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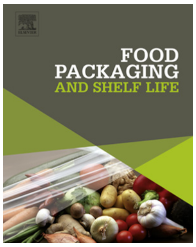

Protection of methionol against oxidation by oxygen scavenger: An experimental and modelling approach in wine model solution

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ABSTRACT

The aim of this study was to evaluate the impact amount (1% and 3%) of oxygen scavengers (os) incorporated in a PET matrix on methionol oxidation in model wine solutions with different initial oxygen concentrations. At saturated oxygen concentration, the studied amount of oxygen scavenger did not affect the methionol preservation. In more realistic oxygen concentration of wine (0.117 mmol L^{-1}), methionol was only protected after contact with 3% of oxygen scavenger. For a minimal concentration of oxygen (0.024 mmol L^{-1}), the presence of scavenger slowed down the methionol degradation by 1.2 and 1.9 times for 1osPET and 3osPET respectively. For the strongest oxygen concentrations, a mechanistic model was proposed to predict methionol degradation in relation to scavenger amount. This model based on second order reactions for methionol degradation and oxygen consumption by scavenger fitted well with the experimental data. An improvement of this model has been developed for the low initial oxygen amount.

1. Introduction

High oxygen exposure of wine is known to be detrimental to the organoleptic quality, inducing changes of colour and aromatic profiles (Câmara, Alves, & Marques, 2006; Karbowiak et al., 2009; Lee, Kang, & Park, 2011; Ugliano, 2013). Oxygen plays a negative role with a loss of freshness and fruitiness occurring concomitantly to the development of off-flavours described as "honey-like", "boiled potato", "cooked vegetable". The main aroma compounds responsible for this pronounced oxidized feature of wine are Strecker aldehydes (such as phenylacetaldehyde, methional and sotolon) (Culleré, Cacho, & Ferreira, 2007; Escudero, Cacho, & Ferreira, 2000; Ferreira, Aznar, López, & Cacho, 2001). Phenylacetaldehyde and methional result from the oxidation of their corresponding alcohols, phenyl-2-ethanol and methionol, which obtained from amino acids phenylalanine and methionine by the Ehrlich pathway during the fermentation of wine (Ugliano & Henschke, 2009). Methionol is characterized by soup, cabbage and boiled potato notes (Escudero, Hernández-Orte, Cacho, & Ferreira, 2000). But because of its high detection threshold, i.e. 1000 $\mu g\ L^{-1}$ in 11% (v/v) alcoholic solution (Ferreira, Lopez, & Cacho, 2000) and its usually lower concentration in wine, the aromatic impact of methionol is negligible. On the contrary, methional which is characterized by "boiled potato" notes, displays a very low threshold around 0.5 $\mu g\ L^{-1}$ (Escudero, Hernández-Orte, et al., 2000) and is considered as a marker of oxidation. Protecting wine against oxidation is one of the objectives of wine makers to avoid off-flavour development

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during the winemaking process as well as bottles storage. The monitoring of methional formation or methionol degradation could be a good marker of oxidation in wine.

Alternatives to glass bottles, such as Bag-In-Box® (BIB), laminated carton or plastic bottles to package wine have emerged for many different reasons: improved distribution efficiency, enhanced end-use convenience, and increased cost-effectiveness than glass (Fradique, Hogg, Pereira, & Pocas, 2011; Fu, Lim, & Mc Nicholas, 2009; Giovanelli & Brenna, 2006; Hopfer, Ebeler, & Heymann, 2012; Peychès-Bach, Moutounet, Peyron, & Chalier, 2009). These changes from glass to synthetic polymers for wine packaging increase the problematic of wine oxidation due to the non-null O_2 permeability of these materials (Ghidossi et al., 2012; Lee et al., 2011). The use of PET-based bottles for medium and long-term shelf life is currently challenging due to low-weight bottles and recycled solutions being more eco-friendly than glass. To face the problem of O_2 permeation through standard PET materials, different furnishers have proposed PET-based solutions to package wine, including multilayers with high barrier layer or monolayer PET including oxygen scavenger systems. The use of these packages was found efficient to preserve the organoleptic quality of wine during a limited time of storage depending on the type of wine or on the amount of scavenger (Mentana, Pati, La Notte, & del Nobile, 2009). For instance, it was shown that the aromatic profile of red and white table wines was not affected by using PET bottles containing oxygen scavenger during 7 months of storage (Mentana et al., 2009). Ghidossi et al. (2012) compared the behaviour of sotolon, methional, phenylacetaldehyde, the current aroma compounds associated to the wine oxidative evolution, in a white wine packaged in glass, Bag-In-Box®, monolayer or multilayer PET bottles (multilayer contained oxygen scavengers). After 18 months of storage at 20 °C, the highest concentrations of these aroma compounds were observed in monolayer PET bottles and BIB, followed by multilayer PET bottles. This study proved that wine ageing during storage is influenced by PET oxygen barrier properties and can be limited by the inclusion of oxygen scavengers in PET. Numerous types of oxygen scavenger system exist, the most used are iron oxidation based systems, but they can also be based on catechol, ascorbic acid, oxidative enzymes such as glucose oxidase, or unsaturated hydrocarbons and polyamides systems (Charles, Sanchez, & Gontard, 2006; Ozdemir & Floros, 2004; Rooney, 1995; Smith, Ramaswamy, & Simpson, 1990).

Although O_2 scavengers are commercially available and commonly used, information on their absorption characteristics is still limited. To package fresh banana slices, Galdi and Incarnato (2011) have studied the scavenging properties of a monolayer PET active but they did not have conclusive results about the absorption mechanism and did not propose any mathematical model of this absorption to quantify the effect of O_2 absorption on oxidation reactions. Charles, Sanchez, and Gontard (2003) had determined the absorption capacity and absorption rate constant of a scavenger based on iron powder. Then, they combined this absorption equation to a Fick-based model for mass transfer and Michaelis–Menten equation to model vegetable respiration in order to predict evolution of gases concentration in modified atmosphere packaging. The authors proposed a first order reaction kinetic for O_2 adsorption by iron-based scavengers which was confirmed by Braga, Sarantópoulos, Peres, and Braga (2010); Feng, Luo, Shao, Wu, and Ying (2013) and Sängerlaub et al. (2013) on other iron-based absorbers. Di Felice, Cazzola, Cobror, and Oriani (2008) worked on PET bottles with or without oxygen scavengers and filled with distilled water. These authors proposed a model to determine the kinetic rate of the absorber based on a second order reaction (oxygen and scavenger amount) and validated the predicted value by experimenting with various scavenger amounts. They affirmed that it is now possible to 'design' the correct bottle for a specific requirement, knowing its O_2 diffusivity, permeability, size, thickness or shape by utilizing a specific scavenger material characterized by its kinetic constant k, with the appropriate value of initial concentration. As far as we know, the studies of Charles et al. (2003) and Di Felice et al. (2008) were the only two studies that quantitatively couple O_2 absorption to mass transfer and shelf-life model equation.

In the previous studies on wine packaging with active PET (Ghidossi et al., 2012; Mentana et al., 2009), O_2 scavenging properties were never quantitatively related to oxygen content and to the oxidation reaction of an oxygen sensitive aroma compound such as methionol.

The objective of this work is to evaluate the impact of the initial oxygen content (0.28, 0.12 and 0.02 mmol L^{-1} simulating three bottling conditions) on methionol oxidation and to determine if the presence of 1 or 3% of oxygen scavengers incorporated in a PET matrix had an impact on the preservation of methionol by limiting its oxidation. The oxidation of methionol was then tentatively modelled on the basis of hypothesis about its reaction pathway. O_2 absorption of scavenger-based PET samples was also modelled and both models were coupled in order to predict the evolution of O_2 content and methionol content in wine model solutions for different initial O_2 contents. Possible interferences due to ethanol oxidation were also evaluated.

2. Materials and methods

2.1. Material

Pieces of monolayer PET bottles containing 1–3% of oxygen scavenger (named 1osPET and 3osPET) were used for this study. Both active PETs were cut from 75 cL wine bottles supplied by SIDEL Blowing Service (France). The weight of both bottles was 38 g, thickness around 350 μm for bottle body and increasing until 470 μm for the lower part and 700 μm in the top of the bottle shoulder. Samples were cut in the top of the body bottle to have the same thickness (350 μm) in all experiments.

Dichloromethane, internal standard, 4-nonanol, and methionol were provided by Sigma–Aldrich, France. Absolute ethanol was purchased from AnalaR NORMAPUR, VWR PROLABO, France. Anhydrous sodium sulfate was provided by MERCK, Germany.

To prepare the model solution, salts were used. Potassium phosphate, calcium chloride, magnesium sulfate, copper sulfate, iron sulfate, and tartaric acid were provided by Sigma–Aldrich, France, potassium sulfate by Fulka, France, and sodium chloride by Carlo Erba, France.