and social benefits resulting from lower alcohol consumption, has given rise to the development of techniques for alcohol reduction or elimination in beverages. The main difficulty is the development of a low alcohol content product with sensory properties similar to the original one. This work presents a preliminary study on the production of alcohol free beer (alcohol content ≤ 0.5 %vol) by osmotic distillation technique, which allows to operate at low temperature and atmospheric pressure, using water as ethanol stripping agent. To this goal, a lab-scale plant equipped with a commercial membrane contactor with hollow fibers was set up. The effect of different stripping agents for ethanol removal on dealcoholization kinetics and on chemical and physical properties of the dealcoholized beer (i.e. alcohol content, colour, pH, polyphenols, antioxidant activity) was investigated. Finally, the ethanol mass flux through the membrane during the dealcoholization process was measured and theoretically calculated with a good agreement.

1. Introduction

Beer is one of the most popular alcoholic beverages and its origin dates far from a very old period until nowadays. The market supply of non-alcoholic beverages has experienced an increasing trend in the last years. This trend resulted from the new consumption practices of reducing the alcohol intake for several reasons, such as: the preference of a healthier lifestyle, new restrictive driving/drinking regulations, religion reasons, etc. There are two main strategies to produce alcohol free (≤ 0.5 %vol) beer: biological and physical processes (Branyik et al., 2012). The former involves the production of alcohol free beer by methods which reduce the ethanol formation, i.e. changed mashing process, arrested or limited fermentation process, use of special yeast. The physical processes, consisting of technologies applied for ethanol removal from regular beers, can be divided into two groups: thermal and membrane processes. Among the processes applied on the industrial scale, the first one comprises vacuum evaporation or distillation and spinning cone column. With respect to biological processes, these allow to completely reduce the ethanol content (even lower than 0.05 % vol) in beer, but have the main disadvantage of the loss of aroma compounds from beer besides to the high costs of investment and operation. With regard to the membrane processes, dialysis and reverse osmosis are the beer dealcoholization technologies industrially used. The membrane processes with respect to physical processes have less thermal impact on beer, but at the same time they require significant capital and running costs.

An alternative membrane process, which was recently applied to partial (Liguori et al., 2012; Diban et al., 2008) and total wine dealcoholization (Liguori et al., 2013) is the osmotic distillation. In osmotic distillation either side of a microporous hydrophobic membrane is separated by two aqueous solutions (feed and stripping solution) having different solute (i.e. ethanol) concentrations. Osmotic distillation has the potential to operate at ambient (or lower) temperature and atmospheric pressure without causing product damage (Nagaraj et al., 2006).

The present work proposes this technique for producing an alcohol free beer. To this aim, we used as stripping agent pure water or aqueous solutions with low alcohol concentrations. During the process, the chemical and physical properties (i.e. alcohol content, colour, pH, polyphenols, antioxidant activity) of dealcoholized beers were evaluated and compared with regular beer. Moreover the ethanol mass flux through the membrane measured during the dealcoholization process was theoretically calculated with a good accuracy.

2. Theory

In the osmotic distillation process, the ethanol removal consists of three steps: evaporation at feed side, diffusion across the membrane and condensation at stripping side. The driving force for such transfer is the difference in ethanol vapour pressure at the two sides of membrane. During osmotic distillation, ethanol transfer from feed to the stripping side originates concentration profile from the bulk solutions to the membrane surface.

The classical expression for component flux J^i across the membrane in OD is:

$$J^i = K_{ov}^i (p_f^i - p_s^i) \quad (1)$$

where p_f^i (Pa) is the partial pressure of component i in the feed phase, p_s^i (Pa) is the partial pressure of component i in the stripping phase and K_{ov}^i ($\text{g Pa}^{-1} \text{m}^{-2} \text{s}^{-1}$) is the overall mass transfer coefficient of the component i through the membrane. In order to calculate the overall mass transfer coefficient an hypothesis of three resistances in series was considered: i) mass transfer resistance in feed boundary layer, ii) membrane resistance through the air gaps in the membrane pores, and iii) mass transfer resistance in stripping boundary layer.

The mass transfer coefficients in the feed (k_f) and stripping (k_s) phase can be estimated by using the following empirical correlation:

$$\text{Sh} = A (\text{Re}^a \text{Sc}^b) \quad (2)$$

where A , a , and b are constants, Sh , Re and Sc are respectively Sherwood, Reynolds and Schmidt numbers. In the case of feed solution flowing inside the fibres, the mass transfer coefficient k_f was estimated by the following correlation that has been shown by several investigators to predict tube side mass transfer coefficients with reasonable accuracy (Gabelman and Hwang, 1999) :

$$\text{Sh} = 1.615 \left(\text{Re} \cdot \text{Sc} \cdot \frac{d_h}{L} \right)^{\frac{1}{3}} \quad (3)$$

For the mass transfer at the shell side k_s (flow parallel to the hollow fibres), it was used the equation found by Prasad and Sirkar (1988) which takes into account the packing of the fibres:

$$\text{Sh}_s = \beta \left[\frac{d_h(1-\phi)}{L} \right] \text{Re}^{0.6} \text{Sc}^{0.33} \quad (4)$$

where d_h (m) is hydraulic diameter, L (m) is module length, $\beta = 5.8$ for hydrophobic membrane, ϕ is the packing density.

The mass transfer coefficient in membrane was determined according to the transfer in a porous medium as described by Dusty gas model (Alves and Coelho, 2004) in which the molecule-pore wall and molecule-molecule collisions are considered in the diffusion mechanism in the membrane pore. The membrane mass transfer coefficient K_m ($\text{g Pa}^{-1} \text{m}^{-2} \text{s}^{-1}$) was calculated as follows:

$$K_m = \frac{M^{\text{EtOH}}}{RT\delta} \left[\frac{1}{D_k^{\text{EtOH}}} + \frac{1}{D_{m-\text{air}}^{\text{EtOH}}} \right]^{-1} \quad (5)$$

where D_k^{EtOH} $D_{m-\text{air}}^{\text{EtOH}}$ (m^2/s^2) are respectively the Knudsen effective diffusivity of ethanol and the molecular diffusivity of ethanol in air.

3. Materials & Methods

3.1 Materials

The membrane module was 1x5.5 Liqui-Cel with the following characteristics: polypropylene membrane, 1800 cm^2 surface area, 42 μm thickness and 14 cm length, 40% porosity, 0.03 μm membrane pore diameter. It consisted of 2300 fibers with dimensions: 11.5 cm length, 220 μm inner diameter and 300 μm

outer diameter. A lager pale beer (5 %vol) was purchased from a local market. All reagents used for chemical analyses were analytical grade by Sigma Aldrich.

3.2 Experimental setup and conditions

The apparatus consists of a membrane module in which feed (i.e. beer) and stripping (i.e. water) streams flowed in recycle mode, respectively, in the lumen and shell side. The temperature of both streams was controlled by a thermostatic water bath and the temperatures of retentate (dealcoholized solution) and permeate (water enriched in ethanol) were monitored by K-type thermocouples. Feed pressure was measured by a manometer.

Preliminary dealcoholization tests were performed on hydroalcoholic solutions (used as feed stream) at concentrations ranging from 0.8 to 5 %vol. In all the tests, the feed volume was 500 mL, the stripping to feed volume ratio (V_s/V_f) was fixed to 2, the feed and stripping flow rates were respectively 70 and 140 mL/min, the process temperature was 10°C. Different stripping agents were used: i) pure water and ii) alcoholic solutions at different concentrations obtained as permeate by previous dealcoholization steps. The ethanol concentration profile during time in both streams was evaluated to determine the process time. As will be discussed in the following the dealcoholization process was carried out in cycles at the end of which the stripping solution was renewed.

Beer dealcoholization tests were then performed in subsequent cycles, of which length was determined by dealcoholization tests of hydroalcoholic solutions.

3.3 Analyses

Chemical and physical analyses were carried out on beer and dealcoholized samples. The pH was measured by pHmeter, whereas the alcohol content was measured by pycnometer. Beer colour was analyzed according to the standard method (EBC, 2008) using an UV/Vis spectrophotometer (Perkin Elmer). The colour was calculated in accordance with the following expression:

$$\text{EBC color} = A_{430} (10 \text{ mmcell}) * 25 \quad (6)$$

The phenolic content was determined by Folin-Ciocalteu method (Singleton & Rossi, 1965): every beer samples (1 mL) was mixed with 15 mL Na_2CO_3 (20%) and 7.5 mL Folin-Ciocalteu reagent and the final volume was made up to 100 mL with distilled water. After 2 h of reaction at room temperature, in the dark, the absorbance at 765 nm was determined.

DPPH radical scavenging activity of different samples of beer was determined according to the method of Brand-Williams et al. (1995) with minor changes: diluted beer sample (0.1 ml) was added to 2.9 ml of $6 * 10^{-5}$ mol/l DPPH solution (dissolved in methanol). The absorbance at 515 nm was measured after the solution had been allowed to stand in the dark for 40 min. A blank experiment was also carried out applying the same procedure to a solution without the test material and the absorbance was recorded. The antioxidant activity was expressed as percentage inhibition of DPPH and then calculated according to the following equation:

$$(\%) \text{ inhibition of DPPH} = 100 * \left(\frac{A_{\text{blank}} - A_{\text{sample}}}{A_{\text{blank}}} \right) \quad (7)$$

The final results were expressed as percentage of antioxidant activity/ μl of beer.

3.4 Statistical Analysis

Dealcoholization trials and analytical measurements were carried out in triplicate and mean values and standard deviation values were reported. Monofactorial variance analysis was used to determine significant differences ($p < 0.05$) among beer (5 %vol) and dealcoholized beer samples by Analysis Lab software.

4. Results and discussion

4.1 Dealcoholization tests

The temporal profile of ethanol concentration starting from a hydroalcoholic solution at 5%vol and using pure water as stripping agent was reported in figure 1a. Differences between ethanol concentrations of feed and stripping streams progressively decreased during time, until (about 100 min) the concentration in both streams approached the equilibrium. It is worth noting that after 60 min, the difference in alcohol content between the two streams was about 1.3 %vol and changed slightly with respect to the equilibrium condition. On the basis of these results, the dealcoholization process was divided in cycles and 60 min

was chosen as the duration of 1st cycle. The 2nd cycle time was set up on the basis of dealcoholization kinetics results starting from a hydroalcoholic solution at 2.5 %vol (Figure 1b). The streams approached the equilibrium condition in a shorter time (about 80 min) and the ethanol concentration difference between the streams was about 0.7 %vol already at 45 min which was chosen as duration of the 2nd cycle. Similar results were obtained starting from 1.3 and 0.8 %vol hydroalcoholic solutions, respectively, so the last two cycles lasted 45 min each one.

On the basis of previous results, the beer dealcoholization process was performed in 4 cycles, in order to produce a dealcoholized beer (≤ 0.5 %vol) starting from an alcohol content of 4.95 %vol (Figure 2a). The alcohol concentration was halved (2.77 %vol) after 1st cycle and it decreased progressively up to 0.5%vol in the dealcoholized beer. At the end of each cycle, the alcohol content in stripping agent was approximately equal to alcohol content removed from the beer.

During beer dealcoholization, ethanol flux was measured and the values were compared with those of hydroalcoholic solutions at the same concentrations estimated by means of empirical correlations (Eq. 1-5). The ethanol flux decreased with the reduction of the ethanol concentration difference at membrane sides (Figure 2b). It is worth noting that, except for the first cycle, the differences between the theoretical and experimental values were small, and hence the correlations were able to well describe the ethanol flux found experimentally. So the behavior of the beer can be described with a good accuracy with that of a hydroalcoholic solution, without taking into account other substances that may interpose and influence the ethanol flux through the membrane.

In order to limit water consumption, the beer dealcoholization was performed using as stripping agents the alcoholic solutions (permeate) obtained by a previous dealcoholization process. To this purpose, the permeate solutions obtained from the 2nd, 3rd, 4th cycle (respectively at 0.77, 0.41 and 0.17 %vol ethanol concentration) were used as stripping solutions respectively for the 1st, 2nd and 3th cycle of the new process.

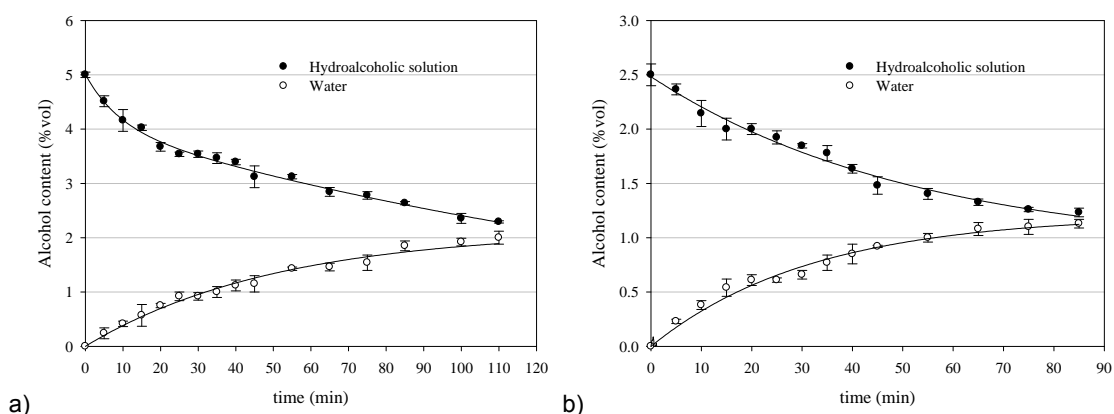


Figure 1. Dealcoholization kinetics of hydroalcoholic solution at 5%vol (a) and 2.5%vol (b).

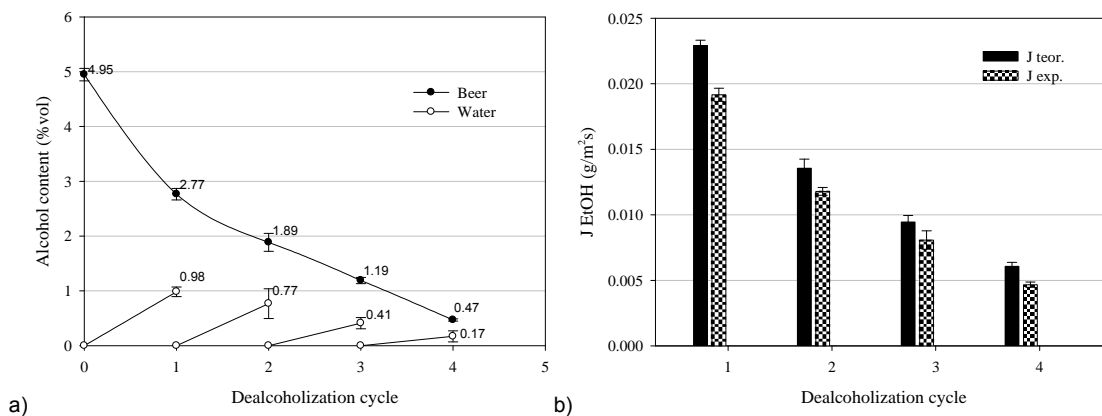


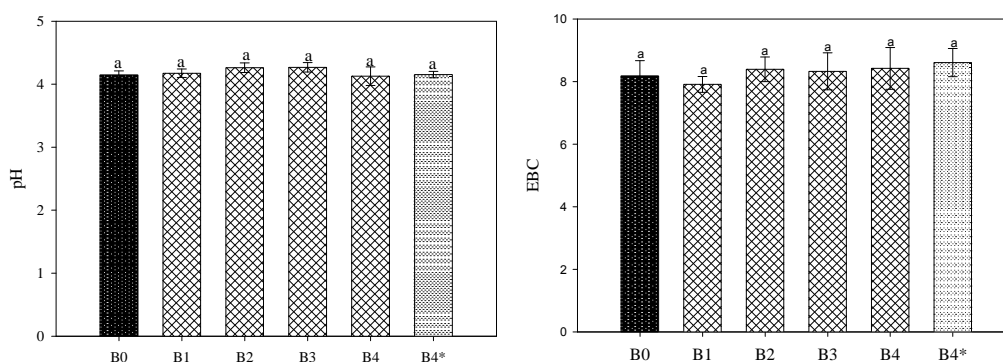
Figure 2. Dealcoholization kinetics of beer (a) and comparison between experimental and theoretical ethanol flux (b).

The stripping agent for the 4th cycle (0.08 %vol) was obtained by diluting the permeate of the 1st cycle. The duration of the cycles was maintained constant except for the 1st and 2nd cycles which was increased to 75 min and 60 min respectively, in order to take into account the reduced difference in concentration between feed and stripping solution. At the end of the 4th cycle a dealcoholized beer at 0.46 %vol ethanol was obtained.

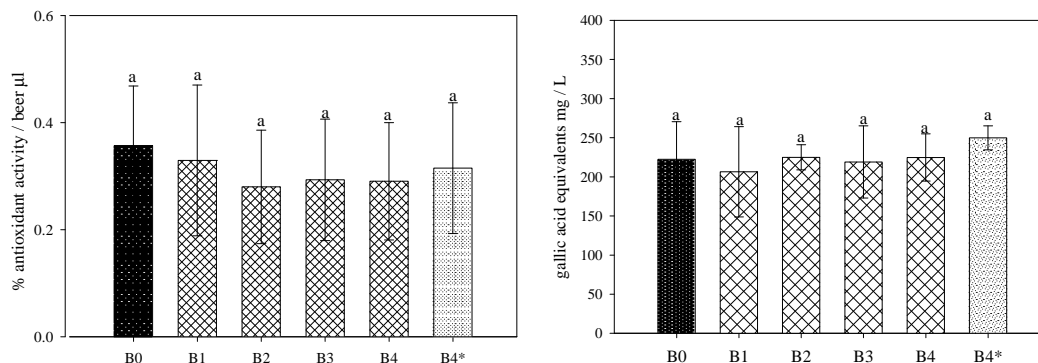
4.2 Chemical and physical analyses

Alcoholic and dealcoholized beer samples were analyzed for some chemical and physical properties. In particular, pH, colour, antioxidant activity and phenols content.

The pH of beer is an important parameter because low value causes a good aroma stability and resistance to microbial contaminations (Smedley, 1992). Figure 3a showed pH values of initial beer (B₀) and of beer samples at different alcoholic concentrations, obtained at the end of each dealcoholization cycle for both dealcoholization process with pure water (B₁-B₄) and with permeate solutions (B₄^{*}) as stripping agents. pH values did not vary significantly ($p < 0.05$) during dealcoholization, and also for dealcoholized (< 0.5%vol) beer samples, which values were similar to those reported in other studies (Harmanescu et al., 2006; Branyik et al., 2012). The colour together with the foam is the first parameter used by consumers during the quality evaluation of the beer. Data of alcoholic beer and beer samples at different concentrations were expressed according to the scale EBC and reported in figure 3b. Colour changes of the alcoholic and low alcohol content beers appeared to be not statistically significant ($p < 0.05$). Similarly, no significant differences ($p < 0.05$) between alcoholic and dealcoholized beer obtained with permeates as stripping solutions were found. The obtained values were in the range 4-18 (EBC scale) of pale lager beers (Shellhammer, 2009). The antioxidant activity and polyphenols content contribute both improving beer flavor stability and preventing free radical generation (Zhao et al., 2010). Moreover, the antioxidant capacity of foods and beverages has attracted researchers' interest due to their protective properties against several diseases. As reported in figure 4a, the antioxidant activity remained approximately unchanged during the dealcoholization process, taking into account that the error on measurement was of the same order of the error between the samples. The values obtained were comparable to those reported by Harmanescu et al. (2006), which showed values in the range 0.0026-0.3498 (% μl^{-1}).



a) b)
Figure 3. pH (a) and EBC colour (b) of beer and dealcoholized beer samples at the end of different cycles.



a) b)
Figure 4. Antioxidant activity (a) and phenolic content (b) of beer and dealcoholized beer samples at the end of different cycles.

Phenolic compounds play an important role both in flavour and colloidal stability of beer besides to represent an important source of antioxidants in beer (Vanderhaegen et al., 2006). As expected, phenolic compounds did not undergo significant changes when compared to alcoholic beer (Figure 4b). Phenols, in fact, are molecules with a high molecular weight that do not cross the membrane in vapour phase. The polyphenol content of the beer was in agreement with values reported by Zhao et al. (2010) which found values ranging from 152.01 to 339.12 mg gallic acid equivalent (age) / L in 34 beer samples.

5. Conclusions

Osmotic distillation was found as a feasible technique to produce low alcohol content and dealcoholized (≤ 0.5 %vol) beers. Preliminary results about pH, colour, antioxidant activity and polyphenols content on the dealcoholized beer with the two types of stripping agents (pure water and alcoholic solutions) highlighted properties similar to those of regular beer. The selection of permeate solutions of previous process as stripping agent is a valid alternative in order to reduce water consumption and minimize the environmental impact of the process, even though with slightly longer process time. Moreover, ethanol recovery from the stripping solutions can be further used as a potential blending stock in the manufacture of alcoholic beverages. Future works will be focused on the study of aroma profile of dealcoholized beer.

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