



Variation of oxygen isotopic ratio during wine dealcoholization by membrane contactors: Experiments and modelling



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ABSTRACT

Due to the increasing trend of ethanol level in wines produced in different regions, partial dealcoholization (up to 2% v/v) has become a common practice in wine industry. Membrane contactors employing water as stripping agent represent a promising technology for implementing dealcoholization at the industrial level. This work investigates the effect of the treatment on the oxygen isotopic ratio ($^{18}\text{O}/^{16}\text{O}$) of the wine water. Notably, European Union prescribes the use of stable isotopic ratio analyses as official methods to detect the illegal additions of compounds in wines and authentication of geographic origin, and year of vintage. Experiments were performed with wines and water with different $^{18}\text{O}/^{16}\text{O}$ ratio and in the presence of non-volatile solute (glycerol) to alter the net water flux through the membrane. Experimental results clearly showed that the water flux through the membrane does not contribute significantly to the isotopic ratio change, which can be adequately explained by the diffusion of the isotope, according to the models commonly used to describe the exchange of ethanol or other components. A model has been developed herein, which accounts for the diffusion of ethanol, water and isotopic. The role of concentration polarization as well as the transport mechanisms are also discussed.

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1. Introduction

Through the last 40 years, “stable isotope ratio” analysis has been applied to determine food authenticity and geographical origin assignment [1]. “Stable isotopes” are defined as isotopes which do not decay over time. Of the several isotopes normally present in natural compounds, the light ones are more abundant than the heavy ones. For instance, in water, ^{16}O represents the large part (typically 99.757%) of the oxygen, whereas ^{18}O represents the 0.205%. The natural isotopic ratio of the bio elements shows variations due to physical and biochemical isotopic fractionation, which can be used to gather information about the history and provenance of the material. Climatic and environmental differences, among different wine growing regions, or different vintages, produce wine with different $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ ratio. For instance wines from southern countries are richer in heavy isotopes as compared to wines produced in northern countries; in the same geographical location the isotopic ratio

changes from vintage to vintage, depending on average temperature, rain, air humidity [2]. The isotopic analysis is currently applied to control wines for illegal additions of compounds: $^{13}\text{C}/^{12}\text{C}$ and D/H values of ethanol are used for checking “chaptalization”, i.e. the addition of beet or cane sugar before or during must fermentation. The wine water $^{18}\text{O}/^{16}\text{O}$ ratio is used to detect addition of spring water, with is typically characterized by a much lower ^{18}O concentration than grape juice [3]. European Union provides an official database for wine isotope parameters provided by all the wine-producing member states [4]. The wine sample is defined “not authentic” when its isotopic values do not fall within the natural range of variability yearly determined upon reference samples officially collected and analysed in each European state. Stable isotope data are generally expressed as “delta-values”, which represent the deviation of the rare to common isotope ratio, X , of a substance from that of commonly accepted reference materials:

$$\delta = \left(\frac{X_{\text{sample}}}{X_{\text{standard}}} - 1 \right) 1000 \quad (1)$$

In the case of oxygen isotope, $X = ^{18}\text{O}/^{16}\text{O}$ and the recognised standard is the “Vienna Standard Mean Ocean Water” (VSMOW),

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established by the International Atomic Energy Agency as $X_{standard}=0.0020052$. Since the isotopic analysis is applied to control wines for illegal additions of compounds, and to ensure compliance of a wine with its labelled geographical origin or year of vintage, eventual variation of isotopic ratios due to oenological practices (e.g. partial dealcoholization) must be verified and quantified in order to avoid incorrect judgment.

The reduction of ethanol level in wines represents a critical issue in oenological industry, as ethanol excess represents a problem for wine quality and balance, as well as consumer health and appreciation. On the other hand, the ethanol level in wines shows an increasing trend in all the wine regions due to several causes, such as global warming and longer grapes ripening, which increase the must sugar content and hence the ethanol level in the final product. European regulation [5] allows for the reduction of ethanol level up to 2 vol%. Several approaches have been attempted to produce wine with a lower ethanol content [6], which can be grouped in three main strategies: reducing the sugar level of the grapes in the vineyard [7], lowering the ethanol produced during fermentation [8–10], and applying technological protocols to reduce the ethanol level in the final product [11]. The partial removal of ethanol from wine represents a versatile way to tackle the problem of high alcohol levels in wines and many technological solutions are now available. Spinning cone column [6], reverse osmosis, nanofiltration [12–14] and pervaporation [15] have been proposed.

Membrane contactors have been regarded with increasing interest for the ethanol removal from wines [11,16–21]. The technique is based on porous hydrophobic membranes in contact on both sides with non-wetting liquids at pressures lower than the minimum entry pressure. Volatile compounds can pass across the membrane as vapours, whereas non-volatile solutes are retained. In the application presented herein, the feed stream comprises wine, whereas the stripping fluid is water containing eventually the same volatiles at lower concentration with respect to the feed. The driving force of the process is represented by the vapour pressure difference between the volatiles on the wine- and water-side of the membrane. The technique has been also referred as “osmotic distillation”, “osmotic evaporation”, “isothermal membrane distillation”, and “evaporative pertraction”. The last term might be more appropriate in the case of dealcoholization [16]. To date, the effect of this treatment has been mainly evaluated for sensory quality and for aroma volatile compounds in wine or model wine solutions [17–21].

Recent studies [22–24] have noticed that dealcoholization by membrane contactor can change the isotopic relation of a wine. Schmitt et al. [24] reported that the alcohol reduction by 2% v/v, entails the change in $^{18}\text{O}/^{16}\text{O}$ isotopic ratio equivalent to an addition of 4–9% of exogenous water. On the other hand, published work provides proof that, during alcohol removal, simultaneous water transfer occurs through the membrane [24]. Diffusion of water towards the wine is expected owing to the difference of water activity in the two fluids facing the membrane. It is therefore spontaneous to relate the two phenomena and attribute the isotopic ratio change to the watering, i.e. to the mixing of water diffusing through the membrane with the wine water. To the best of our knowledge, the impact of dealcoholization treatment on the stable isotope ratio has not yet been investigated in depth, and the mechanism is not clear; many oenologists tend to relate the isotope ratio change to the water transfer in wine compartment [22].

This work investigates the effect of dealcoholization on the oxygen isotopic ratio ($^{18}\text{O}/^{16}\text{O}$) of the wine water via a combined experimental and theoretical analysis of the mass transfer phenomena involved. The experiments presented herein enabled to inspect the possible relationship between the isotopic ratio change

and the net water flux through the membrane. Indeed, in addition to conventional dealcoholization experiments wherein wine was contacted with water, we conducted experiments using pure water with different isotopic ratios on the two sides and experiments in which a non-volatile solute (glycerol) was added to the stripping water or to the feed. The glycerol was selected in view of its thermodynamic properties in aqueous solutions; since it greatly affects the partial pressure of the species [25], it was used to induce variations of the driving force for water transport, in order to compare the oxygen isotopic ratio change in the presence of different net water fluxes.

A model describing the diffusion of ethanol, water and of the isotopic water (H_2^{18}O) is presented. The comparison between the whole experimentation and the transport model allows us to draw a final univocal conclusion about the overall mechanism governing the variation of the oxygen isotopic ratio during dealcoholization by membrane contactors.

2. Mass transfer modelling

2.1. Basic equations

The presented model refers to the dealcoholization operation, wherein a porous hydrophobic membrane is contacted by wine, or a water–ethanol mixture, on one side, and by water on the other side, where the volatile compounds transfer at lower concentration. Since neither liquid wets the membrane, only a gaseous phase, essentially air, exists within the pores of the membrane, and a liquid–gas meniscus is formed at the pore entrances where vapour–liquid equilibrium is established. The partial pressures P_i of volatile components are therefore related to the liquid composition existing in the bulk phases by:

$$P_i = P_i^* x_i \gamma_i \quad (2)$$

wherein P_i^* represents the vapour pressure of each pure component i , x_i its mole fraction and γ_i the activity coefficients. The effect of the interface curvature on the vapour pressure appears negligible, in the present case, as shown in details in Appendix A.

Attention is focussed here on the diffusion of ethanol, water and isotopic water. The activity coefficients of ethanol and water have been calculated with reference to ethanol–water solutions, neglecting the effect of other components of wine, according to the Wilson method [26] (see Appendix B). In the composition range of interest, the activity coefficient of water is essentially unity, whereas values of 3–4 are expected for ethanol depending on composition. Finally, interactions between water and isotopic water were considered ideal; so doing, $\gamma_i=1$ was assumed for both water and isotopic water.

The molar fluxes, J_i , of the species involved can be written as:

$$J_i = K_i (P_{i,v} - P_{i,s}) \quad (3)$$

wherein K_i represents the overall mass transfer coefficient, embodying both membrane and boundary layers transport. According to the “resistance in series” model [16,27]:

$$\frac{1}{K_i} = \frac{1}{K_i^m} + P_i^* \left\{ \frac{\gamma_{i,v}}{k_{i,v} C_{L,v} (d_o/d_m)} + \frac{\gamma_{i,s}}{k_{i,s} C_{L,s} (d_i/d_m)} \right\} \quad (4)$$

wherein K_i^m represents the membrane mass transfer coefficient, and $k_{i,v}$, $k_{i,s}$ represent the mass transfer coefficients in the feed and stripping side respectively. As the overall mass transfer is considered at the average surface, the mass transfer coefficients were corrected by the appropriate diameter ratio, assuming the feed in the shell side and the stripping water in the lumen side, d_i , d_o and d_m represent the inner, outer and average diameter of the fibres,

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