

# Combined Membrane Process for Dealcoholization of Wines: Osmotic Distillation and Reverse Osmosis

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The demand of beverages with low or zero alcohol content is fast growing over the last years for health benefits of drinkers and more restrictive policies in alcohol consumption. Membrane processes are nowadays the most commonly used. They have undoubtedly led to improvements in quality, particularly for the low processing temperatures, but determined volatile compounds loss which in many instances resulted in unsatisfactory sensory quality. This study evaluates the combination of two membrane processes for the production of lower alcohol wines: osmotic distillation (OD) and reverse osmosis (RO). It aims for retain the flavour, preserve the good taste of wine with low alcohol content. A red wine (13.2 %v/v) was reduced in alcohol strength of about -5, -6, -8 %v/v through a RO and OD combined process: the initial wine was firstly treated through RO and was subsequently processed through OD to obtain partial dealcoholized wines. Such wines were then compared with those obtained through OD technique. Low alcohol wines were analysed for chemico-physical parameters and volatile composition. The results showed a better retention of the main chemical properties and volatile compounds in wines with low alcohol content obtained through the combined OD and RO process than those through single OD.

## 1. Introduction

A strong increase in demand for quality low alcohol drinks over the last years has been observed and operators of beverage sectors are stimulated to offer to customers a wide range of choices for these innovative beverages. Some people like a reduced alcohol intake in beverages during business lunch, others for religious or healthy reasons without avoiding alcohol completely. Thus, the possibility of drinking low alcohol wines seems to be a good alternative. However, alcohol reduction in wine tends to reduce its complexity and therefore consumer acceptance. This is especially valid for red wines, whose complexity is correlated with numerous olfactory notes and pleasantness. The production of low alcohol wine is an ongoing challenge in order to preserve taste and flavour. The techniques for reducing alcohol in wines are various: viticultural strategies, pre-fermentation and microbiological strategies as well as post-fermentation techniques (Liguori et al., 2018a; Varela et al., 2015; Schmidtke et al., 2012). The last, applied at the end of fermentation process, relying on ethanol removal from already formed wine, are the most common practices, based on thermal or physical principles. The best technology for alcohol removal should fit an effective control of alcohol reduction, with low energy consumption and minimal impact on wine quality (Varela et al., 2015). Nowadays, spinning cone column and reverse osmosis (RO) are the most employed methods at industrial scale, to produce lower alcohol wines. The main drawbacks of these technologies are high energy consumption. In fact, in RO, water and alcohol move through the membrane when the pressure difference across the membrane is higher than the osmotic pressure difference (Schmidtke, et al., 2012). Osmotic distillation (OD) is a membrane-based technology that shows promising results for low alcohol or no alcohol beverages (*i.e.* wine and beer) (Ferrari et al., 2016; Liguori et al., 2015; Diban et al., 2013; Russo et al., 2013). In OD process,

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wine and water, as ethanol extractive agent, are fed in counter-flow on either side of a membrane module; the driving force is the vapor pressure and the greatest partial pressure of the component (*i.e.* ethanol) allows it to permeate the hydrophobic microporous membrane. The main advantages of this technology are low working temperature and low energy consumption (no pressurization of the system is required). Various scientific papers focused the effect of OD on the chemico-physical characteristics, sensory quality and volatile compounds in low alcohol wines (Longo et al., 2017; Lisanti et al., 2013). Only a recent study compared the use of a combined RO-OD process for wine partial dealcoholization, with wines obtained by grapes early harvest, by evaluating volatile and sensory profiles of dealcoholized wines (Longo et al., 2018). The aim of the current study was to compare the effects on red wine of partial dealcoholization performed through a combined membrane process, RO and OD, and through single OD. For this purpose, the main wine parameters and volatile composition of low alcohol wines were evaluated.

## 2. Materials and methods

### 2.1 Dealcoholization process

A red wine (*cv. Montepulciano d'Abruzzo*) with alcohol content of 13.2 %v/v ( $W_0$ ) was used for partial dealcoholization. In the combined process the wine was first treated in a RO semi-pilot plant equipped with a membrane module of 100 Da, and operating at a pressure  $p=70$  bar, and then in an OD semi-pilot plant equipped with membrane module (1.7 x 5.5, Liqui-cel). In this latter (Figure 1), wine (1 L) flowed into shell side at 1.5 L/min; the stripper was water (0.5 L) flowing at 0.5 L/min in the lumen side. The streams were fed into the module in counter-current and in recycling mode, at 10 °C. Two OD cycles were performed: each cycle lasted 40 min, at the end of each cycle the stripper was renewed with pure water. Low alcohol wines were codified as follows:  $WRO_1$  is the wine obtained by the first RO treatment, and  $WROD_i$  (with  $i=2,3$  is the cycle number) are those obtained in the subsequent OD cycles.

Further dealcoholized wine samples were obtained through OD. In this case the OD process was performed in 3 cycles, with the same conditions as before. At the end of each cycle, the partially dealcoholized wines as  $WOD_j$  (with  $j=1, 2, 3$  is the cycle number).

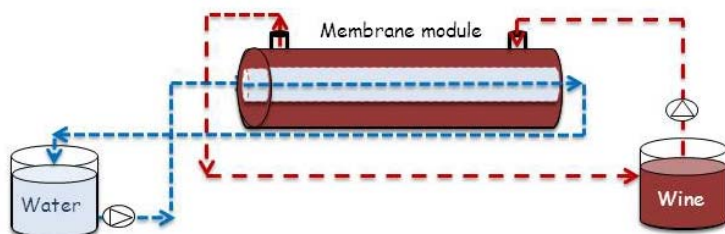


Figure 1: Scheme of OD semi-pilot plant equipped with membrane module (1.7 x 5.5, Liqui-cel).

### 2.2 Chemico-physical analyses

Alcohol content, total and volatile acidity, tartaric acid, pH were determined by means of a Winescan (FOSS, Napa), according to the OIV Compendium of International Methods of Analysis of Wine and Musts (2007). Total phenols (TP) amount in wines was determined with the Folin–Ciocalteu reagent (Singleton & Rossi, 1965; Liguori et al., 2018b; 2016). Total anthocyanins (TA) concentration was determined by spectrophotometry according to Corona et al. (2015), expressed as mg malvidin-3-glucoside equivalents/L and calculated as follows:

$$TA = \frac{MW}{\varepsilon} E_{540} 50 \quad (1)$$

with  $\varepsilon= 33.70$ ,  $MW/\varepsilon = 16.17$  for malvidin-3-glucoside in methanol–HCl (Wulf and Nagel, 1979).

Colour parameters were evaluated according to Glories method (1984), through a Perkin Elmer UV/VIS Spectrometer equipped with Lambda Bio 40 software.

Volatiles organic compounds (VOCs) were determined on 25 mL of wine, through an elution on 1 g C<sub>18</sub> cartridge (Isolute, SPE Columns), with gas chromatography (Perkin Elmer Autosystem XL) and gas chromatography-mass spectrometry (Agilent 6890 Series GC system, Agilent 5973 Net Work Mass Selective Detector), both equipped with a DB-WAX column (Agilent Technologies, 30 m, 0.250 mm i.d., film thickness 0.25 µm), as described by Corona et al. (2010).

### 2.3 Statistical analysis

Tests of dealcoholization and chemical analyses were carried out in triplicate; mean values and standard deviation values were reported. Monofactorial variance analysis was used to determine significant differences ( $P < 0.05$ ) among *Montepulciano* wine and low alcohol wines by Analysis Lab software. Principal component analysis (PCA) on some volatile compounds of wine samples was performed by SPSS 13.0 software.

## 3. Results and discussion

The red wine, *Montepulciano d'Abruzzo*, was dealcoholized at three different alcohol degrees (about -5, -6 and -8 %v/v). The main chemico-physical properties of low alcohol wines obtained through combined RO-OD and single OD membrane process are reported in Table 1.

Table 1: Chemico-physical characteristics of original wine ( $W_0$ ) and partial dealcoholized wines.

Parameter	$W_0$	$WRO_1$	$WROD_2$	$WROD_3$	$WOD_1$	$WOD_2$	$WOD_3$
Ethanol (%)	13.23±0.02 <sup>a</sup>	9.0±0.01 <sup>e</sup>	7.08±0.01 <sup>e</sup>	5.50±0.01 <sup>f</sup>	8.31±0.01 <sup>b</sup>	6.95±0.01 <sup>c</sup>	5.41±0.01 <sup>d</sup>
Total acidity (g/L)	5.30±0.15 <sup>a</sup>	4.96±0.06 <sup>b</sup>	4.96±0.06 <sup>b</sup>	4.86±0.06 <sup>b</sup>	5.50±0.07 <sup>a</sup>	5.40±0.00 <sup>a</sup>	5.30±0.10 <sup>a</sup>
Tartaric acid (g/L)	2.35±0.02 <sup>a</sup>	2.03±0.05 <sup>b</sup>	1.94±0.05 <sup>b</sup>	1.71±0.05 <sup>b</sup>	2.40±0.05 <sup>a</sup>	2.38±0.01 <sup>a</sup>	2.30±0.01 <sup>b</sup>
pH	3.36±0.02 <sup>a</sup>	3.53±0.01 <sup>b</sup>	3.50±0.01 <sup>b</sup>	3.50±0.01 <sup>b</sup>	3.32±0.04 <sup>a</sup>	3.33±0.01 <sup>a</sup>	3.31±0.01 <sup>a</sup>
Volatile acidity (g/L)	0.46±0.01 <sup>a</sup>	0.33±0.01 <sup>d</sup>	0.30±0.01 <sup>e</sup>	0.28±0.01 <sup>f</sup>	0.42±0.01 <sup>b</sup>	0.43±0.01 <sup>b</sup>	0.36±0.00 <sup>c</sup>
Colour intensity	0.80±0.01 <sup>a</sup>	1.07±0.01 <sup>b</sup>	1.07±0.01 <sup>b</sup>	1.04±0.02 <sup>b</sup>	0.71±0.08 <sup>a</sup>	0.74±0.06 <sup>a</sup>	0.80±0.01 <sup>a</sup>
Hue	0.61±0.02 <sup>a</sup>	0.56±0.01 <sup>b</sup>	0.55±0.01 <sup>b</sup>	0.55±0.01 <sup>b</sup>	0.63±0.01 <sup>a</sup>	0.62±0.01 <sup>a</sup>	0.63±0.01 <sup>a</sup>
TA (mg/L)*	296±29 <sup>a</sup>	223±10 <sup>b</sup>	231±11 <sup>b</sup>	223±10 <sup>b</sup>	269±27 <sup>a</sup>	282±21 <sup>a</sup>	312±11 <sup>a</sup>
TP (mg/L)**	1263±110 <sup>a</sup>	1547±74 <sup>b</sup>	1498±343 <sup>b</sup>	1354±83 <sup>b</sup>	1108±176 <sup>a</sup>	1219±98 <sup>a</sup>	1097±67 <sup>a</sup>

\*TA: Total Anthocyanins expressed as (mg malvidin-3-G/L); \*\* Total phenols expressed as (mg GAE/L). Values are expressed as average ± standard deviation. Different letters (a, b...f) mean significant differences ( $P < 0.05$ ).

The original wine ( $W_0$ ) with an alcohol content of 13.23 %v/v dealcoholized through the combined membrane process had a reduced alcohol content of -4.2 %v/v after the RO step ( $WRO_1$ ), and then of -6.1 %v/v ( $WROD_2$ ) and -7.7 %v/v ( $WROD_3$ ) after the subsequent OD cycles.

For the wine samples dealcoholized through osmotic distillation it was obtained a similar reduction in alcohol strength ( $WOD_1$  = -4.9 %v/v,  $WOD_2$  = -6.2 %v/v,  $WOD_3$  = -7.8 %v/v).

No significant differences in total acidity, tartaric acid and pH were observed between the original wine and those processed by OD, whereas a significant decrease in total acidity and tartaric acid and an increase in pH was detected in wine treated by RO. A similar trend in pH after RO was also reported elsewhere (Catarino, 2010). In the subsequent OD cycles, pH value in wine ( $WROD_2$ ,  $WROD_3$ ) remained almost unchanged. Tartaric acid and total acidity have confirmed this trend. A slight decrease in volatile acidity was then detected, which could be explained by acetic acid loss during the OD process and its low rejection in wine in RO process. A significant decrease of total anthocyanins (TA) was detected in wine after RO process probably due to interaction phenomenon with membrane; then, the amount remained unchanged after two OD cycles ( $WROD_2$  and  $WROD_3$ ). The concentration of the non-permeable compounds was evident for total phenols (TP) amount in  $WRO_1$  sample due to permeation of both ethanol and water during RO. TP content remained constant in the subsequent OD cycles, hence the OD process did not influence the amount of these compounds during the wine dealcoholization, as reported elsewhere (Lisanti et al., 2013; Liguori et al., 2013). The colour parameters (colour intensity and hue) were found statistically different ( $P < 0.05$ ) respect to  $W_0$ , more in wine dealcoholized through RO than OD process.

Since the quality of wine depends on the balance between ethanol content, acidity, aroma and taste, the dealcoholized samples were submitted to volatile composition analysis. In the volatile profile of the initial wine 44 compounds were identified, belonging to five main groups: alcohols, esters, acids, phenols and lactones (data non reported). The volatile compounds play an important role in the flavour of wine and the alcohol removal may cause their decrease depending on the process conditions and VOCs chemico-physical properties (i.e. chemical structure, boiling point, water solubility, hydrophobicity, volatility), as well as the interaction with wine matrix, the alcohol concentration and, the affinity to the membrane (Longo et al., 2017).

In OD process, ethanol diffuses across the hydrophobic membrane and, using distilled water as stripper, the volatiles transfer is encouraged across the membrane due to the high difference in volatiles concentration between the two sides of membrane. In RO membrane, ethanol and water and low molecular weight molecules permeate the membrane against the osmotic pressure and are recovered in the permeate side. On the other hand, larger molecules, mostly remain in the retentate side (concentrated wine) in dependence on membrane permeability.

The percentage loss of the main classes of volatile compounds was reported in Table 2. It is possible to highlight how the preliminary treatment on wine by RO allowed to retain a good amount of volatiles compounds (negative loss in Table 2) due to concentration phenomenon in wine. Hence, in the subsequent OD cycles, the volatiles amount remained almost unchanged in WROD<sub>2</sub> and WROD<sub>3</sub> samples. On the other hand, the low alcohol wine (WDO<sub>1</sub> at 8.31 %v/v) presented lower losses of volatiles that those reported in other papers (Lisanti et al., 2013; Diban et al., 2013; Liguori et al., 2013) with the same technique. This difference is probable due to different membrane and operating conditions used in these studies.

Table 2: Percentage loss of the main classes of volatile compounds in partial dealcoholized wines.

	WRO <sub>1</sub>	WROD <sub>2</sub>	WROD <sub>3</sub>	WOD <sub>1</sub>	WOD <sub>2</sub>	WOD <sub>3</sub>
Alcohols	-30	-27	-17	3	0	2
Esters	8	15	22	15	18	19
Phenols	-13	-18	-16	5	10	7
Lactones	-14	-14	-14	7	16	25
Acids	-22	-24	-19	18	25	23

The volatile compounds contribute differently to wine aroma depending on their odour activity value (OAV) calculated as ratio of concentration to odour threshold. As reported elsewhere (Zea et al., 2007), compounds that exhibited OAV>1 are considered to contribute individually to the wine aroma. Hence, the OAV of volatile compounds was calculated (data non reported) and the Principal Component Analysis (PCA) was performed on compounds with AOV>1 (i.e. ethyl hexanoate, ethyl octanoate, isoamyl acetate, 2-phenylethanol, 4-ethylguaiacol) and on typical compounds of grapes variety ( $\alpha$ -terpineol) or that influence taste and aroma of Montepulciano wine (i.e. phenethyl acetate, guaiacol, 4-ethylphenol) (Figure 2).

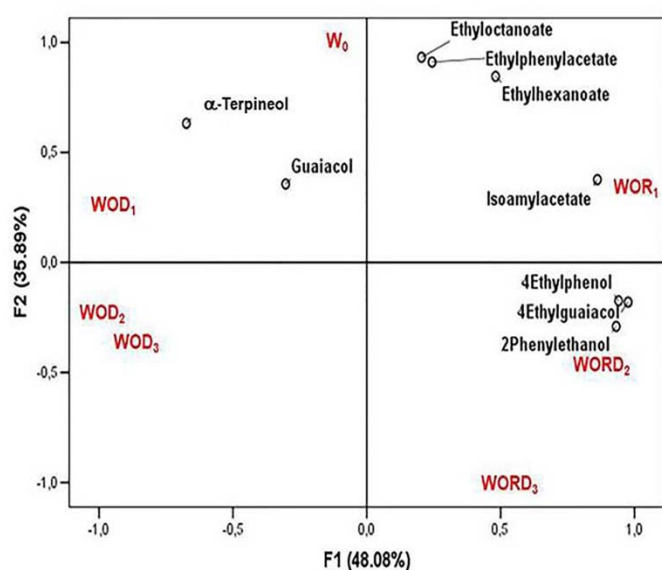


Figure 2: PCA plot of the relationship between some key odour impact compounds and wine samples.

The first two components of PCA analysis explained 84% of data variability (48.08% and 35.89% respectively). Esters compounds are located in the positive quadrants of PC1, instead  $\alpha$ -terpineol and guaiacol on the negative side one. The low alcohol wines obtained by combined membrane processes showed a clear opposition respect to wine samples obtained by OD process and, the initial wine  $W_0$  is approximately in the centre of PCA plot. The selected volatile compounds are well correlated with low alcohol wines ( $WRO_1$ ,  $WROD_2$  and  $WROD_3$ ) obtained by combined membrane process and negatively correlated on the PC1 with wine samples obtained by OD ( $WOD_1$ ,  $WOD_2$  and  $WOD_3$ ). Original wine ( $W_0$ ) and those with about -5 %v/v reduced alcohol content ( $WRO_1$  and  $WOD_1$ ) showed a good correlation on PC2 axis, whereas the other wines with a lower alcohol content were negatively correlated on the second factor of PCA.

#### 4. Conclusions

The effect of different degree of dealcoholization on *Montepulciano d'Abruzzo* wine performed through osmotic distillation (OD) and a combined membrane process, RO and OD, was evaluated. No significant differences in total acidity, tartaric acid and pH were observed between the original wine and those processed by OD, whereas a significant difference was detected in wine treated by RO. The RO process also significantly affected total anthocyanins which decreased in the dealcoholized wine, and total phenols which increased. However, the subsequent OD cycles did not influence the amount of these compounds during the wine dealcoholization. The colour parameters were also found statistically different ( $P < 0.05$ ) respect to  $W_0$ , more in wine dealcoholized through RO than OD process.

An increase of total volatiles content occurred after the RO step which decreased in the subsequent OD cycle. But at the end of the combined process, an overall increase in volatiles content was observed. On the contrary, the OD process alone determined a decrease in volatiles as the level of dealcoholisation increases. In conclusion, the combined treatment seems to better preserve the volatile qualitative characteristics of the initial wine after dealcoholisation. Further study will investigate the effect of the combined process on the sensory quality of the partial dealcoholized wines.

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