THE PROTECTIVE ROLE OF DISSOLVED CARBON DIOXIDE AGAINST WINE OXIDATION: A SIMPLE AND RATIONAL APPROACH

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Abstract

Aims: During wine making, oxygen and carbon dioxide are often simultaneously present in the liquid phase. We propose a simple rational approach, based on usual chemical engineering and thermodynamic principles, to provide understanding and practical rules for controlling the effects of these two dissolved gases, and especially their inter-relationship. Furthermore, this study proposes an explanation for the "protective" effect against oxidation, which is reported when high concentrations of carbon dioxide are present in musts and wines.

Methods and results: The theoretical quantitative relation, termed "binary gas equilibrium line", between the maximum possible concentration of dissolved oxygen in respect to dissolved carbon dioxide was derived and, in our experiments, corresponded to $C_{O_{2max}} \cong -0{,}005\ C_{CO_2} + 7{,}9\ mg.L^{-1}$. Specific saturation experiments using simultaneous injection of air and gaseous carbon dioxide were performed and the experimental results allowed us to validate this theory in the case of gas bubbling in a liquid.

Conclusion: It is shown that complete protection is only obtained when carbon dioxide is generated by the fermentation in the liquid. An interesting parallel conclusion is that micro-oxygenation is totally inefficient in such periods. In the case where there is no production of CO_2 but where a high initial dissolved carbon dioxide concentration is present, the "protective" effect acts only by reducing the rate of oxygen transfer.

Significance and impact of the study: The physical understanding of this phenomenon can be found in the fact that as soon as a gaseous air or pure oxygen phase is in contact with a carbon dioxide saturated liquid, the dissolved carbon dioxide, which is not at equilibrium with the gaseous phase, tends to escape into this gaseous phase. This study points out the complexity of the gas-liquid equilibrium when two dissolved gases are simultaneously present in a liquid and its implication in the winemaking process.

Key words: dissolved gases, micro-oxygenation, carbon dioxide, oxygen, wine making

Résumé

Objectifs : Au cours de la vinification, l'oxygène et le dioxyde de carbone sont souvent simultanément présents à l'état dissous dans la phase liquide. Nous proposons ici une approche simple et rationnelle, basée sur les principes usuels du génie chimique et de la thermodynamique. On peut ainsi avoir accès à la compréhension et à des règles pratiques pour maîtriser les effets de ces deux gaz dissous, et en particulier de leur interaction. Cette étude propose ainsi une explication de l'«effet protecteur» contre l'oxydation que l'on constate lorsque le dioxyde de carbone dissous est présent à forte concentration.

Méthodes et résultats : On a pu établir dans cette étude une relation théorique quantitative, appelée «droite d'équilibre de saturation binaire», qui relie la concentration maximale possible pour l'oxygène dissous à la concentration en dioxyde de carbone dissous. Pour notre domaine expérimental, cette relation correspond à $C_{O_{2max}} \cong -0{,}005\ C_{CO_2} + 7{,}9\ mg.L^{-1}$. Des expérimentations spécifiques de saturation d'une phase liquide hydro-alcoolique, où de l'air et du dioxyde de carbone sont simultanément injectés, ont été réalisées et les résultats expérimentaux ont permis de valider cette approche dans le cas du bullage dans un liquide.

Conclusion : Cette étude montre qu'une protection complète du vin contre l'oxygène n'est obtenue que lorsque du dioxyde de carbone est produit in situ par la fermentation des levures et donc dans le cas où celui-ci est à saturation dans la phase liquide. En parallèle, il est intéressant de noter qu'une micro-oxygénation serait totalement inefficace en de telles périodes. Dans le cas où il n'y a aucune production du CO_2 mais où une concentration dissoute initiale élevée en CO_2 est présente, l'effet « protecteur » agit seulement par une réduction du taux de transfert d'oxygène dans le vin.

Signification et impact de l'étude : La compréhension physique de ces phénomènes réside dans le fait que, lorsqu'une phase d'air gazeux ou d'oxygène pur est en contact avec un liquide saturé en dioxyde de carbone dissous, ce dernier, qui n'est pas à l'équilibre avec la phase gazeuse, désorbe dans la phase gazeuse. Cette étude appréhende la complexité de l'équilibre gaz/liquide quand deux gaz dissous sont simultanément présents dans un liquide et met en lumière son implication dans le procédé de vinification.

Mots clés : gaz dissous, micro-oxygénation, dioxyde de carbone, oxygène, vinification

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INTRODUCTION

Carbon dioxide (CO$_2$) and oxygen (O$_2$) are very often present simultaneously, in the form of dissolved gas, in many steps of wine making. The quality and the organoleptic perception of a wine are affected by their presence. Indeed, the sparkling effect of dissolved carbon dioxide is likely to enhance the perception of the fragrance of the wine. As for dissolved oxygen, its presence at high concentration directly governs the oxidation rate of specific components of the wine, leading either to beneficial or detrimental effects on the organoleptic perception (Singleton, 1987; Dubourdieu and Lavigne, 1990; Schneider, 1998; du Toit *et al.*, 2006; Li and Wang, 2008; Lopes *et al.*, 2009).

It is commonly accepted that there is an interrelation between the effects of these two dissolved gases: when high concentrations of carbon dioxide are present, the wine is "protected" from oxygen, and thereby from oxidation phenomena (Ribereau-Gayon *et al.*, 1998; Jackson, 2008). The influence of dissolved carbon dioxide during the process of micro-oxygenation, especially on the kinetics of oxygen dissolution, has also been recently reported (Devatine *et al.*, 2007).

In this work, we have tried to propose a simple rational approach, based on usual chemical engineering and thermodynamic principles, to provide understanding and practical rules for controlling the effects of these two dissolved gases, and especially their inter-relationship.

Indeed, oxygen transfer into the wine can occur in two ways:

1) not desired and results from accidental or uncontrolled contact with air during manipulations, such as transfer in different tanks (Vidal *et al.*, 2001 and 2004; Castellari *et al.*, 2004);

2) desired and results from the controlled addition of oxygen. Oxygen should be introduced into the wine in controlled quantities and at a controlled rate in order to induce the necessary oxidation reactions of the wine (Atanasova *et al.*, 2002; Drinkine *et al.*, 2007). This is, for instance, the case of micro-oxygenation, a commonly implemented treatment, which aims at providing oxygen in a way equivalent to the slow diffusion of oxygen through wood barrel walls, as used for wine ageing (Gomez-Plaza and Cano-Lopez, 2011).

The contact of wine with oxygen may also occur, willingly or not, when high concentrations of carbon dioxide are present. Here also, two cases must be considered:

1) The carbon dioxide concentration remains constant because of the constant production by growing yeasts, compensating for the possible stripping by contact with a gaseous phase. This is, for instance, the case when micro-oxygenation is performed during the alcoholic fermentation step;

2) There is no in situ production of carbon dioxide and its concentration is likely to decrease by stripping. This case has already been addressed in previous works (Devatine *et al.*, 2007; Devatine and Mietton-Peuchot, 2009) and the main results are recalled here. Indeed, in this case, significantly lower values of the volumetric oxygen transfer coefficient ($k_L a$) were found, indicating a strong decrease of the transfer efficiency, where the oxygen transfer yield drops from 77%, when the wine is initially carbon dioxide free, to 9%, when it is initially carbon dioxide saturated (Devatine *et al.*, 2007). It was hypothesized that massive desorption of dissolved carbon dioxide into rising bubbles would lower the partial pressure of oxygen and thus the driving force for the interphasic mass transfer. Using this hypothesis, mathematical modelling of oxygen transfer around tiny rising bubbles yielded computed values of the transfer yield which were in close agreement with experimental ones, validating the initial proposed hypothesis (Devatine and Mietton-Peuchot, 2009). Note that in this case, because the stripped carbon dioxide was not replaced, its concentration progressively decreased during the course of the experiment, reaching zero, thus leading to slower but complete saturation by oxygen.

These last results suggest that such effects (*i.e.*, lower oxygen partial pressure) may also occur when the concentration of dissolved carbon dioxide is kept constant, and this, in addition to lower kinetics, would yield lower oxygen concentration at equilibrium. This may be described and demonstrated using very conventional thermodynamic principles of gas-liquid equilibrium, as presented below.

THEORETICAL APPROACH

Let us consider a gaseous space in contact with a liquid containing dissolved oxygen and dissolved carbon dioxide, and let us consider that the system has reached equilibrium.

The total pressure is the sum of the partial pressures of air and carbon dioxide:

$$P_T = P_{air} + P_{CO_2} \tag{1}$$

The presence of nitrogen is implicitly accounted for in the partial pressure of air: it is assumed to be at solubility equilibrium and does not intervene in the equations. At equilibrium, the concentrations of dissolved gas in liquid are given by Henry's law:

$$C_{CO_2} = \frac{P_{CO_2}}{H_{CO_2}} \tag{2}$$