Must concentration by new zeolite membrane (KonKer™) technology

Matthias Schmitt[1,a], Monika Christmann[1], Nobuhiko Ueno[2], Tomohiro Kyotani[2], and Hiroyuki Kakiuchi[2]

[1] Hochschule Geisenheim University von Lade Straße, 65366 Geisenheim, Germany
[2] Mitsubishi Chemical Corporation, 1-1, Marunouchi 1-chome, Chiyoda-ku, Tokyo

Abstract. In this work in this work the must concentration by pervaporative dehydration through a new In In this work in this work the must concentration by pervaporative dehydration through a new of zeolite membrane was compared to the common treatments of chaptalization and must concentration by nanofiltration. Must and wine analysis were conducted to assess if the new pervaporative dehydration process by zeolite membrane effects the must and wine composition, in another way than the other tested authorized processes. In general, the must and wine composition was not changed by the new procedure compared to the usual technologies. Sensory evaluation proof that results. The panelists were not able to distinguish the respective test variants significantly from each other.

1. Introduction

Wines coming from poor vintages often lack of alcohol. The influence of ethanol on the wine's sensory profile is very complex. It has gustatory, olfactory and trigeminal stimulating properties [2–4]. Generally, alcohol gives the wine a certain body sensation. The direct sensory perception of ethanol is sweetness, bitterness and due to thermal effects a certain heat perception. Wines with higher alcohol contents often appear beefier and full-bodied. For many product categories these are desired characteristics. So the increase of alcohol is a common practice in many wine regions worldwide. Especially in Europe, the traditional practice is to add sucrose. Furthermore concentrated grape must or rectified grape must concentrate can be added to increase the later alcohol content. Another strategy to increase the alcohol content is to concentrate the must by partly extracting water. Must concentration got authorized by the OIV resolution 30/2000 and resolution codes of international oenological practices: OENO 2/98 based on regulation (EC) 1234/2007. The extraction of water is usually done by reverse osmosis, cryo-extraction or by vacuum distillation.

Another approach is the must concentration by pervaporative dehydration with zeolite membranes. This new technology bases on high-silica chabazite type zeolite membrane. The driving force of the pervaporation process is the difference in water vapor pressure on both sides of the membrane. The water molecules permeate as vapor through the membrane. Therefore, unlike reverse osmosis treatment, no pressure is applied for the pervaporation process. Due to the vaporization the must temperature gradually decreases during the pervaporation process. So this process potentially a very careful and gentle treatment of the must.

[a] e-mail: Matthias.Schmitt@hs-gm.de

2. Material and methods

The trials were conducted at the Hochschule Geisenheim University with two different Riesling musts. Prior to the treatment the must was clarified by sedimentation and 40gm/l of SO2 was added.

The pervaporative dehydration was performed with a set of tubular high-silica chabazite type zeolite membranes (KonKer™ DH) produced by Mitsubishi Chemical Corporation (Japan, Tokyo). This membrane is suitable for the constant treatment of musts with low pH values.

In this study the KonKer™ DH with dimensions of 12 mm outer diameter and 9 mm inner diameter and 400 mm length.

In 2014 the dehydration by zeolite membranes was done with one module consisting of 8 membrane elements. In 2015, the trial plant was equipped with three of modules with 20 membrane elements each. The effective membrane area of each of the modules was 0.26 m^2.

The must dehydration treatment was conducted by immersing the module into the must. On the inner side of the membrane tube a constant vacuum of less than 10mbar was applied. The water vapor that permeated through the membrane was collected in a cooling trap with liquid nitrogen. The trial plant could treat 25l per day. After the treatment the membranes were cleaned by just rinsing with 50 °C water.

Parallel to the treatment by the zeolite membranes, a variant was concentrated by nanofiltration. As non technical variant, a chaptalizazion in the range of the targeted concentration was. The chaptalization was done by adding sucrose.

For the nanofiltration one spiral-wound membrane module was used (Toray/Münchenstein/Switzerland). The membrane had a surface area of 7.4 m^2 and a salt retention of 98% MgSO4 took part by a spiral wound module.

Chart 1. Process parameter 2015 must trials.

Date	Must sample	Initial sugar content (g/L)	Dehydrating time (h)	Must temperature change °C during dehydration (start⇒end)	Pressure on permeate side (mbar)	Initial Must amount (L)	Concentrated must amount	Dehydration amount (L)	Water permeation flux (kg/m² h⁻¹)
Oct. 20th	A	168	7.1	18.0 ⇒ 7.7	5 – 10	25.0	22.44	2.56	0.46
Oct. 21st			8.5	11.1 ⇒ 6.2	4 – 9	25.0	23.49	1.51	0.23
Oct. 22nd	B I	223	7.2	20.8 ⇒ 8.0	4 – 8	25.0	22.44	2.56	0.46
Oct. 23rd	B II		8.9	20.0 ⇒ 7.2	6 – 9	25.0	21.57	3.43	0.50
Oct. 24th	B III		8.0	19.9 ⇒ 9.5	5 – 9	25.0	22.65	2.35	0.38
Oct. 26th	B IV		7.6	20.5 ⇒ 8.7	6 – 8	25.0	22.86	2.14	0.36

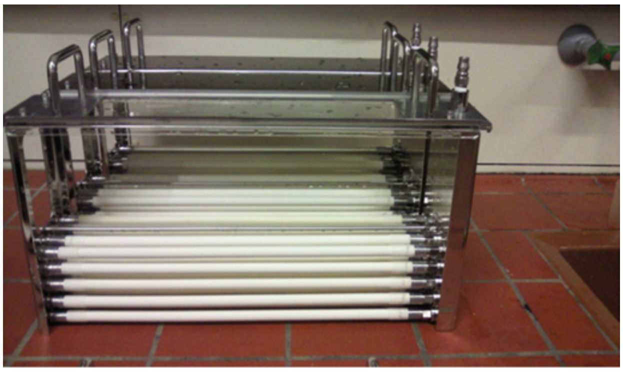

Figure 1. Membrane modules with tubular zeolite membranes.

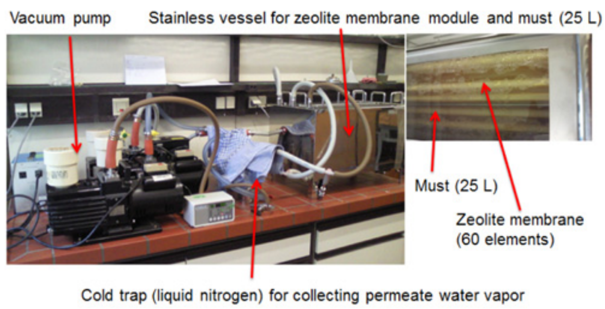

Figure 2. Pervaporative dehydration equipment for must concentration.

The working pressure was 50 bar and the permeate rate was set between 50–60 l during the treatment. The membranes were cleaned after the treatment according to the manufacturer instruction with hot caustic water and citric acid water cycles. Afterwards the membrane was rinsed with water.

All must samples were inoculated by 30 g/hl yeast (Oenoferm Freddo / Erbslöh, Geisenheim, Germany) and the fermentation was monitored in terms of fermentation rate and temperature.

After the fermentation the wines were racked, got sulfured and were bottled. The wine samples from the zeolite treatment of must b were blended. The zeolite membrane treated lots of the first two trial days were blended and the wines coming from the 3rd and 4th trial day were blended as well to get bigger lots of wine.

The basic must and wine parameter analysis were conducted by WineScan SO2 (Foss, Hillerod, Denmark). The calcium and potassium measurements were performed by contrAA 300 Atomic Absorption Spectrometry (Jena Analytik, Jena, Germany).

Chart 2. Overview sensory results.

Test	Answers taken	Answers right	Risk
Control A / Zeolite A	**21**	**7**	**0,5814**
Control A / Zeolite A	**21**	**6**	**0,7514**
Control B / Zeolite B I	**21**	**10**	**0,1248**
Control B / Zeolite B II	**21**	**7**	**0,5814**
Zeolite A / Chaptalization A	**21**	**9**	**0,2399**
Nanofiltraiton A / Zeolite A	**21**	**10**	**0,1248**
Zeolite B I / Chaptalization B	**21**	**7**	**0,5814**
Zeolite B II / Chaptalization B	**21**	**6**	**0,7514**

The sensory analysis were done according to ISO 4120:2004 and ISO 8589:1988 (iso.org). Triangle tests were used as discriminative tests, to evaluate if the different methods to increase the must's sugar content differ from each other.

3. Results and discussion

The process parameter shown in chart 1 indicates that the KonKer™ DH membranes could successfully concentrate the must by extracting water. In the first trial with must A the sugar content was increased by 8 g/l. The must B was concentrated to a higher extent. The sugar content of must sample BI and BII was increased by 16 g/l and samples B III and IV were increased by 26 and 27 g/l. Within 7–8 hours 1.5–3.4 l of water could be extracted from the must by the trial plant. The dehydration performance per hour was between 0.5 and 0.36 kg/m^2. The nanofiltration used could separate 6.75 kg/m^2 and 8.1 kg/m^2. The water flux was bigger with higher temperatures. Furthermore, the concentration performance generally decreased during the treatment due to membrane fouling. That layer could be washed off after each treatment day. The cleaning of the zeolite membrane was much more convenient and took part without any chemical cleaning agents, unlike the cleaning of the nanofiltration membrane that was used in comparison. During the process the must temperature generally decreased from cellar temperature (15–20 °C) to values below 10 °C. The must concentration by reverse osmosis or nanofiltration is generally connected by a certain heat loading. Weber (2006) outlines must temperatures of 40 °C due to the concentration treatment without continuous cooling.

The working pressure on the permeate side was 4–10 mbar. Usual plants for must concentration by vacuum distillation run at pressures of 30 mbar [5].

 DOI: 10.1051/bioconf/20160702009

The analysis of the must and wine samples showed that the trial plant with the zeolite membranes could deliver repeatable results. The targeted concentration could be reached in the trials. Due to the concentration, the content of the most important must parameters was increased due to the water extraction [cf. 1,6,7].

The measured content of potassium and calcium indicated that the permeate of the zeolite membrane treatment was much more pure than the permeate from the nanofiltration treatment.

All tested treatments to increase the sugar content did not affect the measured amount of gluconic acid.

The sensory tests that were done half a year after the must treament showed that there were no significant differences between the different variants. There was no case where the panelists could find a difference between the control and the other variants.

The pervaporative dehydration did not change the sensory character of the must.

4. Conclusion

The must trials at the Hochschule Geisenheim University showed that the process of pervaporative dehydration by high-silica chabazite type zeolite membranes (KonKer^{TM}) is in general suitable for the targeted concentration of must.

The must and wine analysis show no clear shift of the basic wine parameters due to the new dehydration process. The water fraction separated by the pervaporation process through the zeolite membranes appeared more neutral than the permeate from the nanofiltration treatment. The cleaning of the tested zeolite membranes was much faster and thorough than the tested spiral wound nanofiltration module. The storage of the membranes until the next treatment can be seen as a critical factor. The biofilm degradation by microorganism is a hazard for the wine quality. Several cases of off-flavours arising from insufficiently cleaned and incorrectly stored membranes can proof that concern.

A scale up of the plant can allow the must concentration in a greater extend.

References

[1] Clos, D. (2003) Chemische und Sensorische Auswirkungen physikalischer Konzentrierungs-verfahren auf Most und Wein, Dissertation, Technische Univer-sität Kaiserslautern

[2] Green, B.G. (1987) The sensitivity of the tongue to ethanol. Annals of the New York Acadamy of Science, 510, 315-322

[3] Mattes, R. D., DiMeglio, D. (2001) Ethanol perception and ingestion, Physiology and Behaviour, 72, 217–229

[4] Yu P. & Pickering G.J. (2008) Ethanol Difference Thresholds in Wine and the Influence of Mode of Evaluation and Wine Style, American Journal of Enology and Viticulture, 59, 146-152

[5] Weber, D. (2006) Einfluss verschiedener Traubenmostkonzentrierungsverfah-ren auf die Weinqualität, Dissertation, Fakultät Wissenschaftszentrum Weihen-stephan für Ernährung, Landnutzung und Umwelt der Technischen Universität München

[6] Zürn, F. (1979) Anwendungsmöglichkeiten der Umkehrosmose (Hyperfiltration) zur Qualitätsverbesserung von Most und Wein, Dissertation Justus Liebig Universität Gießen