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Chemical compounds and mechanisms involved in the formation and stabilization of foam in sparkling wines

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ABSTRACT

The visual properties of sparkling wine including foam and bubbles are an indicator of sparkling wine quality. Foam properties, particularly foam height (FH) and foam stability (TS), are significantly influenced by the chemical composition of the wine. This review investigates our current knowledge of specific chemical compounds and, the mechanisms by which they influence the foam properties of sparkling wines. Grape and yeast proteins, amino acids, polysaccharides, phenolic compounds, organic acids, fatty acids, ethanol and sugar are examined with respect to their contribution to foam characteristics in sparkling wines made with the Traditional, Transfer, and Charmat and carbonation methods. Contradictory results have been identified that appear to be due to the analytical methods used to measure and quantify compounds and foam. Biopolymer complexes are discussed and absent knowledge with regards to thaumatin-like proteins (TLPs), polysaccharides, amino acids, oak-derived phenolic compounds and organic acids are identified. Future research is also likely to concentrate on visual analysis of sparkling wines by in-depth imaging analysis and specific sensory analysis techniques.

KEYWORDS

Sparkling wine; foam; proteins; polysaccharides; phenolic compounds; organic acids and fatty acids

Introduction

Sparkling wines are defined as an alcoholic beverage of grape origin, which have dissolved carbon dioxide (CO_2), and typically form a bubbly, attractive beverage with condensed bubbles that form a foam on the surface of the wine. Sparkling wines are produced in most of the winegrowing areas in the world including Brazil, USA, South Africa, Canada, Australia, New Zealand, Argentina and England, with traditional production focused on the European producers in France, Italy, Spain and Germany. Sparkling wine consumption in many cultures is associated with 'celebration' or special occasions, and thus command a unique and high quality space in the competitive wine market. The visual properties of sparkling wines are of utmost importance for quality, and thus provide a parameter, which wine producers can modify to increase the quality of their wines.

Sparkling wines constitute a wide range of styles due to climate, soil types, grape varieties and production methods, with different levels of alcohol, sugar and carbon dioxide (CO_2) (Kemp et al. 2015a). Typically, fruit-driven styles of sparkling wine are produced from carbonation or the Charmat method, whereas sparkling wines that are more complex are achieved because of a second fermentation in a bottle and/or the yeast lees aging process used in the transfer method and traditional method (Fig. 1; Culbert et al. 2017). These production methods are the origin of CO_2 in the wine, which can arise from the fermentative power of yeasts or from deliberate addition into still wine.

Natural sparkling wines whose CO_2 originates from a single alcoholic fermentation include Vinho Verde, *Pétillant naturel, Méthode Ancestrale*, Asti Spumante. *Méthode Ancestrale* (i.e. Clairette de Die produced from Muscat Blanc à Petits Grains (75% minimum) and Clairette grapes in France), begins with the alcoholic fermentation in a tank, and the wine is bottled during the first alcoholic fermentation that continues in the bottle. In contrast, the Asti method is a modified version of the Charmat method. Here, after crushing and pressing of wine grapes, the juice is filtered and then, fermented in pressurized steel tanks where the gas is incorporated until the desired alcohol level is reached (Bordigo et al. 2013; Caliari et al. 2015). Carbonated sparkling wines are made with added carbonation where exogenous CO_2 is added into a still wine, with CO_2 pressure levels that often reach only 3.5 atmospheres (atm) (Buxaderas and López-Tamames 2003; Gallart et al. 2004).

Sparkling wines can undergo a second alcoholic fermentation (for example; Champagne, Cava, Prosecco, Sekt, Cap Classique), and are produced using the Charmat, Transfer or Traditional methods (Fig. 1). A further method found in this category, albeit it to a lesser extent, is the Russian Continuous method, an adaptation of the Charmat/Tank Method (Stevenson and Avellan

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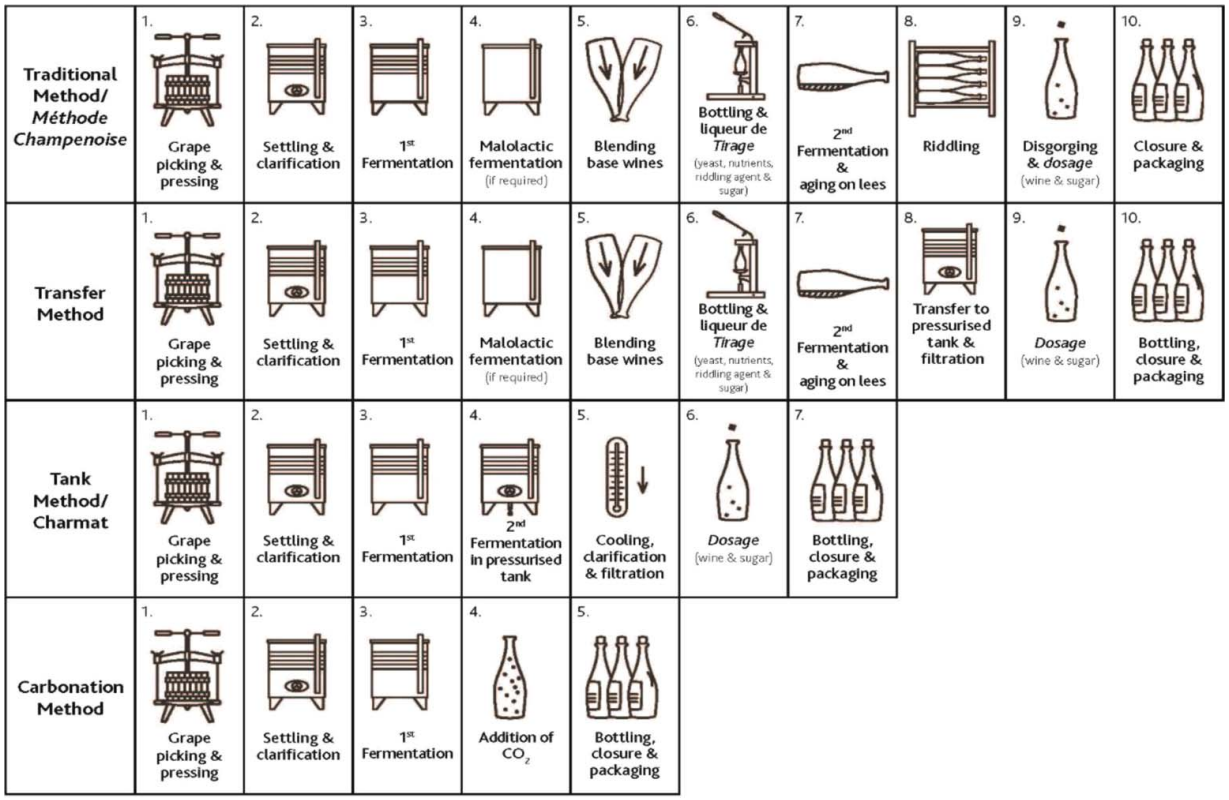

Figure 1. Summary diagram of the four dominant sparkling wine production methods.

2013). These production methods allow stable and efficient introduction of CO_2 into the wine, and the choice of method depends on tradition, culture and, availability of equipment and budget.

The concentrations of CO_2 in sparkling wine ranges from 2 to 12 g/L depending on the style and production method used. The CO_2 pressure is related to temperature. In a closed bottle of sparkling wine, the pressure is 5 – 6 atmospheres (atm) at 10°C, depending on the gas lost during aging on yeast lees and disgorging, but approximately 7 – 8 atm at 20°C (Liger-Belair 2017). Mathematically, the equilibrium concentration of CO_2 in liquid is defined as C_b. When wine is poured into a glass, it desorbs CO_2 molecules to reach a new equilibrium concentration, Cg. A "saturated" solution means that further CO_2 cannot be dissolved in it, so it is in a dynamic state. However, a "supersaturated" solution (as is the case for most sparkling wine), contains more CO_2 at a given temperature than a saturated solution. The saturation ratio is defined as, $\alpha = C_b/C_g$ and the super-saturation as $\sigma = \alpha - 1$ (Lubetkin and Blackwell 1988). For most sparkling wines, C_b is 8 – 11 g/L of CO_2 and C_g is 1.5 – 2 g/L of CO_2 so super saturation ranges from 4 to 9. The dynamic range of these values must be taken in context with the wine matrix, where it forms bubbles and foam.

Biophysically, sparkling wine foam is considered a weakly stabilized foam that irreversibly evolves with time because it contains only gas and liquid phases. The mechanisms involved in foam stabilization and destabilization, specifically the surface-active compounds have been the subject of fundamental studies (Maurdev, Saint-Jalmes, and Langevin 2006; Pugh 2016). Wet foams, like that of sparkling wine, are stabilized by a range of different types of surface-active compounds that adsorb at the interface and, reduce the free energy and tension. It is the adsorption kinetics, the type, as well as the amount, of surface-active compounds at the gas-liquid interface that play an intricate role in the generation, stability and longevity of foam (Saint-Jalmes 2006; Pugh 2016). The composition of the wine is thus of considerable importance to the foaming of the sparkling wine in question (Gallart et al. 2004; Culbert et al. 2017).

Basic wine parameters can significantly influence foaming. Betolli and La Belle (1915, 1917) conducted studies that linked common wine components such as sugar, tartaric acid, citric acid, tannin and glycerol to wine foam early in the 18th century. While the experiments were of a basic nature, sugar, tannin and glycerol exerted a marked effect on effervescence, but with tartaric and citric acids the effervescence appeared to be slow. The influence of temperature, alcohol and sugar content on CO_2 solubility in aqueous-ethanol solutions was established later (Agabaliantz 1954; Agabaliantz 1963). Maujean et al. (1990) and Gomérieux (1989) increased our understanding of the impact of wine composition on foam properties by utilizing a new system. They reported the existence of complexes between the CO_2-dissolved molecules and wine compounds, but did not go further to investigate the wine composition and biochemistry or the effect on foam and bubble parameters. It is possible to estimate the foam potential of a wine based on the chemical and biochemical of juice analysis at the start of wine production (López-Barajas et al. 1997). However, the ability to adjust the wine during winemaking according to production method means the winemaker has more tools to adjust the composition, and thus visual parameters of the resultant wine.

Extensive studies have investigated the formation, physics and chemistry of bubbles in sparkling wine, particularly the

involvement of external factors that influence foam. These include the loss of dissolved CO_2 through the cork and during serving, the type of glass the wine is served in, interior glass particles, the kinetics of CO_2 fluxes and bottle size (Lehuédé and Robillard 1997; Liger-Belair et al. 1999; Marchal et al. 2008a; Marchal et al. 2008b; Beaumont, Liger-Belair, and Polidori 2013; Polidori, Jeandet, and Liger-Belair 2009; Liger-Belair et al. 2012; Liger-Belair and Villaume 2011; Liger-Belair 2017). These factors have been well reviewed elsewhere.

The focus of this review is the influence of chemical composition on foaming properties. The compounds implicated in foam quality and oenological treatments that are able to modify the quality of the foam are of great importance. Here, we review the methods available to analyze sparkling wine foam, and the chemical compounds in sparkling wines that negatively and positively influence foam to identify areas for further research.

Terminology of sparkling wine foam

The Organisation Internationale de la Vigne et du Vin (OIV) define sparkling wines as "special wines produced from grapes, musts or wines processed according to techniques accepted by OIV, characterized on uncorking by the production of a more or less persistent effervescence resulting from the release of carbon dioxide of exclusively endogenous origin" (OIV 2015). The excess pressure of this gas in the bottle is at least 3.5 bars at 20°C. Nevertheless, for bottles of a capacity less than 0.25 L, the minimum excess pressure is 3 bars at 20°C (OIV 2015). Additionally, Gallart et al. (2004) defines sparkling wine as a liquid in which carbon dioxide is present in a state of super-saturation.

Although some bubbles are visible before opening, the foam emerges when the pressure is released, most typically when the bottle of wine has the closure removed. In some cases, release of pressure results in the wine gushing out of the bottle, and is the result of uncontrolled foaming. Gushing of sparkling wine is the rapid, excessive and spontaneous foaming that causes both financial loss and wine loss but is not the focus of this review. Once a portion of wine is poured into a wine glass, the measures of foam and bubbles as defined in this review can be observed.

The term effervescence refers to the formation of bubbles, and their ascent towards the surface of the wine (Fig. 2). Nucleation denotes any process that leads to the formation of a bubble. At the liquid's surface, the bubbles form a ring around the inside of the glass referred to as a collar (Fig. 3). The two foremost terms used in foam analysis are foam height (FH), and foam stability (TS), with FH being the height of foam upon pouring, measured from the base of the collar to its' highest point. TS refers to the time the bubbles take to entirely collapse, and hence the foam to disappear and is measured over time (seconds) (La Gatta et al. 2016).

Effect of CO_2 on the sensory characteristics of sparkling wine

The linking of sensory characteristics to sparkling wines by sensory panels have produced descriptive lexicons for the perception of carbonation, carbonation-related attributes, a visual bubble assessment as well as descriptive analysis and temporal check-all-that apply (TCATA) {whereby specific descriptors

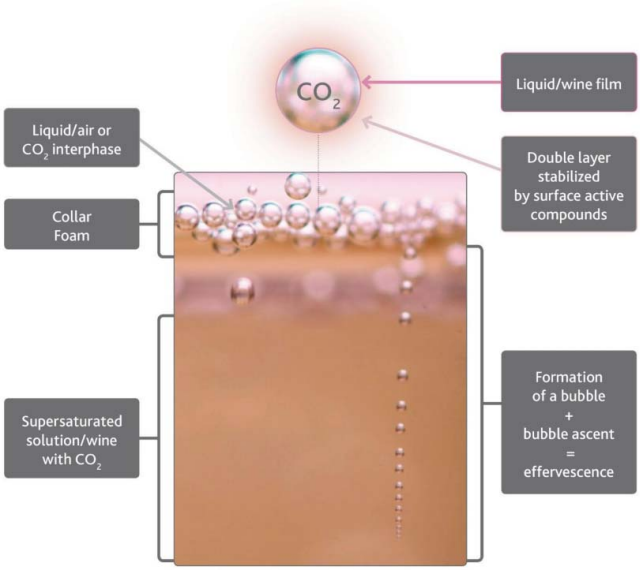

Figure 2. A visual representation of foam terminology.

are assessed over time} (Harper and McDaniel 1993; Kappes, Schmidt, and Lee 2007; Le Barbé 2014; McMahon et al. 2017a). Visual assessment of foam has included a range of attributes for effervescence and foam evaluation but it requires panelists to be trained in specific descriptors. Studies have used different attributes and vary in their definitions of them due to a lack of explicit and universally agreed definitions (Gallart et al. 2004; Buxaderas and López-Tamames 2010; Hood White and Heymann 2015). Foam stability and pressure levels affect the organoleptic qualities of sparkling wines. Although these depend on aroma and flavour, in the case of sparkling wines it is contingent on the wine's capacity to create foam (Buxaderas et al. 2010).

The impact of CO_2 on the tongue is due to carbonic anhydrase activity that has been attributed to trigeminal tactile and chemical impacts (H^+ content) confirmed by studies using carbonated water (Cowart 1998; Simons et al. 1999; Wise et al. 2013). Studies have provided evidence of the influence of carbonation on multimodal interactions from gustatory, olfactory and trigeminal origin on sensory perception (Hummel and

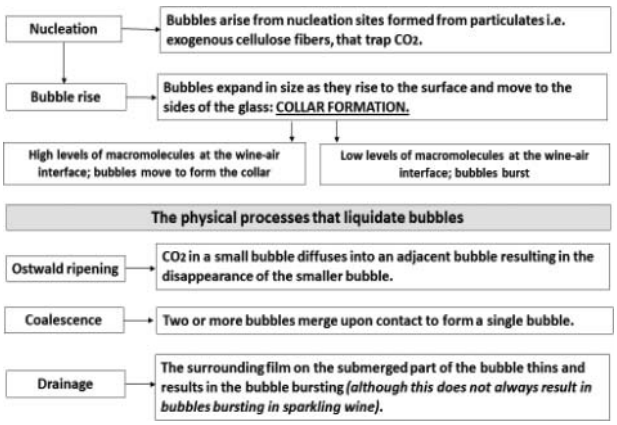

Figure 3. The mechanisms involved in the formation and evaporation of sparkling wine bubbles.

Livermore 2002; Jacquot, Monnin, and Brand 2004). Carbonation has been reported to increase sourness perception and CO_2 is known to be a trigeminal stimulus in model carbonated beer (Hewson et al. 2009), carbonated water (Cowart 1998), and carbonated grape juice (Balaswamy et al. 2011). Clark et al. (2011) found that CO_2 significantly reduced the perception of sweetness in model beer, and Thuillier (2007), confirmed the impact of CO_2 on the perception of sugar and acidity. Interaction between ethanol and CO_2 suggests competition between the trigeminal aspects of both stimuli, which was been reported to suppress the perceived warmness of the beverage, and therefore the perception of ethanol (Clark et al. 2011). Carbonation in wine (Traditional Method) has been found to be perceivable at a concentration >1.2 g CO_2/L. However, carbonation levels were lower than commercial sparkling wines made by the same technique (McMachon et al. 2017b).

Effect of other environmental factors on foam in sparkling wine

Temperature

Wine foam is particularly affected by temperature throughout its production for example, the wines' temperature during the bottle fermentation was been found to affect the foam of Cava wine (Esteruelas et al. 2015a). At a fermentation temperature of 12°C FH and TS increased compared to wines fermented in bottle at 16°C. This was likely due to a higher total protein content in wines fermented at the lower temperature, particularly the low molecular weight fraction, which suggests a higher level of mannoproteins are released during a low temperature in the course of the fermentation in bottle (Esteruelas et al. 2015a).

The solubility of CO_2 is strongly influenced by temperature while the pressure under the cork depends upon the wines' temperature (Liger-Belair 2017). The serving temperature of sparkling wine generally ranges from 4°C (fridge) to 12°C (cellar) but is subjected to temperature changes once it has been poured into glasses. So when the wine's temperature decreases (4°C, 12°C, 20°C), the foamability of the wine increases. Although the concentration of dissolved CO_2 is only moderately temperature-dependent, the bottle pressure is strongly temperature-dependent (Marchal, Descoins, and Jeandet 2003b; Liger-Belair 2017). The effect of temperature on foam was reported to influence the wine's viscosity far more than sugar addition, especially between 5°C and 10°C (Marchal, Descoins, and Jeandet 2003b). Cold temperatures during wine pouring increases viscosity by way of rheological properties of the foam. Therefore, viscosity and foaming ability are strongly correlated with temperature, and a strong linear correlation has been reported between viscosity and foamability (Marchal, Descoins, and Jeandet 2003b).

Influence of the endogenous particles on foam

To retain foamability, some sparkling base wines are produced without filtration but the consequence of such processes is that tiny particles could remain in the wine. These suspended particles can influence foam due to the presence of colloidal matter (Ross and Morrisson 1988). Hydrophobic solid particles can provide sites for bubble nucleation and depending on their size, shape and concentration, the particles can also act as foam stabilizers or destabilizers (Hudales and Stein 1990; Kumagai et al. 1991). Colloidal particles influence TS according to several processes. Firstly, they can decrease the drainage rate of the foam due to hydrodynamic activity. The dynamic viscosity of a colloidal suspension is usually higher than the suspending one depending on the particles solid fraction (Davis and Acrivos 1985). Since the drainage rate is always inversely proportional to the effective dynamic viscosity, TS is increased by slowing down drainage. Secondly, colloidal particles can also increase the stability of foam films by preventing excessive film thinning either by electrostatic repulsion between the particles and the film surface, or by steric hindrance (Prins 1988). Thirdly, particles can efficiently decrease TS by a bridging phenomenon. Surface-active materials desorbing from the particle surface may spread over the film surface and cause film collapse. Since Senée et al. (1998) few studies have taken place regarding endogenous particles (i.e. tartrate and calcium crystals, yeast from poor riddling) but these have been implicated in gushing of sparkling wines at disgorging (removal of yeast sediment) (Kemp, Wiles, and Inglis 2015b). Additionally, the removal of mono- and diglycerides of oleic acid (de-foaming agent) from wine was studied due to its occasional usage for the prevention of tank overflow during first fermentation. Hardly any de-foaming agent was detected (<0.01 mg/L) in the treated wine so the conclusion was that it was either metabolized or removed from wine by adsorption onto yeast (Caputi, Ribeiro, and Byrne 2000). Unfortunately, the foaming properties of the wines were not examined so there is no information about the possible effect of residual oleic acid on foam.

Foam parameters and characterization methodologies

Foam and bubble parameters

Studies concerning sparkling wine foaming properties has predominantly focused on the measurement of FH and TS, and occasionally, the Bikerman coefficient (Σ). Recently, Condé et al. (2017b) presented a method based on computer vision and image analysis to incorporate foam composition and morphology, whilst measuring several other parameters, such as foam volume, duration, velocity, and foam height. The former methods regarding foam studies discussed the variability found when quantifying TS and FH (Bikerman 1938; Maujean et al. 1990; Robillard et al. 1993). Moreno-Arribas et al. (2000) reported approximately 6% standard deviation for their measurements, while Cilindre et al. (2010) did not mention measurement variability, although their results showed very low standard deviations.

External factors that affect results are the glass (wet vs. dry), the rate of velocity of the gas when introduced into the liquid (Bikerman 1938; Germick, Rehill, and Narsimhan 1994), the pouring process, as well as the temperature of the liquid and concentration of CO_2 (Blom 1937). No influence on the foaming parameters was found from temperature, and humidity fluctuations observed under normal environmental conditions (Phillips et al. 1990; Abdallah et al. 2010).

Several techniques have been used to measure CO_2 during wine and beer production (Calvo-López et al. 2016) but this section of our review focuses on methods to analyze the foaming parameters of sparkling wines.

Bubble parameters

Various approaches have been developed to characterize foam formation and stability, and the ring of bubbles/collar, which remains in a glass of sparkling wines after foam dissipation (Table 1). Effervescence has been investigated by using high speed video cameras and strobe lighting (Liger-Belair 2005), and foam characteristics have been assessed using techniques based on sparging or pouring in addition to the use of laser beams and video imaging systems (Maujean et al. 1990; Jackson 2014; Hood White and Heymann 2015; Kemp et al. 2017; Crumpton et al. 2017). Furthermore, compounds related to the absorption layer of foam, and the formation and stability of the collar have been explored by using techniques such as ellipsometry and Brewster Angle Microscopy (BAM) (Péron et al. 2000; Abou-Saleh et al. 2007, 2009; Aguié-Béghin et al. 2009).

Studies related to the effervescence in sparkling wines are regularly reported (Liger-Belair 2017). These mainly concern the physical factors influencing CO_2 behaviour upon uncorking the bottle, pouring the wine into the glass, and the ascension of bubbles in the glass (Foulk and Miller 1931). The studies have also discussed factors influencing effervescence formation, such as the presence of nucleation sites. However, there is a lack of techniques able to quantify the effervescence objectively, such as measurements of bubble size and bubble speed ascension. New image analysis tools are able to film ascension of bubbles over time, and show a high level of potential in understanding the role of wine composition to these bubble measurements (Condé et al. 2017a). At present, we lack knowledge regarding the impact of oenological practices on the characteristics of effervescence. We know that the quality of foam predominantly depends on the wine's macromolecular composition yet there is no certainty that the winemaking process affects the effervescence of sparkling wines.

Foam characterization methodologies

Methodologies for measuring foam have attempted standardization of the external environment, or standardization of the CO_2 content.

Bikerman method

Foulk and Miller (1931) and Bikerman (1938) first presented foam characterization of food. Their apparatus consisted of sparging the liquid with a gas, in a glass tube, and observing the

Table 1. A comparison of methods used to investigate sparkling wine foam and collar.

Foam method	Measurements	Advantages	Disadvantages	References
Photography/filming	Foam height, foam stability	Low cost Corresponds to the image or the properties as observed by the consumer Pictures can be used for various applications in sensory studies Allows different sensory panels to view the same object limiting experimental error Highly reproducible	Laborious technique Limited foam parameters analyzed	Kemp et al. (2017).
Mosalux apparatus	HM, HS, TS, (Σ)	To study still base wines or sparkling wines after degassing Low cost	Requires prior degassing of sparkling wines Not representative of finished sparkling wines	Maujean et al. (1990); Esteruelas et al. (2015b).
Computerized Assisted Viewing Equipment (CAVE)	Several foam parameters	Mimics wine tasting conditions	Lack of portability, high cost of equipment	Machet, Robillard, and Duteurtre (1993); Viaux et al. (1994); Marchal et al. (2001); Cilindre et al. (2010).
Ellipsometry & Brewster Angle Microscopy (BAM)	Not yet applied for measurements of air-wine adsorption layer parameters (effervescence, foam or collar)	To investigate compounds related to foam, collar formation and stability Can be used for still base wines or sparkling wines after degassing	High cost of equipment and highly skilled personnel required	Péron et al. (2000); Desbat and Castano (2013); Irene (2013); (Abou Saleh et al. (2007, 2009); Aguié-Béghin et al. 2009).
FIZZeye-Robot	Several foam parameters	Portability, low cost of equipment, mimic tasting conditions	Does not quantify effervescence	Condé et al. (2017b).
Visual assessment	Several foam parameters	Low cost Corresponds to the image or the properties as observed by the consumer Assessor training required It is easy to reach a consensus between judges, because it is not as subjective as other senses	Subjective measurement	Hood White and Heymann (2015).

height reached by the foam, as well as the volume formed and foam duration. Subsequently, different methods to characterize foam were developed (Ross 1943; Rudin 1957). Those methods consisted of pouring the liquid from a certain height or sparging gas through the fluid, and afterwards, measuring the volume and height of the foam formed. A few decades after the presentation of this method, Maujean et al. (1990) developed the Mosalux apparatus for application in base and sparkling wine studies. Pueyo, Martin-Alvarez, and Polo (1995) adapted this method and Moreno-Arribas et al. (2000), further automated it. The latter has been used in several studies (Hidalgo et al. 2004; Nuñez et al. 2005).

Mosalux apparatus

The Mosalux apparatus consists of sparging wines in a Rudin tube (Rudin 1957) with CO_2, and recording the height of the foam and time using infrared, and further analysis using a personal computer. The tube is closed at the bottom with a glass plate pore size: 40 – 60 μm (porosity is the empty % of a filtration membrane or glass frit), where foam height is measured over time when the base wine is injected with CO_2 (Maujean et al. 1990). The method was adapted from a previous sparging equipment used for beer (Rudin 1957), and has recently been used to measure foam in Prosecco wine (Vincenzi, Crapisi, and Curioni 2014). Nevertheless, the efficiency and performance of this equipment and its application for sparkling wines studies remains a topic of debate.

The Mosalux equipment has been used in several studies (Brissonnet and Maujean 1991; Andrés-Lacueva et al. 1997; Andrés-Lacueva et al. 1996; Puig-Deu et al. 1999; Senée, Robillard, and Vignes-Adler 1999; Girbau-Solà et al. 2002a; Girbau-Solà et al. 2002b; Cilindre et al. 2007; Esteruelas et al. 2015b; Martínez-Lapuente et al. 2015). Most experiments have been carried out on base wines, most likely due to the difficulties faced when studying wines with effervescence and with the belief that foaming properties of sparkling wines follow the same pattern as that of still wines (Maujean et al. 1990; Brissonnet and Maujean 1991). The latter has been questioned in a recent study reporting contradictory results between foam characteristics in base wines when compared to results obtained by their corresponding sparkling wines (Esteruelas et al. 2015b).

The Mosalux apparatus has been improved to address low reproducibility and to include measurements of TS, foam expansion, and Bubble Average Lifetime (Lf), along with the Bikerman coefficient (Σ), which is defined as the ratio of the foam volume when a constant height is reached on the gas flow (Robillard et al. 1993). Nevertheless, it has been questioned whether the foaming parameters obtained by using sparging methods, such as the Mosalux apparatus, are a good representation of the foam parameters perceived by tasters when tasting sparkling wines (Cilindre et al. 2010; Esteruelas et al. 2015b).

Image analysis with CAVE and fizzeye-robot

Sarker et al. (1998), reported the use of image analysis for studying foam characteristics. The researchers manually counted the bubbles after image acquisition and transformation. The use of image processing and analysis were highly laborious due to low computer memory, thus, its application was very limited. Recent improvements in computer technology has made it possible to apply this technique to a vast array of topics as well as the development of techniques to quantify foam characteristics in sparkling wines, such as the Computerised Artificial Viewing Equipment (CAVE) and Fizzeye-Robot. The CAVE system is an image analysis method where two video cameras capture large and small-scale side views allowing the quantification of foam collapse just after its expansion in the glass. It can capture the speed with which foam thickness increases over time, and the speed with which liquid height changes over time (Machet, Robillard, and Duteurtre 1993; Viaux et al. 1994; Cilindre et al. 2010). Digital cameras are used to take pictures of the foam collar at the surface of the wine (Marchal 2010). When used in combination with a sensory panel, pictures can be assessed for hedonic measures and can reduce experimental errors. Condé et al. (2017b), developed another technique based on a computer-automated system that utilizes a robotic pourer and image algorithms (FIZZeye-Robot). It allows for standardized and accurate measurements while reducing variations in pouring wine from the bottle. The FIZZeye-Robot is portable, does not require the use of laser beams and image analysis is based on algorithms applied to videos taken during sparkling wine pouring. Both CAVE and FIZZeye-Robot provide methods to assess sparkling wines in similar conditions to that used in real time sparkling wine tasting, eliminating the sparging process and providing objective measures of wine quality.

Ellipsometry and Brewster Angle Microscopy (BAM)

The stability of sparkling wine bubbles requires an adsorption layer at the interface with gases (air or CO_2) and macromolecules contribute significantly to the formation of this layer. As sparkling wines are considered protein solutions, the formation of the adsorption layer can be seen using ellipsometry and Brewster Angle Microscopy (BAM). Ellipsometry is the method that enables the calculation of the ellipticity coefficient of the adsorption layer that is proportional to the layer thickness. Brewster Angle Microscopy (BAM) uses the properties of the ellipticity coefficient at the Brewster angle to visualize the 2-D organisation of heterogeneities due to variations in the thickness or in the refractive index of the adsorption layer (Abou-Saleh et al. 2007). The uncovered substrate appears dark in the BAM images, whereas all parts covered by adsorption layers appear less bright. This light reflectivity technique can study foam at the molecular level and has been used to study the wine adsorption layer because ethanol lowers the surface tension to such a degree that tensiometry cannot be used (Péron et al. 2000; Péron et al. 2004; Abdallah et al. 2010). Measurements are carried out using a spectroscopic phase-modulated ellipsometer to study wine compounds that influence collar stability, likely because of the ephemeral nature of foam formation and dissipation (Abou-Saleh et al. 2007, 2009; Aguié-Béghin et al. 2009). The lifetime of isolated bubbles was measured to evaluate the stability of the liquid film binding the airside of the bubbles. After pouring the sparkling wine, the stability of the bubble collar was quantified through a kinetics analysis of the fraction of the cylindrical flute surface covered with

bubbles. The ratio of the area covered with bubbles to the total area of the flute surface was defined as Rc, the ratio of the collar as determined by analysis of the pictures. The idea is that the stability of the liquid film that forms the boundary of the bubbles on the airside is determined by the surface concentration of the adsorption layer.

Macromolecules in sparkling wine and the effect on foaming

Foam duration is directly related to bubble stability, and stability itself is reliant on the composition of the film that supports it (Buxaderas and López-Tamames 2010). The film acts as an elastic barrier formed by proteins, polysaccharides and fatty acids that provide viscous and elastic properties (Casey 1995; Bamforth 1985; Buxaderas and López-Tamames 2010).

Proteins

Despite low concentrations of protein in sparkling wines (4 to 16 mg/L), several studies have shown that proteins are the principal compounds associated with foam properties of sparkling wines. The first study that suggested proteins in base wine effected foam was Maujean et al. (1990), who reported a positive effect of protein content on foamability using a Mosalux apparatus. Brissonnet and Maujean (1991) reported a relationship between protein content and sparkling wine foam ability and found that when protein concentration increased by 20%, foam height increased (Brissonnet and Maujean 1993). Supporting this result, Malvy, Robillard, and Duteurtre (1994) found that the protein concentration of a sparkling wine constituted a limiting factor for the foaming properties of wine. The type of protein is also important because hydrophobic proteins are more concentrated in sparkling wine than hydrophilic proteins (Brissonnet and Maujean 1993). Vincenzi, Crapisi, and Curioni (2014) used a reconstitution experiment to study the specific contribution of purified grape proteins to foamability in Prosecco wine (Charmat method). Ultra-filtered wines deprived of molecules larger than 3.5 kDa did not produce any measurable foam confirming that wine foam is due to the presence of macromolecules (Aguié-Béghin et al. 2009). Wines with the highest MW fraction containing glycol-compounds and yeast mannoproteins had higher foaming ability compared to wine with grape berry proteins only. The highest foamability was found when all fractions were combined suggesting a synergistic interaction between yeast mannoproteins and grape proteins (Vincenzi, Crapisi, and Curioni 2014; Coelho et al. 2009; Coelho et al. 2011a). The authors explained that the interaction of negatively charged mannoproteins with the positive charge of the grape PR-proteins, which at the pH of wine is below their isoelectric point (pI), was responsible for the results (Verhnet et al. 1996; Marchal, Bouquelet, and Maujean 1996; Vincenzi, Crapisi, and Curioni 2014).

The stability of sparkling wine bubbles requires the presence of an adsorption layer at the interface with the gases, and macromolecules contribute to the formation of these layers (Maujean et al. 1990; Brissonnet and Maujean 1991; Malvy, Robillard, and Duteurtre 1994). During foam formation, bubbles trap substances such as proteins to stabilize their interfaces (Douillard, Lefebvre, and Tran 1991; Graham and Philips 1979). If these components are lacking, then the films are not stable. The surface tension is high and coalescence takes place more easily (Jordan and Napper 1988). At the beginning of foam formation, the physico-chemical equilibrium has little time to establish. This means that during the first 80 seconds, the foam films are not yet stabilized because it takes time for the surface-active components to diffuse toward the film interfaces as the bubble increases in diameter thereby increasing the size of the interface protein concentration. Macromolecules in the 5–100 kDa MW range are capable of forming an adsorption layer and monosaccharide analysis of hydrolysed fractions indicated the presence of mannose, galactose, arabinose and glucose in decreasing proportions (Péron et al. 2001; Abdallah et al. 2010). Ellipsometry measurements on Pinot noir fractions (10 – 30 kDa and 30 – 100 kDa) indicated the formation of non-homogeneous and slightly reduced adsorption layers with both fractions. The kinetics of the former being faster than the latter, indicating that adsorption layers are formed within various molecular ranges and are the result of complex poly-macromolecular associations rather than the result of a single family of compounds (Abdallah et al. 2010).

Fast Protein Liquid Chromatography (FPLC) then Capillary Gel Electrophoresis (CGE) has been used to fractionate and characterize proteins at different stages of sparkling wine production (Luguera et al. 1997; Luguera et al. 1998). No changes in protein profiles in the first 18 months of lees aging was reported but continued release of proteins and peptides at 270 days after bottling base wines was reported (Martìnez-Rodriguez et al. 2002). To detect low levels of proteins in Champagne wines without purification, or a pre-concentrated step, Combinational Peptide Ligand Library (CPLL) technique has been used (Cilindre et al. 2012). However, the study could not differentiate between grape varieties but a wide range of proteins was identified. Since TS is related to hydrophobicity of polypeptides, proteins with high hydrophobicity would stabilize the films existing between bubbles (Brissonnet and Maujean 1993; Ferreira et al. 2005).

Future research is likely to further investigate, and identify the protein type in a range of grape varieties, their MW and their concentrations during sparkling wine production for a range of production techniques.

Grape proteins

While mannoproteins come from yeast, base wines contain a large quantity of grape berry glycoproteins (Dambrouck et al. 2003; Hsu and Heatherbell 1987; Feuillat et al. 1988; Paetzold, Dulau, and Dubourdieu 1990; Ledoux, Dulau, and Dubourdieu 1992; Pueyo, Dizy, and Polo 1993; Marchal, Bouquelet, and Maujean 1996). Most of them have a pI ranging from 2.5 to 4.5, and MWs ranging from 12 to 65 kDa (Brissonnet and Maujean 1993; Marchal, Bouquelet, and Maujean 1996). Grape invertase (62/64 kDa), is an *N*-glycoprotein enzyme that retains its activity in wine and has a high hydrophobicity and a pI of 3.9 though its effect on foam is unclear (Marchal, Bouquelet, and Maujean 1996; Hovasse et al. 2016). We know that pectic enzymes negatively affect foaming properties, but the effect of commercial protease enzyme products remains unclear (Lao

et al. 1999). A plant lectin exhibiting hemagglutining activity was found in a sparkling base wine but little research has been focused on it since then (Berthier et al. 1998).

The majority of grape proteins present in base wines have been identified as chitinases and thaumatin-like proteins (TLPs), but from 50 wines studied, only one had chitinases in it, probably due to their instability compared to TLPs (Culbert et al. 2017). Chitinase proteins have been identified as the most significant proteins involved in heat-induced haze in white wines due to their low melting temperature. Whereas TLPs not only cause protein haze in white still, table wine (not in sparkling wines) but also play a role in plant-pathogen interactions (Falconer et al. 2010; Marangon et al. 2014). Chitinase activity during fermentation decreases and no measureable activity in the final sparkling wine has so far been described (Manteau et al. 2003; Culbert et al. 2017). In a recent study, the maximum foam volume (FizzeyeRobot) of Traditional Method wines was found to vary the most (by as much as 94 mL) compared to Transfer, Charmat and carbonated wines, from 80, 57 and 35 mL respectively (Culbert et al. 2017). Foam stability, on average, was highest for the carbonated wines (11.2 sec) followed by the Traditional Method (10.2 sec), then the Transfer wines (6.5 sec) and finally Charmat wines (5.7 sec). Foam stability was expected to be highest for Traditional Method and Transfer wines, since these wines were highest in proteins and polysaccharides. Some studies suggested foamability is inversely correlated with TS, and is therefore negatively correlated with protein content but the previous studies used the Mosalux on grape juice, base wines and degassed wines (López-Barajas et al. 1998; Andrés-Lacueva et al. 1996; Andrés-Lacueva et al. 1997). Carbonated wines were high in TS overall but one carbonated wine contained significantly higher concentrations of TLPs but overall carbonated wines had elevated free amino acid concentrations than the other wines (Culbert et al. 2017). The difficulty with proteins is that even if numerous proteins are isolated and characterized (MW, pI, hydrophobicity, glycans, amino acid composition, origin), information would still be lacking concerning some specific macromolecular sized proteins and their contribution to foam. The molecular factors that affect preferential adsorption of proteins at an air-water interface are unknown, although it could be due to differences in their surface hydrophobicity, hydrophilicity and rate of adsorption that is involved. Tkachenko, Drevova, and Gural (2017) stated that foam height and foam stability (Mosalux apparatus) depends on the biopolymeric complexes. They identified that the proteins were the main components involved in the complexes followed by carbohydrates and partially, to a lesser extent, phenolic compounds.

Yeast proteins

Yeast mannoproteins (MPs) released during fermentation and aging on lees are major foam-active compounds due to their structure and composition that favours their adsorption on the gas-liquid interface (Nuñez et al. 2005, 2006; Blasco, Viñas, and Villa 2011; Vincenzi, Crapisi, and Curioni 2014; Medina-Trujillo et al. 2017a). The adverse conditions encountered during the secondary fermentation require yeast strains to be selected for their ability to grow at low temperatures and under pressure in ethanol (10 – 11% v/v), but also have strong flocculating ability (Valade, Laurent, and Moulin 1983). A detailed explanation concerning yeast autolysis can be found in a review by Alexandre and Guilloux-Bénatier (2006) and is not the focus of this review. However, the determination of the yeast strains' autolytic capacity and the foaming properties of the autolysates attained was investigated by Mártinez-Rodriguez et al. (2002). The strains that had the greatest autolytic capacity were those that released the highest quantity of proteins.

Until González-Royo, et al. (2015) studied non-*Saccharomyces* yeasts (*Torulaspora delbrueckii* and *Metshnikowia pulcherrima*), sparkling wine studies had focused primarily on *Saccharomyces cerevisiae* and their foaming capacity of base wines using the Mosalux apparatus. In their study, *T. delbrueckii* Bodiva^{TM} was found to have a positive effect on foaming properties of Cava wines, when used for the first fermentation, while *M. pulcherrima* increased TS. Sequential inoculation using *T. delbrueckii* and *S. cerevisiae* produced base wines with higher foaming potential than *S. cerevisiae* alone (Medina-Trujillo et al. 2017b). This was attributed to a greater release of proteins from the *T. delbrueckii* cells, particularly the low MW fraction. Further studies regarding their influence on foam from their use in the second alcoholic fermentation is likely. Immobilized yeast can be used for alcohol fermentation (first and second) to avoid "riddling" but so far studies have focused on second alcoholic fermentation and sensory affects not on their influence on foam parameters (Torresi, Frangipane, and Anelli 2011). In addition, magnetized yeast requires further investigation concerning their impact on proteins and foaming properties of sparkling wines (Berovic et al. 2014).

Commercial products of MPs, or enriched cell wall preparations, have been used in winemaking to protect wine against protein haze, to improve tartaric salt stability and to increase foaming ability (Moine-Ledoux and Dubourdieu 1999, 2002; Dupin, et al. 2000; Waters et al. 2005). To study the effect of yeast macromolecular extracts on wine foam, Nuñez et al. (2006), used thermally and enzymatically treated yeast cell walls. Model wine supplemented with thermal extract had the highest foaming properties with a linear relationship between the extract addition and the foam parameters in accordance with previous studies (Vanrell et al. 2002; Nuñez et al. 2005).

Regarding the addition of yeast lees and their impact on foam, La Gatta et al. (2016) added different volumes of yeast lees recovered from the first fermentation of Bombino to the *"liqueur de tirage"* for the second fermentation of the same Bombino base wine in Italy. Using the Mosalux apparatus, the control (without lees addition) had the highest foam height and stability. These results are in agreement with Pérez-Magariño et al. (2015b), who reported that addition of dry yeast autolysates (DYA) did not modify foam height of sparkling white wines and only a slight difference was found in rosé wines. The ability of β-glucanase to effect yeast lysis in sparkling wines aging on lees (Traditional Method) was investigated but it was found that additions did not substantially influence either the content of total proteins, or foam characteristics (Torresi et al. 2014). These studies suggest that addition of yeast lees and exogenous proteins prior to the second alcoholic fermentation does not exert an effect on foaming parameters.

To select yeast strains, genetic determinants of the release of MPs was studied to improve MP production from autolysis and increase sparkling wine foam (Gonzalez-Ramos and Gonzalez 2006). Wine made with strain IFI473I, produced the wine

with the highest foamability when compared to other treatments. This was ascribed to higher levels of proteins and highly glycosylated glycoproteins released by the strain (Nuñez et al. 2005). Thirty-six yeast autophagy-related genes have been identified, with *ATG1, ATG17* and *ATG29* being the main ones along with FPG1, the gene involved in foam formation in *Saccharomyces cerevisiae*. These are the principal genes studied in relation to foaming and autolysis which is likely to be the topic of further in-depth yeast and foaming studies in the future (Blasco, Viñas, and Villa 2011; Chew et al. 2013; Perpetuini et al. 2016).

Amino acids

Free amino acids in sparkling wines (Traditional Method) have been correlated with foaming parameters by Moreno-Arribas et al. (2000) and Martinez-Lapuente et al. (2015) but Medina-Trujillo et al. (2017b) reported no correlation when comparing the foam fraction to the wine that remained after the foam was removed. Additionally, Brissonnet and Maujean (1991) added amino acids to base wine then used the Mosalux to assess the foam and also reported no impact from amino acids. Culbert et al. (2017) investigated amino acid concentration in sparkling wines and reported that carbonated wines had significantly higher total amino acid levels than sparkling wines derived from Charmat, Transfer or Traditional Method production techniques. This essentially reflected the considerably higher proline levels of carbonated wines, as well as elevated levels of arginine and alanine. Proline is generally accepted to be the principal amino acid present in must and wine (Waterhouse, Sacks, and Jeffery 2016) although for some grape varieties, arginine, or arginine and proline dominate (Huang, and Ough 1991; Stines et al. 2000). Significant correlations were reported for TS and three of the amino acids studied: histidine ($r = 0.443$), arginine ($r = 0.325$), and tyrosine ($r = 0.332$) (Culbert et al. 2017). However, the mechanism by which they contribute to foam stability remains unclear. In addition to this, even though amino acids correlated to protein content in the study by Culbert et al. (2017), which in turn is correlated with foaming ability, it does not mean that an addition of amino acids will increase foam whereas protein addition does (Brissonnet and Maujean 1991). Amino acid composition can vary according to vineyard management, water availability, and nitrogen application, with proline accumulation considered to be a physiological response to stress (Bell and Henschke 2005; Bertamini et al. 2006). During alcoholic fermentation, amino acids provide nitrogen for yeast metabolism, either as free amino acids or via degradation of grape proteins, but are also released during yeast autolysis (Waterhouse, Sacks, and Jeffery 2016; Lehtonen 1996; Martínez-Rodriguez et al. 2002; Alexandre and Guilloux-Benatier 2006). Because most grape-derived amino acids are consumed during fermentation, the higher amino acid levels observed in carbonated wines (which do not undergo a second alcoholic fermentation and lees aging) were not unexpected. In contrast, sparkling wines produced via the Traditional Method, Transfer, and Charmat (which do undergo a second alcoholic fermentation) had similar free amino acid concentrations, on average, being 931 – 976 mg/L (Culbert et al. 2017). However, the authors found that variation existed amongst wines produced from the same method. In the case of carbonated wines, amino acid levels ranged from 471 to 1924 mg/L and these differences were attributed to grape variety and/or vineyard management practices. Carbonated wines are more likely to be produced from higher yielding vines, lower quality fruit, and/or riper fruit, with fruit maturity being another factor that influences amino acid concentration (Stines et al. 2000). Winemaking practices, in particular the addition of diammonium phosphate (DAP), may also influence amino acid metabolism during fermentation. Previous studies have shown that amino acid levels can fluctuate considerably during bottle aging and yeast autolysis, so multiple factors need to be taken into account (Culbert et al. 2017). Importantly, amino acids are known aroma precursors, so their degree of conversion to aroma compounds will also influence the resultant amino acid concentrations in sparkling wine (Feuillat and Charpentier 1982). Biogenic amines are formed from precursor amino acids, mainly by microbial decarboxylation, and have been studied in relation to their influence on sparkling wine foam and no effect on foam parameters has been reported (Guo et al. 2015; Martínez-Lapuente et al. 2015).

Protein reduction

Processes that reduce wine protein concentration influences sparkling wine foam and the action of bentonite, and its' detrimental effect on foam is now well-known (Maujean et al. 1990; Marchal, Sinet, and Maujean 1993; Luguera et al. 1998; Marchal et al. 2003a). In sparkling wine production, bentonite is mainly used to facilitate the riddling process or as a treatment to avoid proteic haze in Cava wine production. Bentonite is also used as a clarification aid to decrease turbidity of still wine prior to filtration (Kemp et al. 2015a). Studies have included a range of grape varieties and varying quantities. Different types of bentonite affect grape varieties in different ways (Vanrell et al. 2007; Sedmak and Grossberg 1977; Martinez-Rodriguez and Polo 2003; Dambrouck et al. 2005). A decrease in total protein concentration from bentonite use was mainly related to proteolytic activity from contact with lees (Leroy et al. 1990). Without bentonite treatment, TS increased in wines after 180 days of aging, which coincides with the release of nitrogen compounds from yeast autolysis (Andrés-Lacueva et al. 1997). Salazar et al. (2008) compared zirconia to sodium bentonite in Chardonnay base wine and reported that zirconia treated wines had better foam qualities. The negative impact of base wine filtration on sparkling wine foaming has been presented in a previous review but in brief, the smaller the filter pore size, the lower the foaming properties (Robillard et al. 1993).

Botrytis cinerea proteins

Botrytis cinerea is responsible for grey rot on grapes with affected wines marked by characteristic mushroom, mold and rotten smells/tastes (Bocquet, Moncomble and Valade 1995, 1996; Marchal et al. 2006). Several studies have clearly demonstrated that an infection of the grapes with *B. cinerea* leads to a decrease of sparkling wine foaming properties because of an altered protein composition (Marchal et al. 2006; Cilindre et al. 2007; Cilindre et al. 2008). One study investigated the effect of *Botrytis* infection on grape berries and the impact on foam using the Mosalux apparatus, CAVE and sensory analysis (Marchal et al. 2001). An absence of a "collar" in wines

produced from infected grapes, despite the presence of effervescence in the glass was reported (Marchal et al. 2001) along with the speed with which the height of liquid (L_s) increased in the glass as the level of rot infection in the Chardonnay grapes increased. The pouring time (P_T) was also considerably reduced when *B. cinerea* infection reached 20% in Pinot noir (−74%) and Pinot meunier (−58%) wines. This is because some proteins secreted by *B. cinerea* possess proteasic activity (Marchal, Bouquelet, and Maujean 1996). Studies have been carried out to find out if the presence of such proteases in grapes can result in alterations of the protein composition of musts and wines to explain their negative impact on foam (Marchal et al. 1998; Marchal et al. 2006; Cilindre et al. 2007; Cilindre et al. 2008). Marchal et al. (1998) reported that the presence of fungal proteins, on grapes with 80% rot infection, resulted in complete degradation of the initial grape protein fraction. A base wine (cv. Chardonnay) was prepared from healthy grape berries and compared to a base wine made from infected grapes (20%) and the rot-free wine had a better capacity to foam (+ 91%) and better TS (+ 50%) (Cilindre et al. 2007). No relationship between protein concentration and loss of foaming properties was found but proteins should not only be considered quantitatively but also on the basis of their biochemical characteristics and their origin.

Penicillium oxalicum proteins

According to the Carlsberg research group, gushing can be divided into two different types with primary gushing occurring periodically and consequently being associated with the raw materials used, and secondary gushing being caused by technological failures during the production process (Gjertsen, Trolle, and Andersen 1963; Gjertsen 1967; Kemp, Wiles, and Inglis 2015b; Vogt et al. 2017). Several authors have suggested that fungal infection by *Fusarium* species, of the malt used for brewing is responsible for primary gushing in beer (Gjertsen, Trolle and Andersen 1965; Amaha et al. 1973; Gyllang and Martinson 1976; Hippeli and Elstner 2002; Vogt et al. 2017). In contrast to beer gushing, the reason for its occurrence in sparkling wine has received little attention. Vogt et al. (2017) found that PDE_04519, and possibly PDE_07106 (protein molecules) are capable of stabilizing gas bubbles in a hydrophobin-like fashion. The authors suggested that gushing in sparkling wines could possibly occur when base wines have been produced from *P. oxalicum* rot-infected grapes. Additionally, Kupfer et al. (2017a) compared the electrophoretic profile of Pinot blanc sparkling wines made from healthy and botrytis infected grape berries. Their in-depth analysis revealed Seripauperin 5 (PAU5), a highly glycosylated protein from *Saccharomyces cerevisiae*. Sparkling wines made from grapes with *B. cinerea* lacked PAU5 and gushed upon opening. Therefore, the authors hypothesized that the glycosylated PAU5 has foam-stabilizing properties similar to the glycosylated form of ns-LTP1 found in beer by Jégou et al. (2000). Further investigation by Kupfer et al. (2017b) revealed that PAU5 plays a role, indirectly as a marker for gushing, but also has a direct impact as a protein that stabilizes sparkling wine against gushing. *B. cinerea* leads to the degradation of PAU5 but heat treatment of must prior to yeast addition *prevented* protein degradation suggesting that fungal enzymes are not stable at high temperatures. Bentonite fining also reduced PAU5 but differences in its', efficacy were reported to be due to the type of bentonite used.

Lysozyme treatment

Hen egg lysozyme protein is a natural protein with bactericidal activity and therefore, used in some wine regions, to prevent malolactic fermentation (MLF) because *Oenococcus oeni* species are sensitive to the lytic action of this enzyme (Amati, Chinnici and Piva 1994; Benucci et al. 2016). Quantities added to musts and wines range from 250 to 1000 mg/L (Pittoti et al. 1991; Anand and Damodaran 1995; Amati, Chinnici and Piva 1994). Its' effect on foaming properties depends on the protein structure and concentration but when added to Chardonnay and Pinot noir juice foaming ability and foam stability and the wines foaming' ability were similarly diminished (Marchal et al. 2002a). Therefore, when exogenous protein is added to wine, protein concentration is not necessarily associated with foaming properties. Several studies on the kinetics of protein adsorption at the air-water interface have been reported (Castle et al. 1987; Hunter, Carbonell, and Kilpatrick 1991; Xu and Damodaran 1994; Anand and Damodaran 1995). In wine, yeast and grape berry proteins have a wide range of MWs and pIs. Some are composed of amino acids whilst others are glycosylated (Waters, Pellerin, and Brillouet 1994; Marchal, Bouquelet, and Maujean 1996). This complex composition has a buffered effect on wine foam. However, due to its' biochemical characteristics (low MW (14.3 kDa), high pI (10.4)), compact tridimensional structure (four disulphide bonds) and its rigid, hydrophilic and positive charge protein, this is not true for lysozyme (Graham and Philips 1979).

Polysaccharides and oligosaccharides

The quantity and composition of polysaccharides and oligosaccharides in wine depends on a range of parameters such as grape variety, maturity stage, winemaking process and production stage. Their concentration range is 200 to 1500 mg/L, and from 25 to 321 mg/L for polysaccharides and oligosaccharides respectively (Guadalupe et al. 2014; Esteruelas et al. 2015b; Martínez-Lapuente et al. 2016; Jégou et al. 2017; Martínez-Lapuente et al. 2017). Polysaccharides originating from the grape berry cell wall include (i) polysaccharides rich in arabinose and galactose (PRAGs) which comprise type II arabinogalactan-proteins (AGPs), arabinans and arabinogalactans (AGs), (ii) polysaccharides rich in rhamnogalacturonans type I (RG-I) and type II (RG-II), and homogalacturonans (HLs). Yeast polysaccharides, glucans (GLs) and mannans or mannoproteins (MPs) are released by yeast during the first, and second alcoholic fermentations, as well as during aging on yeast lees (Culbert et al. 2017). Nevertheless, the definition of yeast mannoproteins is still controversial with respect to the macromolecule family in which they are classified. In fact, these glycoproteins are called proteoglycans, which are mannan structures covalently linked to a protein or polypeptide moiety, and contain 10% protein and 90% mannose (Waters, Wallace, and Williams 1992; Gonçalves et al. 2002). Thus, according to

the researchers, mannoproteins are defined as proteins (as in section 3.2) or as polysaccharides as in this section.

Several studies have identified polysaccharides as molecules involved in improving foaming properties (Pueyo, Martin-Alvarez, and Polo 1995; Moreno-Arribas et al. 2000; López-Barajas et al. 2001; Abdallah et al. 2010; Coelho et al. 2011a; Martínez-Lapuente et al. 2013). Concerning wine quality, studies on oligosaccharides are still scarce but a positive relationship between oligosaccharides and astringency has been found (Quijada Morín et al. 2014; Boulet et al. 2016). Oligosaccharides can be used for food applications to improve sensory characteristics, and foam stability (Rastall 2010). Thus, their composition could influence the foaming properties of sparkling wines.

Sparkling wine production methods influence polysaccharide composition and the wine's foaming properties (Culbert et al. 2017). Traditional Method and Transfer method wines contained a greater proportion of higher MW polysaccharides (i.e. >200 kDa), which typically represent the yeast-derived compounds, while MW polysaccharides (i.e. 10 – 50 kDa), which typically represents rhamnogalacturonans (RGs) (Culbert et al. 2017).

The level of total polysaccharides has also been studied in Spanish wines made in the Traditional Method, and analyzed at 3 and 26 months after bottling (Andrés-Lacueva et al. 1997). The highest concentrations were detected at 18 months after bottling, owing to the release of polysaccharide compounds during yeast autolysis (Charpentier and Feuillat 1992). Nevertheless, after 18 months a decrease in foaming ability was reported, accompanied by an increase in monomeric compounds, likely due to hydrolytic activity on yeast polysaccharides (Feuillat 1987). A later study that used Verdejo, Viura, Malvasiá, Albarıño, Godello, Garnacha and Prieto Picudo varieties in Traditional Method wines, reported a decrease of all polysaccharide families but an increase in the Mannose/Glucose ratio (Martínez-Lapuente et al. 2013). A difference in the release time of monosaccharide composition and polysaccharide families was reported as mannose increased from 0 to 6 months of aging on lees while glucose increased only between 3 and 6 months of aging (Martínez-Lapuente et al. 2013).

Concerning grape polysaccharides, base wines were composed of grape primarily of PRAGs and with less HLs, indicating that they are more easily released into wine because of their soluble form within grape cell walls (Vidal et al. 2001). Moreover, a base wine supplementation of inactive dry yeasts increased the total polysaccharide concentration during aging on yeast lees (from 0 to 9 months), then constantly from 9 to 18 months, and improved the foaming properties of the sparkling wine (Marti-Raga et al. 2016). The positive correlation observed between polysaccharide content and TS could be due to additional polysaccharide release by inactive dry yeast cell structure. A very recent study concerning the change of polysaccharides and oligosaccharides during the aging on yeast lees of Tempranillo and Verdejo sparkling wines suggested a potential cultivar impact on the contents of yeast polysaccharides and PRAGs of these wines (Martínez-Lapuente et al. 2017). The difference in polysaccharide composition would likely influence the foaming properties of the sparkling wines. Interestingly, oligosaccharides and polysaccharides from yeast could be autolysis markers of sparkling wines.

It has been determined that purification steps can strongly alter the foaming properties of macromolecular fractions (Puff et al. 2001). Coelho, Rocha, and Coimbra (2011b), have studied the effect of the different families of polysaccharides on foam in model wines. Three arabinogalactan (AG) fractions were isolated from a Fernão-Pires white wine and when added to a model wine, exhibited high foaming ability, yet reasons for which remain unclear (Coelho, Rocha, and Coimbra 2011b). A later study to identify which family of polysaccharides influences foaming properties of rosé and white sparkling wines found that total polysaccharides were the only compounds that affected foam stability and yet they did not affect foaming ability (Martínez-Lapuente et al. 2015). Grape polysaccharides showed higher correlation coefficient than polysaccharides from yeast and this effect was attributed to PRAGs while the influence of yeast polysaccharides was probably due to MPs. Jégou et al. (2017) reported that the content of oligosaccharides and polysaccharides in Champagne wines was affected by press fractioning. The polysaccharides decreased during the press cycle but the result was not as clear for oligosaccharides, and the impact of this reduction on foaming properties was not studied. It is also essential to consider the concentration of proteins other than MPs that are released from *S. cerevisiae* i.e. proteins from the periplasmic space and their possible role in foaming (Marchal et al. 2017).

The proteic fraction of MPs and PRAGs have shown an ability to adsorb at the liquid-air interface, and to interact with other (glyco) proteic macromolecules by means of hydrogen bonds, electrostatic forces and/or hydrophobic forces (Blasco, Viñas, and Villa 2011). No one wine polysaccharide family correlated with the foaming ability of sparkling wines yet in contrast, positive correlations were found between foam stability and wine polysaccharides (RG-II and PRAGs were the highest). PRAGs and MPs present hydrophobic (a part of the proteic moiety) and hydrophilic domains (glycan moiety) although some domains of the proteic moiety are also hydrophilic; therefore, they could interact with surface-active materials and be absorbed at the gas-liquid interface. The hydrophilic glycans located at the liquid layer, are capable of increasing the film viscosity and then delay the drainage of the liquid. Proteic fraction of PRAGs and MPs could interact with other proteins to form a more stable film by increasing its viscoelasticity (Blasco, Viñas, and Villa 2011). The fact that PRAGs showed a high correlation coefficient could be due to their structure and composition. PRAGs isolated from champagne wines showed a high content of hydroxyproline (%), a hydrophobic amino acid and PRAGs that had glucuronic acid in the terminal positions could stabilize foam (Doco and Williams 2013).

Grape ripening stage (early and late maturity grapes) showed a significant impact on the content, composition, and evolution of polysaccharides and oligosaccharides of red sparkling wines made from Tempranillo grapes (Martínez-Lapuente et al. 2016). PRAGs, MPs, RG-II, and oligosaccharides in base wines increased with increased grape maturity. The harvest date and therefore, the grape maturity had an effect on the foaming properties of Cava base wines and sparkling wines, the high MW polysaccharides (> 180 kDa) having a negative effect on foam maximum height (foamability) (Esteruelas et al.

2015b). Conversely, no specific trend was shown for oligosaccharides (< 7.5 kDa) and wine foaming properties in this study.

The different behaviour of the polysaccharide families regarding TS is likely due to their different structures, conformations and their charges (Moreno-Arribas et al. 2000; López-Barajas et al. 2001; Nuñez et al. 2006; Coelho, Rocha, and Coimbra 2011b). Polysaccharide levels vary amongst wines and comparison of results must allow for the different analytical methods used to quantify them (Alexandre and Guilloux-Benatier 2006; Jegou et al. 2017; Esteruelas et al. 2015b; Culbert et al. 2017). Improved understanding of their content and release kinetics is necessary and likely to be the focus of future studies.

Sugar additions

Apart from chaptalization (sugar addition to juice) common in some cool/cold regions, sugar addition during sparkling wine production can affect foam at two specific times: 1) the amount added to the wine levels prior to the second alcoholic fermentation and, 2) the amount added in the *dosage* solution (sugar and wine solution) after disgorging (Fig. 1). The addition of sugar prior at bottling for the second alcoholic fermentation is the major contributor to the amount of CO_2 in the final wine. Alcohol levels increase to approximately 12 – 12.5% (the alcohol increase is around 1.2 – 1.3% v/v), so typically a bottle produced by the Traditional Method, will contain 9 grams of CO_2 (if there is no residual sugar) (Liger-Belair 2017). However, after aging on yeast lees (typically 2 to 10 years), disgorging and aging with the cork, the CO_2 content is much lower. At the end of the second alcoholic fermentation, following the Pasteur law, 24 g/L of fermentable sugars produce 12 g/L of CO_2 from a complete fermentation. This means that for a 5-year-old wine, we generally observe around 9 g/L and not 9 g/bottle. It is the amount of sugar added at this stage that determines the pressure level of the bottle at disgorging, which then reduces with CO_2 escape, oxygen ingress and *dosage* addition. American consumer preference for sparkling wine has been found to be segmented based on sweetness preference as opposed to the type of sugar (glucose, fructose and dextrose) used in the *dosage* solution (McMahon et al. 2017b). Additionally, Culbert et al. (2015) reported that sweetness level in an Australian study of Traditional Method, Transfer, Charmat and carbonated wines, was highly correlated to sensory attributes and the main contributor to the differentiation of the wines by sensory analysis. Although foam analysis was not included in either of the studies, the type of sugar, and amount used, in the *dosage* can effect wine viscosity therefore, the foam height (FH) and stability (TS) in the finished wine. TS can directly depend on the viscosity of the liquid because when the liquid's viscosity increases, it impedes the hydrodynamic drainage and coalescence of bubbles (Dale et al. 1999; Gandolfo and Rosano 1997; Magrabi, Dlugogorski, and Jameson 1999; Nguyen 2002). However, in contradiction to this view sugar addition was found not to effect viscosity (+10% for 40 g/L at 5°C) (Marchal, Descoins, and Jeandet 2003b). Yet zero-*dosage* wine (without sugar addition) made by the Traditional Method, was reported to have higher foam height and stability than sparkling wines with sugar addition (residual sugar +/− 8 g/L) (Kemp et al. 2017). However, an English sparkling wine made by the Traditional Method but with low-pressure levels compared to commercially produced wines, was analysed by a modified Mosalux apparatus as well as an imaging method (Crumpton et al. 2017). The authors reported that TS decreased when sugar levels in the *dosage* additions increased, yet foam formation improved. It is probable that sugar and foam trial results differ due to several factors including; the grape varieties/blend, the wine's chemical composition, acidity levels, protein content, time aging on yeast lees, bottle pressure, wine temperature, ambient temperature and the differing foam analysis methods used. Furthermore, sugar addition reduces the alcohol content by 0.2% v/v on the basis of a *dosage* at 12 g/L for example with a "liqueur d'expédition" (sugar solution using wine to dissolve the sugar) at 550 – 600 g/L.

Ethanol

Ethanol concentration, which increases during the second alcoholic fermentation, was reported to influence foam in wines made by the Traditional Method. Ethanol influences the wine foaming properties by decreasing the surface tension of the gas-liquid interface, and by influencing the adsorption of other surface-active compounds (Comelles, Bosch, and Castro 1991; Dussaud et al. 1994b; Senée, Robillard, and Vignes-Adler 1999; Péron et al. 2000; Puff et al. 2001; Glampedaki et al. 2010). A high ethanol content negatively affects the foamability of sparkling wines, as has also been shown for beer (Brierley et al. 1996; Girbau-Solá et al. 2002b; Esteruelas et al. 2015b). However, Andrés-Lacueva et al. (1996) reported a positive correlation between foaming ability and alcohol content for sparkling base wines. Initially, as with other compounds, the timing of harvest will affect ethanol levels due to sugar levels at harvest. Chardonnay and Parellada (AOC Cava) wines made from less ripe grapes in Spain had higher foaming ability due to lower sugar levels at harvest, compared to later picked grapes (Esteruelas et al. 2015b; Kemp et al. 2015a). The surface pressure ($\Pi = 1.5$ mN/m) is the difference between the surface tension of pure water (73 mN/m) and the surface tension of a hydro-ethanol solution. The Π of ethanol in water at 11.3% is 23 mN/m though the surface pressure of ethanol in wine is 24.5 mN/m but the surface tension in sparkling wines ranges from 45 to 48 mN/m (Comelles, Bosch, and Castro 1991; Dussaud et al. 1994a; Péron et al. 2000; Joshi 2011). The difference between surface pressure and surface tension is that the first one corresponds to the surface pressure ($\Pi = 1.5$ mN/m) of other surface-active compounds present in the adsorption layer at the gas-wine interface, principally oligo-peptides, polypeptides, proteins and glycoproteins and lipids. The value of 1.5 mN/m becomes 13.8 mN/m for the same wine with a concentration of ethanol of 2% (v/v) after partial de-alcoholization by rotary evaporation. After adding 1.3% ethanol to a base wine to simulate bottle-fermentation, foaming ability decreased by 50% demonstrating the impact of ethanol content on the adsorption of surface-active compounds at the gas-liquid interface, and the interface gas-liquid is essentially dependent upon the presence of ethanol (Maujean et al. 1990).

Abou Saleh et al. (2007) reported a difference in gas-wine interface by Brewster Angle Microscopy (BAM), which was

attributed to the higher alcohol (1.4% v/v) in the finished sparkling wine compared to the base wine. Once it was confirmed that CO_2 concentration did not interfere with the gas-liquid interface, alcohol concentration was investigated and the assertion made that ethanol was the cause for the air-gas interface differences that would influence foaming. The study however, used bentonite as an adjuvant at bottling, and did not take into account the removal of macromolecules i.e. proteins, so the impact of ethanol on the collar shape might not be responsible for the gas-liquid interfaces variances instead the use of an adjuvant likely contributed to it.

Fatty acids and lipids

Fatty acids and lipids are good candidates for involvement in foaming and bubbles in carbonated beverages, including wine, due to their biophysical properties. Short-chain fatty acids are amphipathic, where one part of the molecules has an affinity for the nonpolar media, here the air interface, and one part that has an affinity for polar media such as water, the main constituent of beverages. The most energetically favourable orientation for these molecules is at the interfaces so that each part of the molecule can reside in an environment for which it has the greatest affinity. Longer chain fatty acids exhibit an extreme kind of adsorption at liquid surfaces and can concentrate in one molecular layer at the surface (Schramm 2005). Short-chain alcohols and short chain fatty acids are mildly surface-active compounds and can stabilize weakly stable, transient foams. These weak "frothers" tend to produce foam films having stabilities in the order of seconds. More strongly surface-active compounds can stabilize quite strong, meta-stable foams. Examples include long-chain alcohols and fatty acids, and proteins. These strong "frothers" tend to produce foam films having stabilities in the order of minutes to hours (Schramm 2005). The involvement of individual fatty acid species to the stability of foam and bubbles in sparkling wine is dependent on the structure of that fatty acid, and as a factor of the concentration of that fatty acid within the complex wine matrix (Table 2).

The effect of lipids on the foaming properties of sparkling wines was been studied by lipid addition to wines (Dussaud et al. 1994b). The lipid composition of three sparkling wines was determined and the lipid content (C_{16} – C_{20}) average value was 308 μg/L of total free fatty acids. When fatty acids were added to wines in varying amounts of ethanol concentrations, (2%, 5%, and 11.3%, v/v), foam decreased in the presence of lipids but all values returned after 3 days. The lipid effect existed only when the ethanol concentration was below 5% ethanol whereas at higher alcohol levels the foam behaviour was mainly governed by the ethanol. The fatty acids may have been molecularly dissolved and not active at the interface. However, when fatty acids were esterified to their ethyl esters, a positive relationship with foaming ability was observed (Gallart et al. 2002). In a study on Portuguese sparkling wines, Coelho et al. (2011a) reported that sparkling wine foam possessed glyceryl ethylene glycol fatty acid derivatives with potential tensioactive properties, glyceryl palmitate and glyceryl stearate. These fatty acid derivatives may be released during yeast autolysis (Pueyo et al. 2000), meaning that production method of sparkling wine could significantly affect foaming and bubble behaviour.

During sparkling production, the introduction of yeast breakdown products depends on the time spent in contact with yeast. A comparative study that investigated sparkling wines made from different production methods found different concentrations of fatty acids and their esters were dependent on production method (Culbert et al. 2017). Although no correlation was found between fatty acid concentration and two foaming measures, octanoic and decanoic acids and their ethyl esters were present in Charmat and carbonated wines at significantly higher concentrations than the bottle-fermented wines, and were negatively correlated with sensory quality ratings. It is likely that the measures of foamability in this study were not sensitive enough to the effects of fatty acids, as foam collar height can be enhanced by the presence of octatonic and decanoic fatty acids, but these same fatty acids negatively affect overall foam stability (Maujean et al. 1990).

The effect of fatty acids on foaming and bubble properties deserves more investigation. Studies of cider show clear effects of fatty acid chain length on foaming (Margolles Cabrales, Arias Abrodo, and Blanco-Gomis 2003), and the possibility to fine-tune the concentrations of these compounds by modulating yeast autolysis by production method shows great promise. Understanding the roles that fatty acid and ester derivatives play on specialized foaming and bubble behaviour is now possible by automated pouring and image analysis (Condé et al. 2017b), as advances in analytical chemistry allows sensitive quantification and precise qualification of fatty acid concentration and structure.

Organic acids: Tartaric, malic, lactic and gluconic acids

Sugar and acid levels are important in sparkling wine grapes and the sugar to acid ratio (°Brix to TA g/L index) shows that at a ratio of 4: 5.5 produces wines with optimal foaming ability. Grapes picked at more mature ripeness levels produce wines with less foaming ability (López-Barajas et al. 1997; Girbau-Solà et al. 2002a). Tartaric acid is the main acid in sparkling wine with malic acid levels being dependent upon climatic parameters, and whether malolactic fermentation (MLF) is carried out to adjust malic to lactic acid. Although it was reported that commercially produced Lambrusco wine had higher levels of succinic and malic acid than tartaric acid (Papotti et al. 2013). Malic acid was found to be high in Lambrusco wines, which are meant to be consumed young and are characterized by a lack of MLF. Traditional and Charmat wines made from Moscato Giallo grapes were higher in succinic acid compared to wines made from the same grape variety using the Asti method of production (Caliari et al. 2015). This is because succinic acid is formed by yeast during alcoholic fermentation from lipid metabolism in the Krebs cycle, and during Asti wine production their first fermentation is stopped.

Organic acids have been implicated in the foaming ability of sparkling wine and malic acid has been found to positively affect foaming height but negatively affect foam stability (Andrés-Lacueva et al. 1996; Andrés-Lacueva et al. 19967; López-Barajas et al. 1998; Girbau-Solá et al. 2002a; Kemp,

Table 2. The influence of fatty acids on foam.

Fatty acid	Structure	Beverage	Concentration range	Effect on foam	Reference
Octanoic (caprylic)	C_8	Cider	—	Positive correlation with foam stability	Margolles Cabrales, Arias Abrodo, and Blanco-Gomis (2003).
Linolenic, pentadecanoic, and palmitic acid	C_{18}, C_{15}, C_{16}	Cider	—	The fatty acids that best define the foam height	Margolles Cabrales, Arias Abrodo, and Blanco-Gomis (2003).
Palmitic acid	C_{16}	Cava	120 – 370 μg /L (360 – 1298 μg/L total)	Foam height increase	Pueyo et al. (1995).
Stearic and linoleic acid	C_{18}	Cava	43 – 118 μg/L (360 – 1298 μg/L total)	Negative relationship with foam formation	Pueyo et al. (1995).
Linoleic and oleic acid	C_{18}	Beer	$>$0.1 μg/mL	Inhibit the foam formation	MacLeod (1977).
Octanoic and decanoic acids and their ethyl esters	C_8, C_{10}	Australian sparkling wine from different production methods	Concentration not reported	No effect on foaming; charmat and carbonated wines at significantly higher concentrations than bottle-fermented wines	Culbert et al. (2017).
Glyceryl ethylene glycol fatty acid derivatives	C_{14}–C_{18}	Red and white Portuguese sparkling wines	Partitioned into the foam fraction	Important for foam stability	Coelho et al. (2011a and b).
Octanoic and decanoic fatty acids	C_8, C_{10}	Added to champagne base wine	0.5 – 2.5 μg/L added	Negative effect on foam stability time, but positively influences foam collar height	Maujean et al. (1990).
Lipid mixture added to wines	C_{16}–C_{20}	Champagne	308 μg/L total free fatty acids	No effect until ethanol added	Dussaud, et al. (1994b).
Free fatty acids C_8, C_{10}, and C_{12}	C_8, C_{10}, and C_{12}	Cava	24–10325 ug/L dependant on species	Negatively affects foam	Gallart et al. (2002).
Esterified C_8, C_{10}, and C_{12} fatty acids	C_8, C_{10}, and C_{12}	Cava	21–1984 ug/L dependant on species	Positively affects foam	Gallart et al. (2002).

Table 3. The influence of tartaric, malic, lactic and gluconic acids on sparkling wine foam.

Organic acid	Influence on foam	Wine	Reference
Tartaric	Positive effect on foam height and foam collar	Cava and Champagne wines	Pueyo et al. (1995); Robillard et al. (1993).
Malic	Positive effect on foam height. Negative effect on foam stability	Cava wines	Andrés-Lacueva et al. (1997); López-Barajas et al. (1998); Girbau-Sola et al. (2002a).
Lactic	Positive effect on foam stability. Negative effect on foam height.	Cava wines	Andrés-Lacueva et al. (1996); Andres-Lacueva et al. (1997); López-Barajas et al. (1998).
Gluconic	No effect on wine foamability. Negatively correlated to wine foam but strongly correlated to the protease activity measured in the wine.	Cava wines	Esteruelas et al. (2015b).

Wiles, and Inglis 2015b). However, MLF is rare in Cava wine production due to low malic acid levels found in grapes at harvest owing to climatic influences. Lactic acid, found in higher concentrations after MLF, has been found to be beneficial for foaming stability but negatively affected foaming height (Andrés-Lacueva et al. 1996; Andrés-Lacueva et al. 1997; López-Barajas et al. 1998). Concerning tartaric acid though, foam height and foam collar have been found to be positively related to its' concentration in wine (Table 3) (Pueyo, Martin-Alvarez, and Polo 1995; Robillard et al. 1993).

Gluconic acid is regarded as an index marker for the presence of *Botrytis cinerea* to the point that some appellations d'origine contrôlées (AOCs) have established a maximum limit in wines (Donèche 1989). Gluconic acid is found at concentrations of mg/L as opposed to g/L of tartaric, malic and lactic acids, and the molecule is always present with proteases. As previously mentioned, *B. cinerea* can affect foaming ability, and Esteruelas et al. (2015b) reported that wines produced from late harvested grapes had higher levels of gluconic acid from rot infection than the earlier harvested Macabeo, Xarel.lo and Chardonnay. These wines were found to have the lowest foam height when analyzed by the Mosalux apparatus. However, gluconic acid does not have a direct impact on foaming ability, even though it was been found to be negatively correlated with foam. It is strongly correlated to the protease activity (released by *B. cinerea* during its growth on the grape berry), which leads to protein degradation, and hence the reason for the impact of *B. cinerea* on foam. When only disease-free, healthy berries were used in a study, Liu et al. (2017) reported contradictory results.

A study focused entirely on organic acids has yet to be conducted, instead their contribution to foam and gushing has been a small part of larger studies (Kemp, Wiles, and Inglis 2015b). While the effects of organic acids on foam have been reported, further research is required to elucidate results reported thus far. It is probable their different chemical structures are responsible for their different foam influences, and their interaction with other compounds. Investigating weaker acids i.e. succinic acid, and wines made from a range of production methods would provide further insight into foam and acid interactions.

Phenolic compounds

One of the two principal types of phenolic compounds in grapes are non-flavonoids. These are predominantly represented by the phenolic acids and their esters and found at low concentrations in grape pulp and wine, with the exception being hydroxycinnamic acids (Kennedy et al. 2006; Kemp 2010). Flamini (2003) explained that the important hydroxycinnamates in grapes are the tartaric esters of caffeic, p-coumaric and ferulic acids, namely caftaric, coutaric and fertaric acid. The other grape phenolic group contains flavonoids which consist of a C15 (C6-C3-C6) three-ring system with a central oxygen-containing pyran ring with different oxidation states (Waterhouse 2002). This benzopyrano moiety is also referred to as a chroman ring and typically bears an aromatic ring at C-2, C-3 or C-4.

Grape variety, vintage differences, soil type, ripeness level at harvest, press fractionation, production technique and the treatment of grapes prior to fermentation have all been found to influence the concentration of phenolic compounds in sparkling wine (Murphey, Spayd, and Powers 1989; Girbau-Solá et al. 2002a; Girbau- Solá et al. 2002b; Chamkha et al. 2003; Pozo-Boyón et al. 2003; Coelho et al. 2011a; Dowling et al. 2015; Esteruelas et al. 2015b; Pérez-Magariño et al. 2015a; Culbert et al. 2017). Additionally, winemaking practices that reduce phenolic compounds can negatively affect foaming i.e. the use of charcoal on juice or base wines to reduce phenolic compounds and proteins (Maujean et al. 1990; Marchal 1995; Marchal et al. 2002a; Parmentier et al. 2013). Grape storage temperature prior to pressing was found to affect the concentration of phenolic compounds in Method Cap Classique (MCC) wines in South Africa (Mafata 2017). Wines produced by the Traditional Method (Chardonnay and Pinot noir), were stored at 0, 10, 25 and 30°C, over two vintages (Mafata 2017). MCC wines made from grapes stored at lower temperatures (0 and 10°C) had lower total phenolic content, colour intensity and total hydroxycinnamates than wines made from grapes stored at higher temperatures (25 and 30°C). Therefore, greater phenolic extraction from grapes stored at 25 and 30°C was reported but any possible effect on foaming is unknown.

In sparkling wine production minimal levels of phenolic compounds are required hence, the light pressing of grapes to acquire a low level of phenolic compounds in must (Chamkha et al. 2003). Juice from press fractions later in the press cycle are known to have higher levels of total phenolics than the earlier, high quality fractions with the first juice fraction having the least (Dowling et al. 2015). Phenolic compounds have been found to affect flavour and are more susceptible to oxidation, but also negatively impact foam (Andrés-Lacueva et al. 1996; Lao et al. 1999; Mailliard 2000; Girbau-Solá et al. 2002a; Serra-Cayuela et al. 2014). However, Hidalgo et al. (2004) reported that rosé sparkling wines (Garnacha Tinto variety) had higher foaming properties than the white sparkling wines studied.

However, as aging time increased, differences in foaming characteristics became smaller. This is likely due to differences in phenolic composition/concentrations as well as the different production technique used for rosé compared to white sparkling wine. Chamkha et al. (2003) reported that phenolic composition in Champagne wines differed in terms of concentrations but not concerning type, class, and total phenolics. Lees aging was found not to influence the concentration of phenolic compounds in Cava sparkling wines possibly because very few monomeric phenolic compounds are absorbed by yeast cells (Pozo-Boyón et al. 2003; Mazauric and Salmon 2005).

Studies regarding the extraction of phenolic compounds from oak during aging in barrels are scarce and any impact on foaming ability is currently unidentified. Although concentrations of phenolic compounds were found to be highest in wines in which the *Liqueur d' Expédition/dosage* was made from still Chardonnay wines aged in oak (12 A.U.) (Kemp et al. 2017). Concerning non-acylated anthocyanins, they had a positive effect on the foaming of rosé sparkling wines while malvidin-3-(6-acetyl)-glucoside had a significant effect on foam stability (Girbau-Sola et al. 2002a). When the total phenolic concentration was considered, no relationship with any foam parameters for rosé or white sparkling wines were found yet there was a negative correlation between total proanthocyanidins and foam regardless of their size, and positive correlations were reported for coumaric acid and isorhamnetin (Martínez-Lapuente et al. 2015). These results were likely due to the interaction of anthocyanins with wine proteins through hydrophobic interactions and hydrogen bonds (Martínez-Lapuente et al. 2015). Links between proteins and polyphenol molecules can lead to an increase in foaming ability and foam stability in model wines by increasing the rigidity of the interfacial air-liquid layers (Sarker et al. 1995). Contradictory results of phenolic compounds in sparkling wines are also likely to be because their analysis has been carried out in model systems, grape juices or base wines, which are all very different mediums to the finished sparkling wines (Sarker et al. 1995; Andrés-Lacueva et al. 1996; López-Barajas et al. 1997; Lao et al. 1999; Girbau- Solá et al. 2002a). Positive effects of monomeric molecules on wine foam could be attributed to their low MW and planar structure, which modulates their polarity leading to hydrophobic molecular interactions through vertical stacking.

Conclusions and further research

This review investigated chemical compounds and the mechanisms we are currently aware of that impact the foaming quality of sparkling wines. Further studies are needed to investigate the relationship between polyphenol composition (white, rosé and red sparkling wines), their concentration and their impact on foam particularly concerning grape varieties, viticultural practices, and sparkling wine production methods. Further investigation would elucidate the possibility that TLPs, although responsible for protein haze in still white wines, might make the most significant contribution of all grape proteins to sparkling wine foam. Studies have demonstrated that wine foam characteristics are complex, and influenced by grape variety, ethanol, proteins, polysaccharides, polyphenols, sugar, organic acids and lipids. A better understanding of foam behaviour could be gained from increased knowledge about the gas-liquid interface combined with the physics of bubbles in conjunction with the chemical composition of sparkling wines. Mechanisms involved in the interaction of organic acids in sparkling wine, and the effect of oak-derived phenolic compounds on foam are areas for future investigation. Information on the factors involved in sparkling wine foam properties are of considerable interest, and winemakers can benefit from understanding how a wine's chemical composition can affect foaming parameters in sparkling wine.

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