Gains in speed, labour and gas consumption for winemakers

Membrane contactors for management of dissolved oxygen and carbon dioxide

Automated dissolved gas management systems using membrane contactors for gas transfer have recently been introduced to the Australian wine industry. They potentially allow for faster and more precise dissolved gas adjustment and reduced gas consumption. In this article, AWRI Senior Engineer, **Simon Nordestgaard**, reviews how they work and compares them with alternatives.

Membrane contactors facilitate mass transfer between two fluids. For wine gas management, wine flows on one side of the membrane and a gas (or vacuum) flows on the other side. Wine doesn't pass through the membrane because the membrane is hydrophobic (water-repelling) and has very small pores (0.03 µm). Gases diffuse through the membrane into or out of the wine depending on the operating conditions.

The basic principles are illustrated in Figure 1. In Figure 1a there is more carbon dioxide (CO_2), oxygen (O_2) and nitrogen (N_2) in the wine than in the vacuum stream, so these gases diffuse out of the wine through the membrane into the vacuum stream. In Figure 1b, there is more CO_2 in the gas stream than in the wine, so the CO_2 diffuses from the gas stream into the wine. O_2 and N_2 are still removed from the wine since they are at higher levels in the wine than in the gas stream. By using a combination of the approaches shown in Figure 1a and Figure 1b it is possible to adjust wine CO_2 concentration down or up to a set level (including full carbonation) while removing a large proportion of O_2 and N_2, all in a single pass.

Dissolved gas management systems for wine that use membrane contactors (e.g. Figure 2) are now being built by K+H, PTI Pacific (which builds systems for 3M) and Juclas. While there are differences between the systems, they all use Liqui-

THEORY

Partial pressure: The pressure exerted by a single component of a gas mixture.

Dalton's law: The total pressure exerted by a gas mixture is equal to the sum of the partial pressures of the individual gases in the mixture.

P = pCO2 + pO2 + pN2

Henry's law: Each gas dissolved in a wine exerts a partial pressure proportional to its concentration, at equilibrium.

p*CO2 = HCO2 . x*CO2   p*O2 = HO2 . x*O2   p*N2 = HN2 . x*N2

The driving force for addition or removal of each gas from a wine in a membrane contactor is the difference between the partial pressure exerted by the gas species in the wine (according to Henry's law) and the partial pressure of that same gas species in the gas/vacuum strip stream. The direction of diffusion being from the side with the higher partial pressure to the side with the lower partial pressure.

Henry's law constants (H) are temperature dependent. They have higher values at higher temperatures meaning that the same concentration of a dissolved gas exerts a higher partial pressure at higher temperatures (i.e. it is less soluble and can be more easily removed).

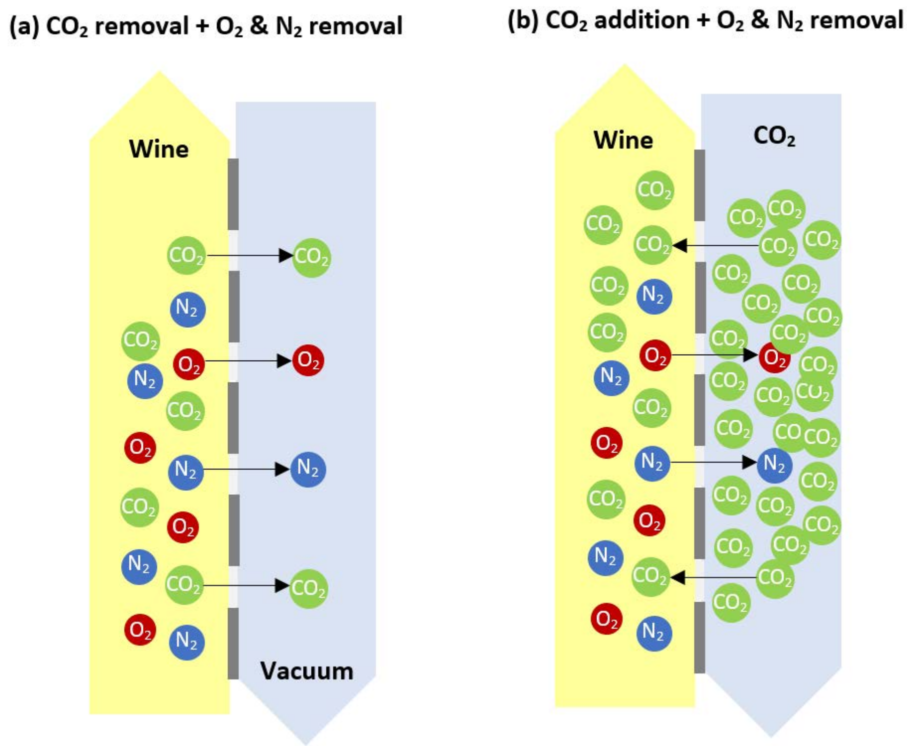

Figure 1. Illustration of gas transfer in a membrane contactor

Cel membrane contactors (Figure 3). Liqui-Cel membrane contactors are manufactured by Membrana, which was purchased in 2015 by 3M. The membranes are in the form of very thin hollow fibres (microporous tubes with an outer diameter of 300 µm) knitted together in an array that is wrapped around a central distribution/collection tube. The gas or vacuum flows through the inside of the fibres and the wine flows across the outside of them. The arrangement of tightly bundled thin hollow fibres provides a large surface area for efficient gas transfer without a large wine pressure drop.

History and adoption

Membrane contactors suitable for industrial gas transfer applications were introduced in the mid-1990s. They have been trialled in wine applications by German and French research organisations since the mid-2000s. There has been significant commercial adoption of the technology recently, with more than 50 new installations for wine gas management in Europe, most of them in Germany.

In Australia, while the use of membrane contactors for wine gas management is new, the same membranes have been used here for dealcoholisation since the mid-2000s. Membrane contactors are used in the Memstar process to remove alcohol from the permeate stream coming from a reverse osmosis separation of wine. The membrane contactor step is referred to as evaporative perstraction and is performed against strip water instead of against a gas/vacuum. It is also possible to dealcoholise wine directly with a membrane contactor without prior RO separation, albeit with some loss of volatiles, particularly when larger reductions in alcohol are made (Diban et al. 2008)

Sensory and chemical impacts

Carbon dioxide concentration has a major impact on wine taste irrespective of the technology used to add or remove it. Red wines are typically bottled with lower levels than white wines, and semi-sparkling and sparkling wines have much higher concentrations.

The method of introduction of CO_2 with membrane contactors is quite different from other carbonation techniques. It involves bubbleless diffusion. There have been suggestions that this technique results in bubbles that are finer and more like those in a bottle-fermented sparkling wine than with other in-line carbonation methods. This is questionable. While there may be bubble differences immediately after carbonation conducted using a membrane contactor compared to another in-line carbonator, it seems likely that the bubble dynamics will be the same after CO_2 equilibration in a bottle for weeks or months prior to consumption (unless there is some influence of different N_2 concentrations – see later section). Finer bubbles in high quality Champagne wines are mainly a consequence of these wines having lost CO_2 during ageing (Liger-Belair 2004); bottle-fermented wines may also have higher levels of surface-active chemicals that influence bubble dynamics.

Loss of aromatic compounds is a potential issue occasionally raised in discussions about gas management. Blank and Vidal (2012) demonstrated that there were negligible losses of esters and some other aroma compounds during treatment of a model wine solution with a membrane contactor and verified this

Figure 2. Automated dissolved gas management system using a membrane contactor (K+H)

further using theoretical analysis. This suggests that loss of desirable aroma is unlikely to be an issue when adjusting wine dissolved gas concentrations with a membrane contactor. Some very volatile reductive aroma compounds like hydrogen sulfide may be removed to some extent.

Oxygen levels in wine after processing with membrane contactors can sometimes be quite low. There is anecdotal evidence that if they are used in conjunction with some new bottling lines that achieve very low O_2 pick-up, the low overall O_2 level could lead to reductive characters developing in-bottle for some wines. To counteract this risk, the K+H system has a mode where O_2 can be added to a target level.

Membrane contactors are being used successfully in Europe for dissolved gas adjustment, but as with any relatively new technology, it would be prudent for Australian wine companies to perform side-by-side trials against existing treatment methods to assess the sensory effects prior to adoption.

Automation

Sensors to measure CO_2 and O_2 concentration in the exiting wine are a typical feature of automated membrane contactor systems. They facilitate control to a set-point (e.g. Figure 4). Optical O_2 sensors are relatively cheap but CO_2 sensors can contribute significantly to overall system cost. CO_2 sensors can also sometimes overstate the CO_2 concentrations at low concentrations, depending on the concentrations of residual O_2 and N_2 and whether the sensor compensates for the partial pressures that these gases exert.

If a unit is to be used in a single pass it is important that the CO_2 and O_2 in the wine exiting the system are always at the correct concentration irrespective of fluctuations in ▸

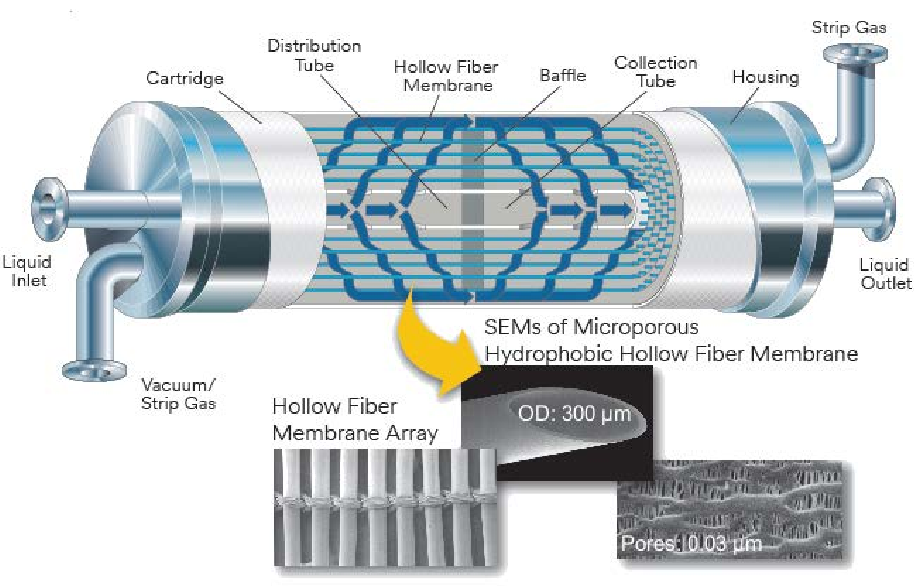

Figure 3. Liqui-Cel membrane contactor module cut-away showing the flow path of liquid/wine (Membrana/3M)

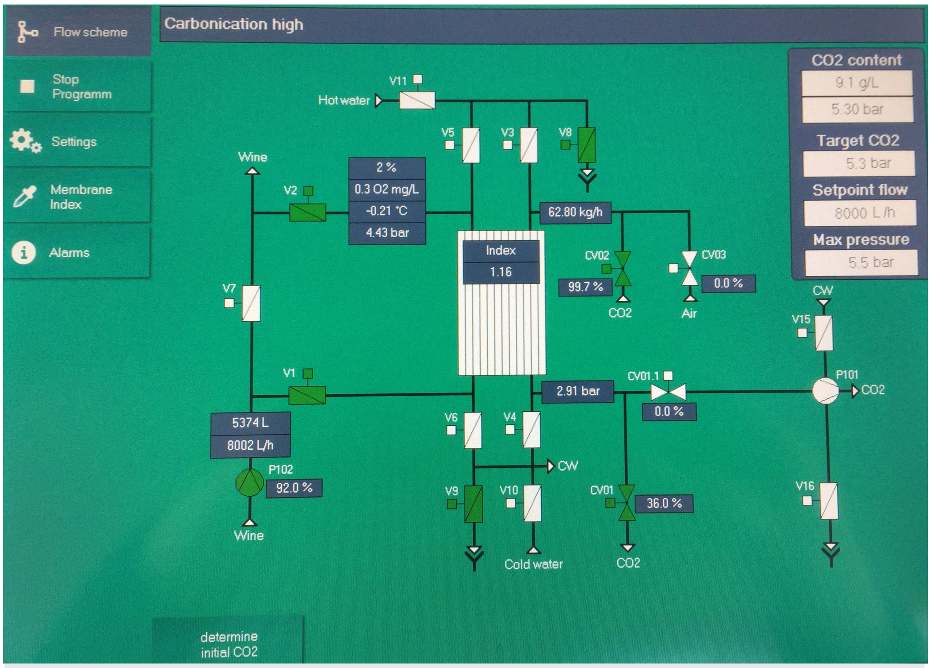

Figure 4. Control screen on a dissolved gas management system (K+H)

wine flow rate, temperature or other conditions, particularly if the system is installed directly on a bottling line. Fast CO_2 sensors are important in this regard. Systems sometimes also employ other control features to manage feed fluctuations. For example, the K+H system employs a mathematical model of gas exchange so that it can adapt to changing feed conditions before the sensors on the wine outlet would detect them.

A common criticism of many traditional carbonators is their poor ability to react to changes in conditions. Membrane contactors with advanced control systems seem to offer an alternative and perhaps lend themselves better to CO_2 sensors because gases are dissolved immediately without bubbles, and they remove N_2 and O_2 that can influence CO_2 sensor accuracy.

Other aspects of some membrane contactor systems are also automated. These include verification of membrane condition, and membrane cleaning, drying and conservation. Flow meters, pressure sensors and temperature probes are amongst the other instrumentation included to automate operation.

It is possible to buy much cheaper membrane contactor systems with less automation, but given some of the complexities of working with membranes manually, this may be a false economy.

Process timing, unit sizing and cost

Wine must be well filtered before it is introduced into a membrane contactor. Pre-filtration to at least 5 µm particle size is the absolute minimum requirement specified by the membrane manufacturer (Membrana/3M 2016), but system suppliers generally specify tighter limits. For example, K+H specifies a minimum pre-filtration requirement of 1 µm . The tight filtration requirements are understandable given that the membrane module consists of an expensive tightly wrapped bundle of 300 µm microporous fibres. The pre-filtration requirements of membrane contactor systems limit when the technology can be used to late in the winemaking/packaging process.

Systems are generally designed to be used in a single-pass (as opposed to during recirculation on a tank). To avoid creating an extra step and to get the most use out of the machine it may be best to place the system in-line with another process, such as on the outlet of a cross-flow filter or on a bottling line. For dedicated packaging facilities receiving wines from off-site, the best place to put a system may be directly on the bottling line as opposed to at the point of tanker off-load. Off-loads are typically performed at higher flow rates than bottling lines, which would require larger systems. Furthermore, facilities may not be certain of the clarity of the wine until after unloading.

Gas management systems should be sized by suppliers based on specific processing requirements (e.g. desired wine flow rates, temperatures, inlet and outlet CO_2 and O_2 concentrations). In Australian trials, it was observed that the K+H unit shown in Figure 2 could carbonate a white wine from 0.95 up to 1.7 g/L (9°C) at >18,700 L/hr and could carbonate a base white wine up to 9.1 g/L (0°C) at 8,000 L/hr but was only able to decarbonate a still red wine from 1.3 to 0.5 g/L (12°C) at 4,000 L/hr. These examples illustrate that if a system is not designed around the required application, it may be over-, or more importantly under-sized. It also suggests that larger systems may generally be required for removal of gases to low levels as might be common in red wine production or in preparation for bag-in-box packaging or bulk flexitank filling.

The cost of a membrane contactor system is dependent on the specific design, but as an indication, the unit shown in Figure 2 was approximately $180,000. A similar capacity unit from another manufacturer was a similar price.

Membrane cleaning and lifespan

There are some restrictions on the chemicals that can be used for cleaning membrane contactors. For example, caustic solutions can be used but some common proprietary cleaning solutions cannot be because they contain additives that would damage the membranes. Solvents and surfactants need to be avoided as they can wet-out the membrane (remove its hydrophobic nature) and oxidising agents like chlorine, hydrogen peroxide and peracetic acid will also shorten membrane life if used too frequently. Water temperature must never exceed 85°C during hot water sanitisation. System suppliers should be consulted for specific cleaning procedures. Guidelines can also be found on the Liqui-Cel website (Membrana/3M 2016). Membrane life will depend on the specifics of use, including cleaning procedures, but a typical lifespan of 3-5 years has been suggested in discussions with suppliers.

Nitrogen, 'fobbing' and bottling line speed

Membrane contactors remove N_2 at the same time as they remove O_2 and add/remove CO_2 (except when N_2 is used as the strip gas, in which case N_2 is added not removed). K+H has suggested that this N_2 removal may reduce 'fobbing' (foaming over) during bottling. It advises that a German customer has been able to increase its average bottling line speed by 10% by installing a membrane contactor system on its vacuum fill line because of reduced fobbing. The customer is bottling large quantities of white wine at 15°C to a specification of 1.5 g/L CO_2 to meet the requirements of a major retailer. Prior to installation of the membrane contactor the company had to add CO_2 in tank to a slightly higher level than 1.5 g/L to counteract losses during bottling and fobbing was experienced (1.5 g/L is close to the solubility limit of CO_2). K+H believes that this is not just due to the bubbleless introduction of CO_2 with membrane contactors but also due to N_2 removal

Nitrogen is mentioned in Australian wine packaging guidelines (WFA 2015) as being one cause of fobbing during filling and the issue is also recognised in soft drink manufacture, where the water used is de-aerated for this and other reasons. Air (N_2 and O_2) provides nucleation sites on which CO_2 bubbles can form (Steen 2006, Molony 2014). N_2 is commonly used in wine production for sparging so it is conceivable that it may be present in wine at reasonably high concentrations relative to its solubility.

For bubbleless CO_2 introduction and/or N_2 removal to have an influence on bottling line speed, fobbing needs to currently be speed limiting. From discussions with a couple of Australian bottlers, it appears that fobbing does not generally limit line speed for nominally still wines, but that it does for semi-sparkling and sparkling wines, so there may be an opportunity for improvement when packaging those wine types. It would be good to independently verify whether these improvements can be realised.

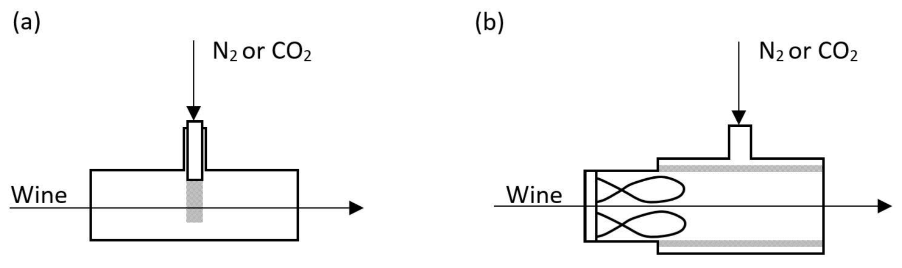

Figure 5. In-line spargers/gas injectors: (a) standard, and (b) with elements to promote turbulence prior to a large surface area sinter tube and gas supply from the outside (simplified concept drawings only - partly based on models sold by W.E. Ware & Co. and WEMS)

From a research perspective, dissolved N_2 is interesting because there does not appear to even be basic data published on typical N_2 concentrations in wine, let alone whether these concentrations can influence bubble dynamics during packaging or consumption.

Comparison with existing sparging/gas injection practices

Introduction of N_2 and CO_2 via sinters is the current method of making small adjustments to O_2 and CO_2 concentration. The sinter surface area is much smaller than with a membrane contactor and the pore size is much higher (typically around 15 μm, compared with 0.03 μm in a membrane contactor). Bubbles of gas are injected and gas exchange occurs at the surface of the bubbles as opposed to in the pores of a membrane.

When wine is sparged with N_2 to remove O_2 and CO_2, the dissolved O_2 and CO_2 diffuse into the N_2 bubbles and leave in the bubbles at the top of the tank. Just as with a membrane contactor, removal of dissolved gases is faster at higher temperatures. Sparging can be performed in-line during transfers and during pumping recirculation of a tank or it can be performed directly in tank via the tank valve or a drop-in sparger. Sparging directly in a tank is easier to set up since no pump and hoses are needed, but it is likely to be slower. The increased agitation that occurs in-line (during transfer or recirculation) tends to create and distribute a larger number of small bubbles with a greater bubble surface area for gas transfer. A typical in-line sparger that costs around $300 is illustrated in Figure 5a. Another in-line sparger design with a larger sinter surface area and elements to create turbulence is illustrated in Figure 5b. Designs like that shown in Figure 5b are more expensive (and therefore not used as often), but still cost less than $1,000 and allow for faster gas adjustment and lower gas consumption (Allen 1991). Wilson (1985) showed that sinter pore size also influences sparging efficiency with 2 μm being more efficient than 15 μm at the same gas flow rate, presumably due to smaller bubbles being released with the 2 μm sinter. However, 15 μm sinters are most commonly used in the wine industry. This may relate to difficulties in achieving sufficient gas flow rate through finer sinters, either due to the size of the pores or clogging of those pores. In support of this theory, staff at one winery noted that they had removed the sinters in many of their sparging fittings altogether because of difficulties in getting enough gas through.

Sinters do have some advantages over membrane contactors for gas adjustment. They are much cheaper to buy and can work with turbid wine. Generally, gas usage with a sinter is higher (Blank and Vidal 2012) and the time to reach the desired level of CO_2 and/or O_2 can be long and/or hard to predict. It can also involve separate steps of injection of N_2 and CO_2 to achieve specifications for both CO_2 and O_2.

Automated sparging/gas injection systems

More sophisticated approaches to using sinters for gas management have also been developed. Around 2012, Parsec introduced a system with an O_2 sensor that is used to control gas injection via a sinter and achieve a set O_2 level. At the end of 2017 it introduced a system with two sinters and both CO_2 and O_2 sensors (Figure 6, CO_2 and O_2 sensors not shown).

These systems can be operated in recirculation mode on a tank or in a single-pass arrangement. For recirculation on a tank, the CO_2 and O_2 and sensors are placed on the wine inlet to the machine. CO_2 and N_2 are injected via the sinters and the system automatically stops once the set-point for the tank has been reached. When the device is used in a single pass, the CO_2 and O_2 sensors are placed on the wine outlet from the machine and these measurements are used to manipulate the injection of CO_2 and N_2.

The obvious question when using a machine like this in a single pass with ▸

Figure 6. Automated dissolved gas management systems using sinters instead of a membrane contactor (Parsec)

O_2 and CO_2 sensors on the outlet only a short distance after injection of bubbles of CO_2 and N_2 is how representative will the dissolved gas concentrations measured at that point be? Will more gas exchange occur after the sensors and will the sensor measurements be influenced by the bubbles? Parsec advises that its system has an auto-compensation mode that takes into account post-sensor gas transfer. It also employs at least 10 m of hose between the two gas injection sinters and in some instances an additional valve to improve dissolution of CO_2 before passing to the second sinter for N_2 injection. The Parsec systems are cheaper than the membrane based contactor system. The single sinter O_2-only adjustment system costs around $40,000 and the two-sinter system that can adjust both CO_2 and O_2 costs approximately $100,000. How well these systems perform in comparison with a membrane contactor based system could only be definitively determined by independent trials.

Conclusions

Automated dissolved gas management systems are new options for the Australian wine industry that potentially offer gains in speed, labour, and gas consumption.

The 2017 Winery Engineering Association National Conference and Exhibition featured the latest membrane filtration technology.

This paper provides a summary based on observations at initial Australian winery trials of one membrane contactor system and from discussions with several suppliers. The Australian industry will no doubt learn more about the technology as equipment is trialled and adopted further. Future trials could further study performance and investigate topics like the influence of removing N_2 on fobbing.

To discuss the technology or share thoughts or experiences please contact Simon Nordestgaard (simon.nordestgaard@awri.com.au, 08 8313 6600).

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Disclaimer

Readers should undertake their own specific investigations before purchasing equipment or making major process changes. This article should not be interpreted as an endorsement of any of the products described. Manufacturers should be consulted on correct operational conditions for their equipment, including cleaning procedures.

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