

2 The use of the membrane contactor in the service of dissolved gases

The role of the MC is the management of the liquid and the gas flow; it makes it possible to control the gas exchange. Reminder, although the gas phase is separated from the liquid phase physically, the transfer of material remains possible. For this, the diffusing species must be mobile in the material that constitutes the membrane. The migration occurs under the effect of a pressure gradient or concentration across the membrane. Adjust the CO₂ concentration while lowering the O₂ concentration. It is possible to dose different gases into liquids and also to dissolve them out again. For example, the concentration of CO₂ can be enriched to impart more freshness to a white wine or just to extract unwanted CO₂ from a red wine. A further application consists of removing O₂ to prevent an early oxidation of the medium.

This process can be used with a buffer tank before the filler, or without a buffer tank and control of the membrane switch by the filler's pump. The flow meter placed on the membrane contactor can meet the demand of the filler.

There are others areas in which CM are used (more performant and economic than other process), in the food industry for soft drinks or beer for example. The fields of action of the CM are deoxygenation/ carbonation of blending water; deoxygenation of water used to brew canned coffee and teas; deoxygenation of water used to reconstitute fruit juices and also concerning beers, O₂ removal from blending water or removal of pushing water, CO₂ control and scrubbing, deoxygenation and nitrogenation of beer. CM is also used to improve the outlet water quality in electrodeionization process, during this process it provides a low maintenance, chemical free and high purity water system.

2.1 Other dissolved gas management techniques

2.1.1 Gas injector

An injector allows the diffusion of liquid products or gas in the musts or in the wines. It allows the carbonation, the decarbonation, the oxygenation of the wines by aspiration of the ambient air and the deoxygenation of the wines. Bubbles of gas are injected and gas exchange occurs at the surface of bubbles as opposed to in the pores of a membrane (Nordeastgaard, 2018).

The gas injector is composed of an injector, and a microporous tube.

Price:454 €HT (<http://www.lasovitec.fr>)

453 €HT with mirror (Air Liquide) and 295 €without mirror



*Figure 18: Gas Injector.
(Lasovitec)*

2.1.2 Carbofresh®

Carbofresh® is a tool for adjusting the CO₂ concentration of wine during transfers (carbonation or decarbonation).

The two main providers are Technica Entwicklungsgesellschaft mbH & Co. KG (Germany) and Michael Paetzold SARL (France).

Carbofresh® :

Product information's from Technica:

- 3 different processors model range (standard, standard to 12.5 m³.h⁻¹ and standard to 30 m³.h⁻¹).
- Maximum CO₂ dosage: 1.8 g.L⁻¹
- Maximum flow performance: 2000 L.h⁻¹, 12500 L.h⁻¹ and 30000 L.h⁻¹
- P_{max}: 7 bar



Figure 19: Carbofresh® (Technica)

Carbofresh® deluxe:

Product information's from Technica:

- Flow rate capacity: 1.000 - 10.000 L/h
- CO₂ dosing : 0 – 11 g/L
- Required pump pressure: at least 5 bar
- P_{max} : 10 bar



Figure 20: Carbofresh® deluxe (Technica)

<http://www.technica-gmbh.de>

2.1.3 EVO1000 Parsec

EVO1000 is a process from Parsec manufactory (Italy) used to deoxygenation, carbonation and decarbonation of wine.

- Adjustment and enrichment of CO₂: 0.1 - 9 g.L⁻¹
- By introduction of gas under pressure: up to 7 g.L⁻¹
- Used 70% for its application of deoxygenation of musts and wine. Removes in a single pass up to 6 mg.L⁻¹
- Single sinter O₂ only adjustment system: 40,000 \$
- Two-sinter system that can adjust both CO₂ and O₂: 100000 \$.



Figure 21: EVO1000 (Parsec)

The processes have evolved over the years, in 2017, 2 sinters are added and also two sensors one for CO₂ and the second for O₂. Two modes are possible, either in recirculation or on a single-pass arrangement (Nordeastgaard, 2018)

In recirculation mode: sensors are placed at the entrance of the wine circuit, the CO₂ and / or N₂ gases are added by sinters and the system automatically stops when the set point has been reached.

In single pass mode: the CO₂ and O₂ sensors are placed at the wine outlet, the measurements are used to adjust the gas injection. (Nordeastgaard, 2018)

<https://www.parsec.com>

2.1.4 DEOS®

DEOS® is a device from Michael Paetzold SARL (France). Device capable of deoxygenation, oxygenation, carbonation and decarbonation wine in vats.

- It allows a precise add of $5 \mu\text{g.L}^{-1}$ to $60 \mu\text{g.L}^{-1}$,
- Carbonation until 100mg.L^{-1} in vats

Decarbonation until 400mg.L^{-1} in vats



*Figure 22: DEOS®
(Paetzold)*

<http://michaelpaetzold.com>

2.2 Alimentary of the membrane

Membrana (USA) is the leader on the market of hollow hydrophobic membrane for use in MC. According to the document provided by the company, the “FDA Compliance Summary of Liqui-Cel® Membrane Contactor” (Annex 1), the principle component of the membrane is the polypropylene.

The treatment of dissolved gases in wines by MC is admitted by the OIV since December 3rd 2013 (Commission implementing regulation (EU) No 1251/2013), and one of the requirement for is: “The membranes used must comply with the requirements of Regulation (EC) N° 1935/2004 and Regulation (EC) No 10/2011 and with the national provisions adopted for the implementation thereof. They must comply with the requirements of the International Oenological Codex published by the OIV”. So the treatment is admitted by the OIV and authorized by the EU since January 14th 2011 (N°10/2011).

Concerning the membrane, it is not yet defined in the International Oenological Codex according to the 2017 edition and has not yet been approved by the EU. For now it has only the US FDA food approval and the only official document is the EU food contact declaration (Annex 2) which states that all responsibility for the use of the Liqui-Cel membranes rests on the end user, this person to check and prove the dietary neutrality of the membrane.

Module Liqui-Cel® composition:

- Potting of fibers: epoxy resin (Ho & Sirkar, 1992).
- Seal: K-UPW, Viton® (rubber quality, copolymer of fluorovinilidene and exafluoropropylene, appropriate to French and foreign food standards (Jeantet Elastomères)) or K-EXT.
- Casing: polypropylene, Teflon

2.3 Operation Modes for Wine: CO₂ and O₂ Adjustment

The membrane contactor can be used under different operation conditions; five different modes are established, Vacuum mode, Combo mode, Carbonation mode, Strip CO₂ mode and Strip N₂ mode; which are explained in detail within the following section (Sengupta et al., 1998; Vidal, Vidal Vila, & Waidelich, 2011).

2.3.1.1 VACUUM Mode

This mode (Figure 23) is used to reduce all the gases (CO₂ and O₂) in the same time by introducing a low absolute pressure in the lumen side. The reduction rate of dissolved gases is dependent of the depression reached and the liquid flow. To obtain the best wine degassing, the depression should be the highest one. The degassing depends on the gas solubility, so the gases are partially reduced according their partial pressure in function of the concentration. Blank and Vidal (2013), have demonstrated the efficiency of the degassing with the vacuum mode. At low liquid flow, the elimination of both gases is better. The vacuum pump removes the gas molecules continuously and thereby a stream is created that strips CO₂ and O₂ from wine. To readjust the CO₂, a second passage is needed using a constant flow CO₂ at a slight overpressure in the lumen side.

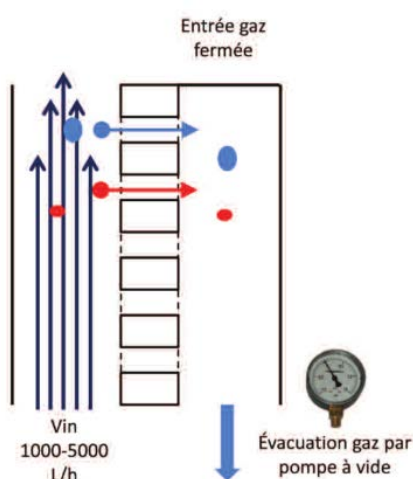


Figure 23: Schema of the Vacuum mode (Blank & Vidal, 2013)

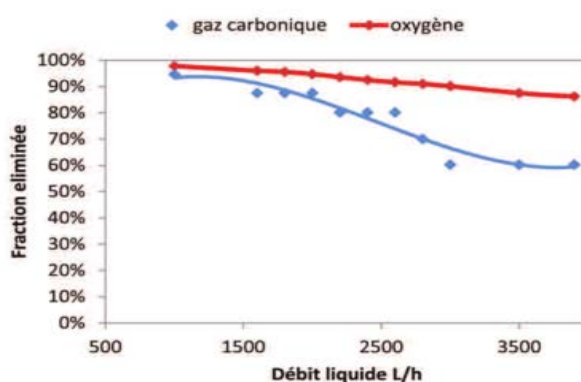


Figure 24: Decarbinication and desoxygenation in vacuum mode according to the liquid flow (Blank & Vidal, 2013)

Also Leiknes and Semmens 2001 studied the use of hollow fibers for a vacuum degassing of aqueous liquids. They derived the following conclusions:

- The mass transfer appears to be controlled by the resistance in the liquid phase. This assumption is verified by many other authors (Gabelman & Hwang, 1999; Mavroudi et al., 2006; Shirazian et al., 2009),
- The driving force is the partial gradient pressure from the liquid to the average partial pressure in the gas.
- The liquid phase boundary layer resistance is determined by the Reynolds number and the liquid properties.
- At Reynolds numbers below 2500 – 3000 the degassing is controlled by the mass transfer, at higher Reynolds numbers the flow inside the fiber lumen, meaning the gas phase resistance is the limiting factor.

All these assumptions and findings are in accordance with the previously mentioned concept of resistances in series for mass transfer in membrane contactors.

Vacuum mode is one of the more efficient to delete the both principals dissolved gases.

2.3.1.2 CARBONATION Mode

This mode is used to increase dissolve CO₂ concentration of wine, for that the gas exit is closed (Figure 25). CO₂ is injected under pressure into the wine, and to have good results, the liquid need to be in slight pressure. The important thing is the gas and liquid regulation pressure in a way to injected CO₂ that dissolves completely into the wine during passage through the membrane.

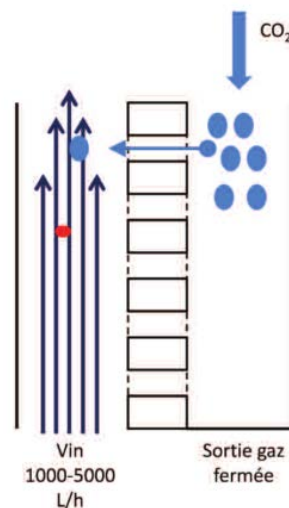


Figure 25: Schema of the Carbonation mode (Blank & Vidal, 2013)

At the beginning of the process it takes some time till the gas phase equilibrium is adjusted on the lumen. During this time the other gases diffuse according to their partial pressure gradient inside or outside the liquid. Steady state is reached when the partial pressures on the lumen side are equal those on the shell side at inlet and outlet. In this situation there is neither oxygen uptake nor stripping. A full saturation of carbon dioxide can be reached. If the input of the gas is bigger than what can be transferred to the liquid the

pressure on the gas side increases, thereby the partial pressure on the lumen side increases and more gas is transferred. The problem is that the gas cannot be dissolved in the liquid. This means, that gas bubbles are created and the gas is lost on the liquid side.

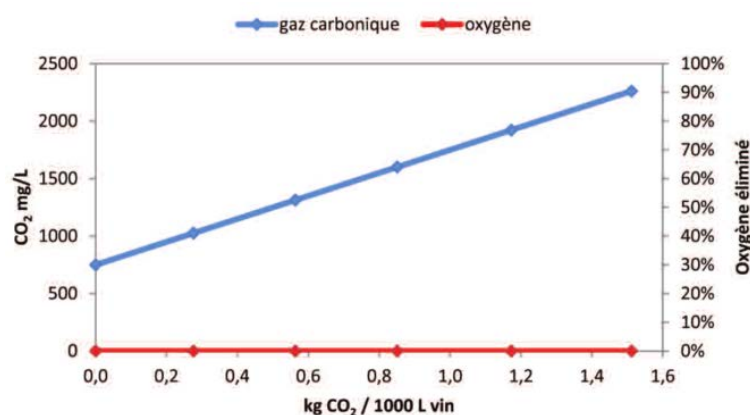


Figure 26: Enrichment of CO₂ and desoxygenation by Carbonication mode (Blank & Vidal, 2013)

The process can be controlled by simple visual observation. If bubbles are visible, the liquid pressure should be increased until bubbles disappearance. To increase gas solubility a counter pressure on the liquid side can also be applied. A decrease of the liquid pressure during the filtration or the bottling, could lead CO₂ desorption and foam apparition in the wine. According to Blank and Vidal 2013, it is easy to master the adjustment of CO₂, more gas is sending to the membrane, more will be dissolve in the wine.

This mode is reserved for high carbonation, because it presents as major disadvantage to not reduce the others gas like oxygen or azote.

2.3.1.3 STRIP CO₂ Mode

This mode is also used like carbonation mode to increase CO₂ content; but the difference between them is that in this mode the gas out is open and so in air contact. According the high affinity and solubility of CO₂ the gas passes through the membrane and is directly dissolved in the wine in function of flow rate, temperature, delta of gas pressure and gas flow rate while oxygen and azote can diffuse through the membrane in the opposite direction as wine towards the vector gas.

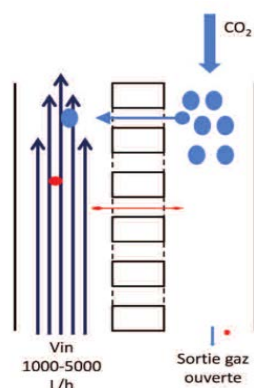


Figure 27: Schema of the Strip CO₂ mode (Blank & Vidal, 2013)

In this mode, the partial pressure of oxygen in the lumen side is practically zero at the entry of the gas, so the oxygen is stripped out of the wine. O_2 and N_2 are evacuated towards the out by an excess of CO_2 which does not dissolved in the wine. The carbon dioxide reacts exactly opposite to this, an excess partial pressure in the lumen side is applied, hence the partial pressures of liquid and gas equalize, meaning that CO_2 is added into the wine.

CO_2 diffuse into the wine until his maximal solubility is reached; so the enrichment in dissolve gas of wine is limited by the maximal solubility like Blank and Vidal 2013 shown in Figure 28.

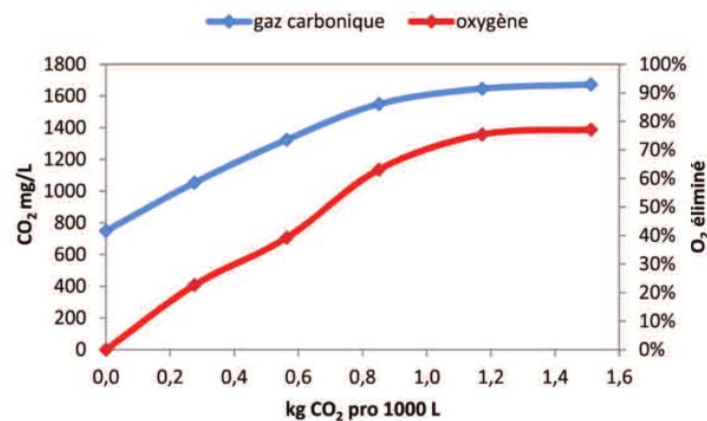


Figure 28: Enrichment CO_2 and desoxygenation by strip CO_2 mode at 12 °C (Blank & Vidal, 2013)

Conversely to what was stated for the Carbonation mode, the Strip mode can carbonate and deoxygenate at the same time. Herein the maximum possible CO_2 level is the solubility of CO_2 in the liquid at the applied pressure. For wine at 20 °C with 12 %vol this solubility is around 1400 mg.L⁻¹.

So the strip CO_2 mode is a good choice to increase it until its maximal solubility, but to obtain the best oxygen elimination, the CO_2 amount that flow in the lumen side should be superior to the quantity to be dissolved.

2.3.1.4 Strip N_2 Mode

This mode is used to reduce simultaneously O_2 and CO_2 ; here nitrogen is the vector gas. As shown in the Figure 29, the gas out stays open, nitrogen flow circulates in the lumen side and drives CO_2 and O_2 that diffuse through the membrane from wine to the lumen side while the N_2 circulates in the opposite way but in small quantities because it is sparingly soluble.

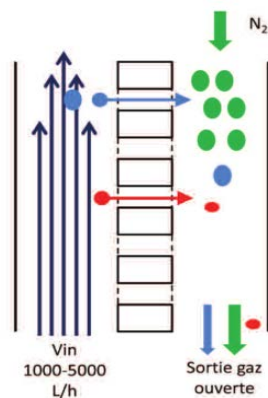


Figure 29: Schema of the Strip N₂ mode (Blank & Vidal, 2013)

The reduction of CO₂ is dependent on the flow rate of nitrogen applied in the lumen side. The dissolved CO₂ content decreases when the nitrogen flow rate is increased. According to the study of Blank and Vidal 2013 at the ratio of 0,1 kg N₂ for 1000 L of wine, the dissolved oxygen content is reduced to 80 % while for a 50 % dissolved CO₂ removal, 0.5 kg of N₂ for 1000 L of wine.(Figure 30)

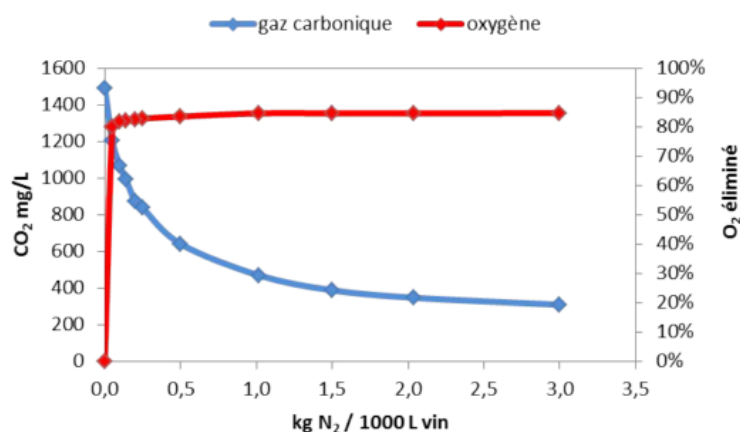


Figure 30: Decarbonation and desoxygenation in Strip N₂ mode (Blank & Vidal, 2013)

In comparison with other techniques, fashion to one advantage is that it does not foam the wines because the gases are separated from the liquid and removed through the membrane.

2.3.1.5 COMBO Mode

The combo mode is a combination of to the strip CO₂ and vacuum mode. Here the vector gas is the CO₂ (Figure 31) and an additional vacuum is applied to reduce the total pressure inside hollow fibers. The aim of this mode is to adjust the carbon dioxide content and at the same time to remove oxygen from the wine.

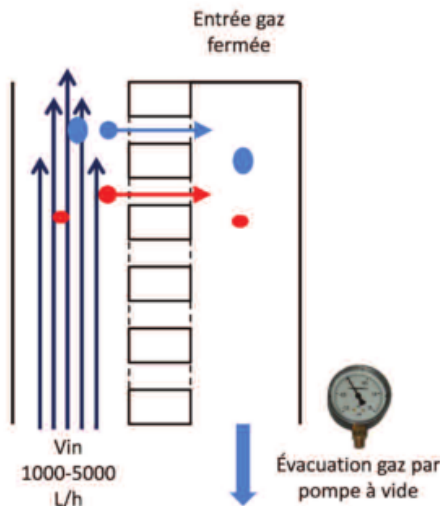


Figure 31: Schema of the Combo mode (Blank & Vidal, 2013)

This mode is usually applied to most efficiently remove oxygen from a wine without using a very high flow of strip gas. The work of Tarafder et al. (2007) is describing reasons for a better transfer efficiency in this mode. Explaining this was done by calculating the ratio between liquid flow and gas flow. It is important in this case to calculate the gas flow in the same unit than the liquid flow, which means in $\text{m}^3 \cdot \text{s}^{-1}$ or $\text{L} \cdot \text{h}^{-1}$ to create the dimensionless ratio for gas flow to liquid flow (L/L). As the law of ideal gases states the volume flow is inversely proportional to the ambient pressure using constant mass flow. By decreasing the pressure by 50 % the volumetric gas flow increases doubles. Tarafder et al. (2007) showed clearly how the transfer coefficients increased using vacuum. They concluded that absolute values of gas flow and pressure did not have a significant influence, just the absolute concentrations of the compounds in the gas and liquid phase. They were using the same type of membrane than in our study just with an active membrane surface of 1.4 m^2 and not 20 m^2 . They did not observe negative effects of using vacuum. Furthermore, in their study, the group did not find an impact of the polarity of the molecule that is stripped.

Vidal et al. (2011) work showed (Figure 32) that according the high affinity and solubility of CO_2 the gas is directly dissolved or decreases in the wine in function of the wine flow rate, the temperature, the delta of gas pressure and gas flow rate. During operation the oxygen is reduced efficiently and irrespective of the target value of dissolved CO_2 . Blank and Vidal (2013) explained in their works that a deliberately excess gas flow will not pass through the membrane but will allow the efficient removal of oxygen. The solubility of CO_2 in wine depends on the vacuum and pressure of the carrier gas, more the vacuum will be intense and lower the pressure of the carrier gas, lower will be the CO_2 solubility in the wine. The vector gas pressure is determined according to the temperature.

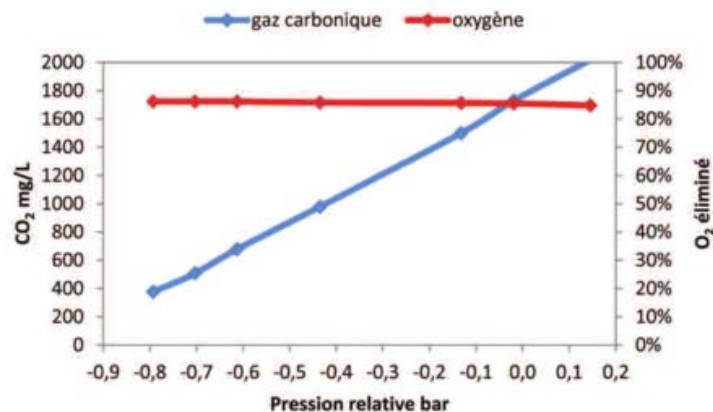


Figure 32: Evolution of the CO₂ content and desoxygenation in Combo CO₂ mode (Blank & Vidal, 2013)

Because of the simultaneous adjustment of the CO₂ and O₂ contents, it is possible to substantially reduce the consumption of inert gas.

2.3.1.6 Comparison of the different mode

Vidal et al. (2011) have firstly concluded the efficiency of the usefulness of membrane contactor and then that the most effective mode is the combo one, that was approved by Waidelich and Vidal (2014). This mode of oxygen and nitrogen reduction with simultaneously adjustment of CO₂ is the most efficient mode for the oxygen removal caused by the sweep effect of the CO₂. No nitrogen is needed and the CO₂ consumption is lower. The tests in different sites have shown that the efficiency in oxygen removal is higher than only degassing with vacuum, which means in addition, it is also much more efficient like with nitrogen diffusion Vidal et al. (2011). In this case even wines with very high concentrations of dissolved oxygen can be easily brought down in-line to vales underneath 0.5 mg.L⁻¹ just before the bottling.

The work of Blank and Vidal (2013), allowed to differentiate the different operating procedures using the same wine, containing 6.1 mg.L⁻¹ of oxygen and 800 mg.L⁻¹ of carbon dioxide so as to compare them at best on the level of dissolved CO₂ and O₂ obtained with the different procedures.

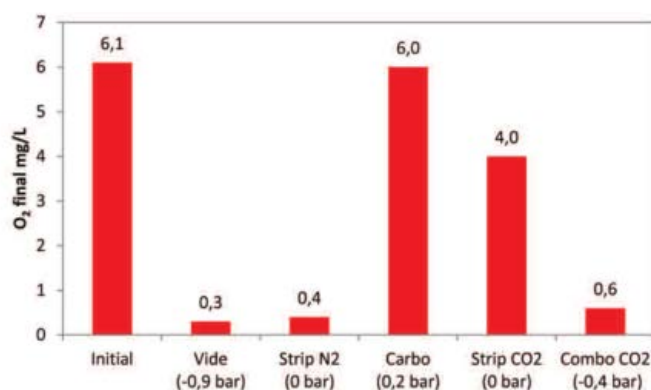


Figure 33: Different operating modes impact on the dissolve oxygen content (Blank & Vidal, 2013)

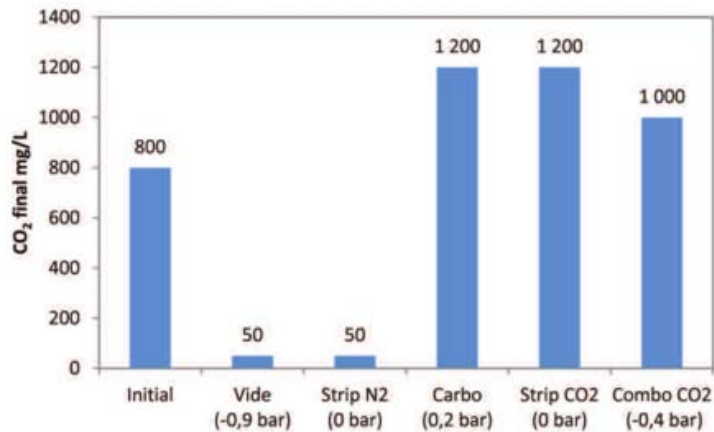


Figure 34: Different operating modes impact on the dissolve carbonic gas content (Blank & Vidal, 2013)

On these Figure 33 and Figure 34, it can be clearly seen that the most efficient modes for removing the two main dissolved gases are the Vacuum and the Strip N₂ mode. The Carbo mode does not remove O₂ from the wine but it permits to increase effectively the dissolve CO₂ content. The Strip CO₂ permits efficiency wine carbonation but the O₂ reduction is not enough. With the combo mode the carbonation is not as efficiency than the Carbo and Strip CO₂ mode but it is efficiency for the oxygen reduction.

In oenology, the objectives to be achieved are at the output of the membrane contactor an O₂ concentration between 0.1 and 0.5 mg.L⁻¹ and a CO₂ concentration between 300 and 1500 mg.L⁻¹.

2.4 Results and State of Market

2.4.1 Comparison of Membrane Contactor and Porous Injector

2.4.1.1 Materials and Methods

The WineBrane pilot from Inoxpa Industry was compared to a porous injector (Blank and Vidal 2012). The objective of this trial is to achieve a comparison of methods between the membrane contactor and the traditional method by porous injector.

The membrane surface is a 20 m² liquid-Cel® membrane contactor, the liquid flow can be controlled from 1000-4000 L.h⁻¹. The porous injector is 55 mm long, and 17 mm diameter with 5 µm pores installed in a DN40 housing. The liquid flow was controlled to 4000 L.h⁻¹.

The comparison of the WineBrane with the Porous injector was performed on industrial scale. A rosé wine was treated before filling in bag in box. The goal was set to keep the carbon dioxide at 800 mg.L⁻¹ while reducing oxygen below at 0.5 mg.L⁻¹. This objective was set by sensorial experience with the type of rosé wine. For the comparison, the WineBrane was operated in Combo mode, as this mode is the most suitable for the desired objective according to (Vidal et al., 2011). The porous injector needs two runs for the desired treatment: a first run with nitrogen to reduce the oxygen content and a second run with carbon dioxide to readjust CO₂.

Table 15: Initial conditions gas consumption study (Blank, 2010)

General Conditions			
T _{air} [°C-K]		27 – 303	
T _{wine} [°C-K]		27 – 303	
Wine		Rosé IGP Cité de Carcassonne	
Alcohol		12.5 %vol	
[O ₂] ⁱⁿ [mg.L ⁻¹]		0.68	
[CO ₂] ⁱⁿ [mg.L ⁻¹]		800	
Liquid flow rate [L.h ⁻¹]		4000	
Porous Injector Operation		WineBrane Operation	
Run 1		Gas	CO ₂
Gas	N ₂	Pressure [kPa]	60
Gas Flow [L.h ⁻¹]	913	Gas Flow [L.h ⁻¹]	350
Run 2			
Gas	CO ₂		
Gas Flow [L.h ⁻¹]	809		

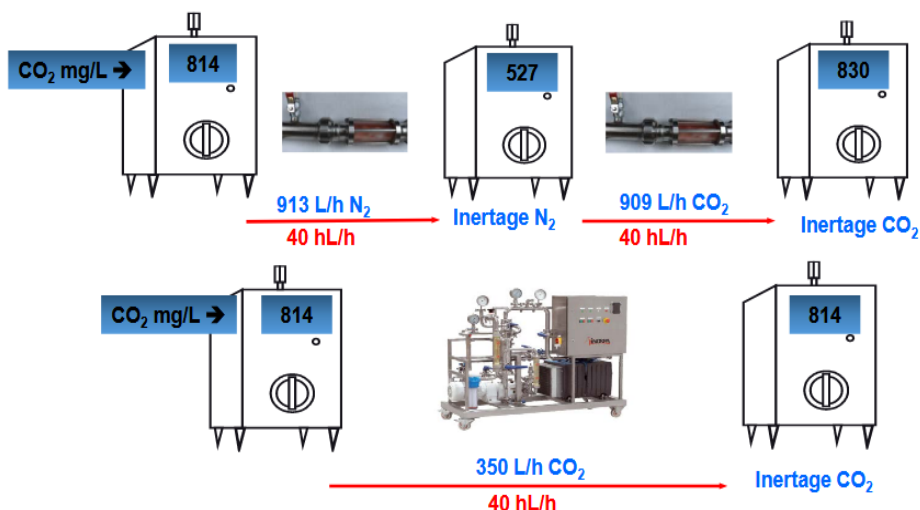


Figure 35: Flow schema of the porous injector and the WineBrane processes

2.4.1.2 **Results**

Table 16: Results of porous injector and WineBrane processes

Treatment by porous injector	Start (Tank 1)	After first transfer (Tank 2)	End after second transfer (Tank 3)	Difference Start/End
Dissolved O ₂ [mg.L ⁻¹]	0.68	0.18	0.38	-44%
Dissolved CO ₂ [mg.L ⁻¹]	814	527	830	1.9%
Ethanol [%vol]	12.59	12.57	12.56	-0.2%
Treatment by membrane process	Start (Tank 1)	After WineBrane	End (Tank 2)	Difference Start/End
Dissolved O ₂ [mg.L ⁻¹]	0.68	0.35	0.40	-41%
Dissolved CO ₂ [mg.L ⁻¹]	814		814	0%
Ethanol [%vol]	12.58		12.52	-0.6%

The different analyzes on esters and alcohols showed that there were no significant losses. The ethanol content hasn't changed too.

The major difference between the two processes is the quantity of gas used. (Table 17)

Table 17: Gas consumption comparison of porous injector and WineBrane per operation and per 50 hL (Blank, 2010)

	Porous Injector		Winebrane	
	Per operation	Per 50 hL	Per operation	Per 50 hL
Inertation Tank	260 L N ₂	260 L N ₂	260 L CO ₂	260 L CO ₂
Transfer Gas	0.23 L/L N ₂	1140L/L N ₂	0.09 L/L CO ₂	450 L/L CO ₂
Inertation Tank	260 L CO ₂	260 L CO ₂	-	-
Transfer Gas	0.20 L/L CO ₂	1000 L/L CO ₂	-	-
Total gas consumption	2660 L		710 L	

The total gas consumption was 2660 L for the porous injector trial and 710 L for the WineBrane process. In the WineBrane trial a similar effect and result is observed using only 27% of the gas and only one transfer is need.

Main points from this series:

- The WineBrane can achieve a deoxygenation while preserving the carbon dioxide content at a desired level in one passage.
- With porous injector the goal of efficient oxygen removal and precise CO₂ adjustment can be reached, but two passages and a 4 times high gas consumption is necessary.
- No analytical significant aroma compound losses could be observed in both variants.

In this trial it could be shown, that a carefully controlled injector using two passages can have a similar use in gas adjustment than the WineBrane. Nevertheless the gas use is more efficient with the WineBrane. Furthermore, no bubbles are created during a WineBrane treatment, hence it can be operated directly serving the bottling line. Using an injector requires minimum 20 m of pipe for a good contact and a buffer tank for the release of the undissolved gas bubbles (Blank & Vidal, 2012).

The membrane contactor is also more economic than the gas injector. The cost is about 1.50 €/hL with a manual CM, 1.25 €/hL with an automated CM, and 2.00 €/hL with a gas injector. This includes CO₂ and N₂ consummation, the heating, cooling, labor and washing tanks and pipes.

2.4.2 Non-exhaustive list of manufacturers

2.4.2.1 Ymélia (www.ymelia.com)

Ymélia is a French wine engineering company, based in Languedoc and specialized in the processing of wine and its preparation for packaging.

Their 3 major axes in the processing of wine and its preparation for packaging are:

- Filtration: tangential filtration, filter pallet,
- Management of dissolved gases in wine: CO₂, O₂, N₂.
- The dosage of the inputs: SO₂, arabic gum, MCR.

Ymélia is the only French supplier.

Pervelys process **Erreur ! Source du renvoi introuvable.** (Réussir Vigne 2017, n°237, p22):

- Membrane surface : 20, 130 and 260 m²
- Maximal flow : 2500, 10000 and 20000 L.h⁻¹
- Flow : 50 / 100 hL.h⁻¹

Still wine :

- O₂ adjustment: reduction of 80 – 99%
- CO₂ adjustment: 0.3 – 2.5 g.L⁻¹

Sparkling wine :

- O₂ adjustment: reduction of 60 – 95%
- CO₂ adjustment: 2.5 – 10 g.L⁻¹



Figure 36: Pervelys process by Ymelia

First price : 125000 €

Known customers: Perrin (Côtes du Rhône); Legras D. contract bottling (Occitanie).

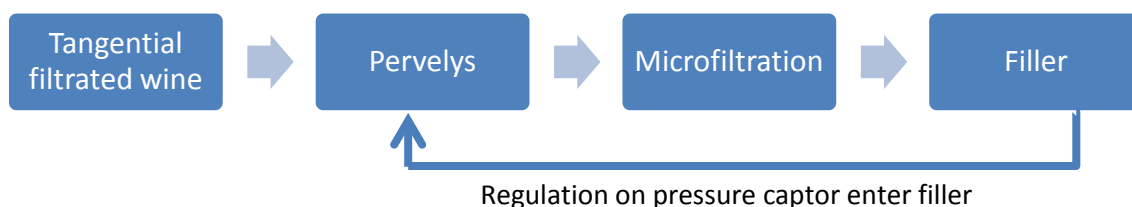


Figure 37: Example of Pervelys integration in a process line

2.4.2.2 Agrovin (www.agrovin.com)

Agrovin (Spain) manufactures, processes, distributes and sells a wide range of products from raw materials to industrial machinery.

Oxy Out processes

- 97% of the dissolved O₂ can be extracted depending on the procedure and the flow rate.
- Eliminate gases of low molecular weight (CO₂, O₂, N₂)
- Controlled by a PC, to select and edit with the possibility of controlling various parameters (dissolved oxygen, dissolved CO₂, temperature, pressure, flow, etc.).

This unit uses Venturi system to make the vacuum; the choice of Venturi system is depending on the desired vacuum. Oxy_Out was tested and evaluated in 2009 by the INRA UEPR.



Figure 38: Oxy_Out process (Agrovin)

2.4.2.3 Kunzmann & Hartmann (www.kh-armaturen.de)

K&H (Germany) produces stainless steel products at 3 production sites today and are a renowned supplier for the drinks, food, pharmaceutical, cosmetic and chemical industries. The worldwide N°1 seller of CO₂ membrane system.

CO₂ membrane system:

- Max product flow 5.000 L.h⁻¹ until 350 hL.h⁻¹
- Max. CO₂ dosing 7 kg.h⁻¹ until 140 kg.h⁻¹
- Membrane surface 20 m² until 2*140 m²
- CO₂ adjustment 0 – 9 g.L⁻¹
- O₂ adjustment 0.5 -10 mg.L⁻¹
- O₂ removal 50 to 99 %
- Around 180000 \$ for the unit shown in (Nordeastgaard, 2018)



Figure 39: CO₂ membrane system (K & H).

Some examples observed (Nordeastgaard, 2018):

- Carbonation on a white wine at 9°C from 0.95 g.L⁻¹ up to 1.7 g.L⁻¹ at a flowmeter > 18700 L.h⁻¹
- Carbonation of a base white wine up to 9.1 g.L⁻¹ at 0°C and 8000L.h⁻¹
- Decarbonation of a still red wine from 1.3 to 0.5 g.L⁻¹ at 4000L.h⁻¹

2.4.2.4 InWag (www.inwag.de)

InWag (Germany) is a service provider for the development of beverage technology equipment, cellar technology, liquid food processing, as well as design of wine cellar equipment and complete wine cellars. OenoMem system uses a precise gas management and alcohol reduction in wine and non-alcoholic beverages.



a)



b)

Figure 40: a experimental pilot, b industrial skid.

OenoMem system

- O₂: < 0.5 mg.L⁻¹
- Reduction of 20 % of the initial alcohol content
- Flow: 10 to 400 hL.h⁻¹
- 3 different sizes: 50 hL.h⁻¹, 100 hL.h⁻¹ and 400 hL.h⁻¹

Price in 2013 for a membrane contactor of 8 m²: 41000 €HT (Figure 40 b)

2.4.2.5 Romfil (www.romfil.com)

Romfil is a German company.

Romfil Gas Contactor (**Erreur ! Source du renvoi introuvable.**):

- Flow rate: up to 70 hL.h⁻¹
- LxWxH: 450 mm x 450 mm x 1630 mm
- Weight: 28 kg
- P_{max}: 7 bar



Figure 41: Romfil Gas Contactor

2.4.2.6 Emrich Edelstahlbau (www.emrich-edelstahlbau.de)

Emrich Edelstahlbau (Germany) proposes a CO₂ management pilot named “Winegas”.



Figure 42: Winegas process from Emrich-Edelstahlbau

3 Others applications of membrane contactor in oenology

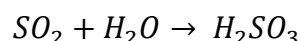
3.1 Some generalities on sulfur dioxide (SO₂) and quantification of it by a membrane contactor technology

The addition of SO₂ is done from the delivery of harvest until the filling tank. It is for its various oenological properties that it is added, it plays the role of protector to the oxidation by antioxidant actions (it traps the oxygen), and anti-oxidase (it inhibits the phenols oxidases); also to germs of alterations such as molds, bacteria, as antiseptic. It also plays a selective role on the yeast population when it is added to the must.

SO₂ has many advantages, however it has a negative point, it is its toxicity. The SO₂ being perceptible by the man from 1 ppm, one can estimate that it already has toxic effects as soon as it is perceived by the user. It can be at the origin of unpleasant tastes and smells of reductions (SO₂, H₂S ...). It is therefore important to master the amount of SO₂ to be added in order to properly protect the wine but while preserving the organoleptic qualities of the product and also the health of the consumer (Bonder, 2014). The challenge for the wine maker is to limit the final sulfite content of these wines as much as possible, while avoiding the risk of a drop in organoleptic quality: oxidation, acescence, Brettanomyces growth.

3.1.1 Generalities on SO₂ in must

SO₂ is added during all the vinification process in the form of sodium met-bisulfite Na₂S₂O₅ in powder form or in the form of an aqueous solution of potassium met-bisulfite K₂S₂O₅ concentrated to 8% (P8) or 18% (P18), or in the form of dioxide of gaseous sulfur. In aqueous solution, the sulfur dioxide forms sulfurous acid according to the following reaction:



SO₂ exists and is present in different chemical forms in wine, HSO₃⁻ bisulfite ions and the SO₂ molecular form known as active SO₂. These two forms constitute the free SO₂ which brings the protective role of wine against microorganisms, oxygen and oxidases.

A part of the bisulfite ions react with certain compounds of the wine (compounds carrying carbonyl functions) and combine. The combined SO₂ has no protective effect because its S-function is mainly involved in a bond, or with ethanal in wines (ITV, 2002) (Figure 43).

All the products formed make up the combined SO₂, and the combination of these two groups constitutes the total SO₂.

$$SO_{2Total} = SO_{2free} + SO_{2combined}$$

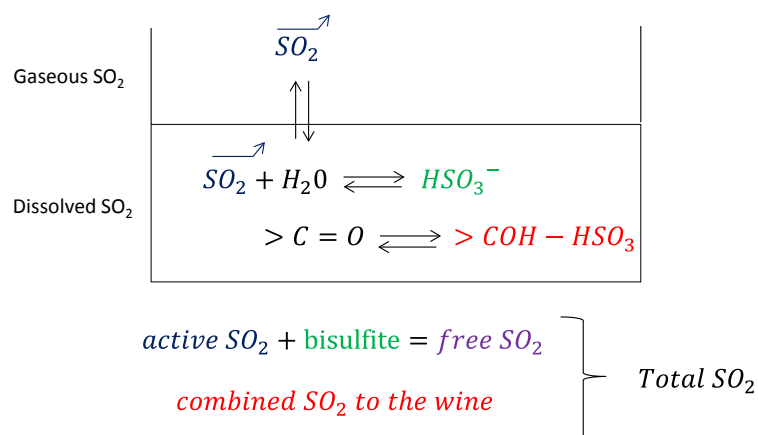


Figure 43: The different fractions of sulfur dioxide in wines.

When wine making and ageing are completed, the wine is sulfited just before bottling in such a way that the total SO₂ regulatory concentration complies with European legislation (less than 200 mg/L of total SO₂ for white wines), and that there is at least 30 mg/L of free SO₂. This ensures, for the conditioned wine, protection for a sufficient time against the chemical oxidation due to the oxygen which diffuses inexorably through the cap, the stopper of the bottle or the film of bag in box.

3.1.2 Extraction and quantification of SO₂ content in wines using a hollow fiber contactor

Currently, there are several instrumental methodologies available for the determination of sulfites such as pervaporation flow injection, capillary electrophoresis, enzymatic, electrochemical and conductimetric techniques. But these methods require an important material and instrumentation. There are also the Ripper method, Monier-Williams method and the aeration oxidation methods. Plaza et al. (2014) have decided to work on a new method for the quantification of free and total sulfite content in wines and other liquid foods using a membrane contactor. This method is used to extract and recover the sulfite content in a receiving NaOH solution which can be analyzed by different techniques.

They worked on the extraction of SO₂ from an acidified wine using a porous hydrophobic membrane. SO₂ is desorbed from the wine and transferred through the gas gap that fills the membrane pores and finally absorbed in a diluted NaOH solution in order to quantify the concentration of SO₃²⁻ (Figure 44). To defined the operational conditions they used a previous work from Schultes (1998).

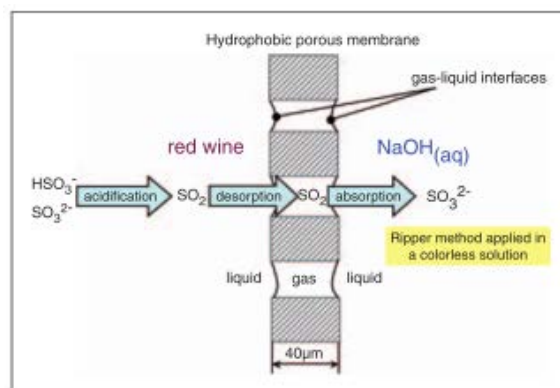


Figure 44: Principle of the membrane process applied to extract the sulfite content from an aqueous solution (Plaza et al., 2014)

This method permits to quantify the sulfite content in wines. It is a technique that can be applicable when the use of conventional methods would be difficult to implement. This method has shown that reliable results on the concentration of free SO_2 and total SO_2 can be obtained. The results of this technique were compared to the conventional methods of analysis, and no significant difference was observed.

The use of a membrane contactor allows a fast and well controlled transfer of SO_2 from the wine to a receiving solution without using any additional chemicals, unlike other methods of analysis. However this remains an experimental study, which requires improvements, and optimizations of parameters, operating variables, such as wine flow, volume of NaOH and H_2SO_4 to be added in the wine.

3.2 De-alcoholization of wine by membrane contactor

Semi-permeable membranes by which alcohol can be separated from fermented beverages have been studied and available since the 70's. In the 80's, several studies were carried out on partial or total removal of alcohol from wines.

Nowadays, various technologies in which a membrane is used for the selective removal of ethanol from beverages have been developed. The most widespread technology for the removal of ethanol from wines is reverse osmosis based on the selective separation of water and alcohol from the wine. But from several years some people are interested by the new method, the osmotic distillation by membrane contactor (El Rayess & Mietton-Peuchot, 2015).

3.2.1 Operation Modes of Osmotic Distillation Process

For wine de-alcoholization, ethanol is selectively removed from wine. The transport mechanism of ethanol in de-alcoholization by osmotic distillation process can be divided into three steps:

- 1) evaporation of ethanol at the membrane pores on the feed side,
- 2) diffusion of ethanol vapor through the membrane pores (Figure 43),

- 3) condensation of ethanol vapor in the stripping solution at the membrane pore exit (Varavuth, Jiratananon, & Atcharyawut, 2009)

Because the vapor pressures of water over the wine and over the strip solution are nearly identical, there is virtually no traffic of water from the strip into the wine.

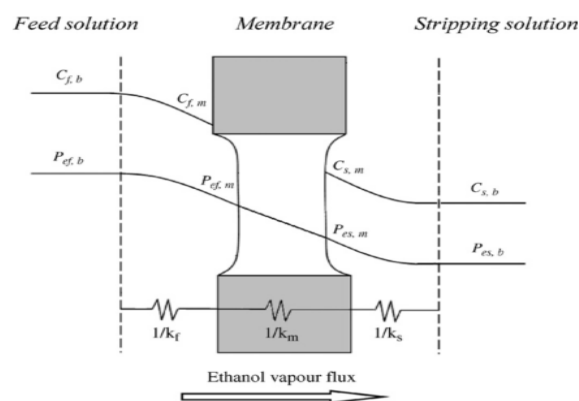


Figure 45: Concentration profile of ethanol in dealcoholization process by osmotic distillation (Varavuth et al., 2009)

The partial pressure difference of the volatile components, in our case it is ethanol, between both phases creates the driving force of the process.

The main advantages of the technology are:

- 1) process can be conducted at room temperature,
- 2) low energy consumption (no pressurization of the system is required),
- 3) cheap and non-hazardous extractor, water, is normally used as stripping phase.

3.2.2 Effect on sensory characteristics

Several studies were done on the subject. Diban et al. (2008) showed that a partial dealcoholization reduction of 2 %v/v of the Merlot wine gave acceptable flavor losses without a perceptible reduction in the quality of the product. They concluded that it is a process that achieves an alcohol reduction of 2 %v/v, without a perceptible decrease in product quality, results also approved few years later by Gambuti et al. (2011).

Diban et al. (2013) deepened the subject, working initially on an industrial scale with a membrane contactor of 20 m² of separation surface. They experimentally observed that the modification of the feed and stripping flow of the working variables (from 600 L.h⁻¹ to 300 L.h⁻¹), the pH of the stripping phase (from 7 to 3) and the ratio (from 1.5:1 to 1:4.7) increased the degree of de-alcoholization by 1.3 to 5 %v/v, while the aromatic losses were maintained at 25-37 % or even reduced to about 20 %. The experimental results validated a mathematical model capable of describing the mass flow through the membrane of ethanol and the most abundant aromatic compounds in wine varieties. Also the model used to study the influence and optimize the operational variables; the results of experiments have shown that it is necessary to work with the flow of wine feeding outside the fiber and therefore the flow of water circulating in the lumen side with a low stripping rate, low pH and a high

charge/stripping ratio. But they also showed that using this process to get high de-alcoholization degrees (> 2 %v/v) causes great sensory modifications on the wine.

But, recently, the European Union regulation has fixed the maximum permitted de-alcoholization level at 2 %v/v.

3.2.3 Effects of process parameters

Varavuth et al. (2009) have worked on the performance of the osmotic distillation de-alcoholization process using three different types of stripping agents (pure water, 50 %w/w glycerol and 40 %w/w CaCl₂) by changing the flow rates of feed and stripping solutions and temperature. They concluded that water is the best suitable stripper providing in term of ethanol flux, removal ethanol performance and water flux. They also showed that the ethanol flux and ethanol removal performance were enhanced by increasing feed, stripping solution rates and operating temperatures. The ethanol concentration in the red wine can be reduced to 34 % of the initial concentration after 6 hours of operation but it lead to significant aroma components loss especially ethyl acetate and iso-amyl alcohol.

The flux obtained from the osmotic distillation be usually expressed by $J_e = K_{ov} * \Delta P$ in which the driving force corresponds to the concentrations for both sides, where J_e is the ethanol flux, $\Delta P = (P_{ef} - P_{es})$ is the ethanol vapor difference between feed solution and stripping sides, and K_{ov} is the overall mass transfer coefficient which can be given by: $K_{ov} = \frac{1}{k_f} + \frac{1}{k_m} + \frac{1}{k_s}$ (with k_f : feed solution transfer coefficient, k_m : membrane transfer coefficient and k_s : stripping solution transfer coefficient) did not damage the final perceived quality of the product. However, aroma compound losses can reach almost 100 % for the most volatile compound when residence time of the feed stream was larger (Figure 45).

In the de-alcoholization process operation, the ethanol vapor transport from the feed side results in the decrease of ethanol concentration at the membrane surface. Therefore, it leads to a concentration difference between the bulk and the membrane surface. This phenomenon is known as concentration polarization affecting the driving force of the process. According to the mass balance across the feed boundary layer at steady state condition, the relationship between bulk concentration ($C_{f,b}$) and the concentration at membrane surface ($C_{f,m}$) is given by:

$$C_{f,m} = \frac{C_{s,b} - (C_{s,b} - C_{f,b})}{\exp(J_e / \rho_e \cdot k_f)} \quad (81)$$

$C_{f,m}$ Concentration at membrane surface on the feed solution side

$C_{s,b}$ Concentration on stripping side

$C_{f,b}$ Concentration of the feed solution

J_e Ethanol flow

ρ_e Volumic mass of ethanol

k_f Transfer coefficient in the feed solution

A study showed that working in lamellar conditions for feed and stripping streams was the optimum ethanol removal condition from 10 %v/v model solutions. Liguori et al. (2013) have also observed a decrease in the flow of ethanol by increasing the ethanol content of the solutions explained by the saturation phenomena. Increasing the temperature accelerates the de-alcoholization process. They noticed no difference between the crude wine and the de-alcoholized wine concerning the chemical analyzes.

The flow of ethanol across the membrane can also be calculated by the following equation (82) according to Liguori et al. (2013)

$$J_e = K_{ov} * P^{sat} * (a_f - a_s) \quad (82)$$

J_e	<i>Ethanol flux</i> [g.m ⁻² .s ⁻¹]
K_{ov}	<i>Overall mass transfer coefficient</i> [g.m ⁻² .s ⁻¹ .Pa ⁻¹]
P^{sat}	<i>Saturation pressure of ethanol at the temperature T</i> [Pa]
a_f and a_s	<i>Ethanol activity in feed and stripping stream</i>