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THE ROLE OF MEMBRANE SEPARATION IN ALCOHOL REMOVING OF WINES AND IN DEHYDRATION OF INDUSTRIAL ALCOHOLS

Thesis of PhD dissertation

LÁSZLÓ TAKÁCS

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Name:	PhD School of Food Science
Field:	Food Science
Head:	Prof. Péter Fodor Corvinus University of Budapest
Supervisor:	Prof. Gyula Vatai Department of Food Operations and Machines Faculty of Food Science Corvinus University of Budapest

The applicant met the requirement of the PhD regulations of the Corvinus University of Budapest and the thesis is accepted for the defence process.

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Signature of Head of School	Signature of Supervisor

INTRODUCTION

The benefits of wine for human health were realized towards the beginning of wine-making, in the ancient times. The Bible, the first written record of wine also mentions the connection between wine and long life. Nowadays this correlation can be proved by the French Paradox based on the cardio-preventive role of wines and its consequences.

The idea of removing alcohol content from wines comes from this recognition and the demand from different social groups to reduce the risk of cardiovascular diseases. All this has further positive physiological impacts on the elimination of negative effects of alcohol.

In my dissertation I showed the place and opportunities of modern membrane technology in alcohol reducing processes. In my work I demonstrated modern membrane separation processes, which can preserve wine quality based on mathematical modelling. However the capability of the modelling of membrane based on pervaporative alcohol reduction has some significance beyond itself. According to this point, I analyzed the questions of etil-, and isopropyl-alcohol dehydration with induction of half empirical formulas into the alcohol industry surround setting. I summarized in my recommendations the principle of modelling of membrane processes in development of complex technologies, which are appropriate for the reduction of alcohol content of wines and for the extracted wine alcohol pervaporative dehydration together in an integrated system based on membrane treatment.

OBJECTIVES

My research focused on two main parts, in which I endeavoured to realize the following considerations:

1. Removing of the alcohol content of wines by laboratory works of membrane processes, which have good retention of the ingredients and its mathematical modelling; optimizing and economical analysing of the

system according to the correlations of basis processes; chemical analysis of the products of membrane methods.

2. Development of complex wine pervaporation by the widening of mathematical modelling and half-empirical formulas of wine pervaporation. According to literature [ATRA et al., 1999a; 1999b] based on ethyl-alcohol and water model mixture, mathematical modelling and determination of characteristic of the wine permeate. Examination of mathematical models for dehydration of isopropyl-alcohol.

MATERIAL AND METHODES

Vacuum pervaporation was applied for the alcohol removing of Tokaji Hárslevelű by organophillic membrane (1060 SULZER). The quantity of product was measured, the pervaporation factors were determined and the distributions of components between wine and products were analyzed by a gas chromatograph.

The test of membrane filtration processes was carried out by the 2^p type plan of experiment according to KEMÉNY and DEÁK (1993). The applied membrane was NF45 nanofiltration membrane with 300 Da cut off (DOW-FILMTECH) for diafiltration of Tokaji Hárslevelű. Nanofiltration of Egri Bikavér was achieved by NF200 polyamide nanofiltration membrane with 400 Da cut off (DOW-FILMTECH). In case of reverse osmosis of Egri Bikavér, a SWHR 30-80 type DOW-FILMTECH reverse osmosis membrane with 99.4 % $NaCl_2$-retentation was applied. The measurement of etil-alcohol content was performed by GIBERTINI equipment based on relative density. The glucose concentration was measured by ABBÉ refraction equipment.

The investigation was based on the experimental data in the etil-alcohol and isopropyl-alcohol pervaporative dehydration system of ATRA et al. [1999a; 1999b], which was analyzed by mathematical modelling of mass transfer and linear resistance model.

SUMMARY OF THE RESULTS

In my research I examined the alcohol removal of Tokaji Hárslevelű by pervaporation. The analysis of the phenomena and the factors of pervaporation by using the mathematical exponential models showed the important role of pervaporation temperature. The economical investigation of wine pervaporative alcohol reduction defined the cost effectiveness of the investment and operation. In the case of low alcohol content wine cost effective production is at its best at 36.5°C and at 39.5 °C for alcohol-free wine.

Development of a new index by the membrane filtration of Tokaji Hárslevelű and Egri Bikavér verified the competence of diafiltration compared with the results of reverse osmosis and membrane filtration of several nanofiltration membranes. The improved hydrodynamic model for the relative resistance of the polarization layer as indicated by the operation parameters shows that the areas determined by different theoretical models can be applied with the same formula.

Gas-chromatographic analysis of the products of wine separation processes showed that the distributions of aroma components of wine in the membranfiltered products are almost of the same ratio, and in case of an average sample of the pervaporative wine permeate, the presence of the aroma components storage is 70%.

The results of isopropil-alcohol and etil-alcohol model solutions, using theoretical mathematical models, confirmed that according to the mass transport coefficients of the applied hydrofil membranes, the best membrane for the pervaporative dehidration is CMC-CA-01. Mass transport determinations of MORA et al. (2003) for organofil membranes have been confirmed, which means mass transfer only is specified by the material and structure of the applied membrane. This is also true in the case of the applied hydrofil membranes. In conclusion, amplification of theoretical models defined that the running of water selectivity corresponds to a hyperbolic function dependence on the feed concentration and it gains maximal value by infinitively high concentration.

NEW SCIENTIFIC RESULTS

1. The results of my wine-pervaporative examinations show that, in the case of increasing temperature, the alcohol concentration of wine is decreased.
   - 1.1. I pointed out that flux is increased and the selectivity of alcohol is dropped by the effect of temperature. The pervaporation separation index grows, because the rising of flux is more intensive than the reducing of the alcohol separation coefficient of membrane.
   - 1.2. I determined the pervaporation activity energy of 1060 SULZER membrane: in case of etil-alcohol it is 39.10 kJ/mol, in the case of other components, it is 43.58 kJ/mol. According to this, I worked out half-empirical models. I extended this model to the process indexes of pervaporation. I found that the running of the indexes of wine pervaporation is corresponding to an exponential function depending on temperature according to 1.1.
2. I calculated connections based on a wine pervaporative model for economical analysis of the preparation of industrial wine pervaporative system regarding investment and operation cost.
   - 2.1. I established that the needed membrane area for the process of pervaporative removing of alcohol is decreased by temperature and its running corresponds to an exponential function. In case of low alcohol content wine needs less membrane area than in case of alcohol-free wine.

$$A = \frac{\rho_P \cdot V_F}{J_0 \cdot e^{\frac{-E_0}{R \cdot T}} \cdot \tau} \cdot \frac{x_{F,E} - x_{R,E}}{x_{P,E} - x_{R,E}} \qquad (1)$$

Where:

A – area of membrane [m^2],

ρ_P – density of permeate [kg/m^3],

V_F – volume of wine in feed [m^3],

J_0 – pre-exponential factor of total permeate flux [$kg/(m^2h)$],

τ – pervaporation time [h],

$x_{F,E}$ – alcohol concentration in feed wine [weight %].

$x_{R,E}$ – alcohol concentration in wine retentate [weight %].

$x_{P,E}$ – alcohol concentration in wine permeate [weight %].

2.2. Based on my calculations, I defined that at higher temperature is better the yield of permeate, but in this phase there are less good components for separation. Besides, at lower temperature more final product can be produced, because different components from alcohol can not go so much to the permeate side.

2.3. Because of different alcohol concentration in the final product can be made more quantity of low alcohol wine than alcohol-free wine, where in the same category you can also remark different quantities depending on temperature under 2.2.

3. I carried out a test with different membranes according to the plan of experiment in case of direct concentration and diafiltration of wines. I compared the capacity of reverse osmosis and nanofiltration membrane processes and I founded that the diafiltration is the best of the examined membrane processes for production of low alcohol content wine.

3.1. I developed a new index for description of membrane filtration resistances, which I called the relative resistance of the polarization layer. Regarding the effects of operation parameters, I confirmed that this index follows the decreasing tendency of recirculation flow rate in higher range in case of higher driving force. I worked out a new model, based on hydrodynamic criteria, for the relative resistance of polarization layer. For this model I determined the wine constants in case of Tokaji Hárslevelű and Egri Bikavér in examined processes.

$$\frac{R_P}{R_M} = a \cdot (Eu \cdot Fr)^b \cdot Re^c \tag{2}$$

Ahol:
R_P/R_M – the relative resistance of polarization layer (in the same temperature) [-],
a, b, c – wine constants [-],
Eu – Euler-number [-],
Fr – Froude-number [-],
Re – Reynolds-number [-].

3.2. I extended the hydrodynamic model to flux, thereby I fixed that the flux of the wine permeate can be determined by pure water flux in the knowledge of wine constants. The formula can be used on the areas, which are determined by different theoretical models in case of different driving forces.

$$J = \frac{\Delta p_{TM}}{R_M} \cdot \frac{1}{a \cdot (Eu \cdot Fr)^b \cdot Re^c + 1} = \frac{J_W}{a \cdot (Eu \cdot Fr)^b \cdot Re^c + 1} \quad (3)$$

Where:
Δp_{TM} – transzmembrane-pressure [Pa],
R_M – resistance of membrane [1/m],
J – flux of wine permeate [kg/m^{2}h],
J_W – flux of pure water [kg/m^{2}h].

3.3. Examining concentration polarization I found that, in case of sweet wine (Tokaji Hárslevelű) the degree of concentration polarization is higher than in case of dry wine (Egri Bikavér). Furthermore the glucose concentration on the membrane is changed by flow rate, which means there is no gel layer on the surface of the membrane.

3.4. I examined the fitting of the theoretical models of osmotic pressure for the measured points of wine membrane filtration. I indicated that, the RAUTENBACH and CHERYAN model are adequate to the osmotic pressure of wine membrane filtration, but van’t HOFF model is not.

4. I analyzed the wine and the separated products by gas chromatograph. I pointed out, that in case of wine retentate of the membrane filtration there are 47% of the wine aroma components and 53% in the wine permeate. Furthermore there were the same components in both phases, but there is higher quantity in the membrane filtrated wine permeate. In case of pervaporative wine permeate the aroma component of total aroma-storage of wine was 70%.

5. According to the results of isopropyl- and etil-alcohol of literature, based on theoretical mathematical modelling, I calculated the characteristics and the mass transfer coefficients of hydrophilic membranes in pervaporative dehydration system.

5.1. I showed that the resistance of the overall membrane processes and the resistance of the membranes are the same technically, which means that mass transport depends on the material and structure of membrane only.

5.2. Dehydration is achieved the most efficiently by CMC-CA-01 membrane at 45 °C, which is true in case of isopropyl- and etil-alcohol, too, where the mass transfer coeffient of the membrane is in case of etil-alcohol $5{,}90\cdot10^{-7}$ mol/(m^{2}Pas), and in case of isopropyl-alcohol $4{,}71\cdot10^{-7}$ mol/(m^{2}Pas).

5.3. I determined the factors of pervaporation of CMC-CA-01, CMC-CE-01, CMC-CE-02, and GFT-2000 type hydrophilic membranes. I fixed, that pervaporative flux and water selectivity falls depending on decreasing feed concentration, and, the pervaporation separation index follows decreasing tendency depending on pervaporation time.

6. I worked out a mathematical model, which is extended to pervaporative flux and selectivity of membrane, too. According to this model I defined that, the running of water selectivity corresponds to a hyperbolic function dependence on the feed concentration and it gains maximal value by infinitive high concentration, under 5.3.

$$\beta_i = \frac{1}{(1-x_{F,i})\cdot(\psi-1)+1} \qquad \psi = \frac{Q_{M,j}\cdot\gamma_j\cdot P_j^0\cdot\rho_{L,j}\cdot M_i}{Q_{M,i}\cdot\gamma_i\cdot P_i^0\cdot\rho_{L,i}\cdot M_j} \tag{4}$$

Ahol:

β_i – „i” component selectivity [-],

$x_{F,i}$ – „i” component concentration in feed [kg/kg].

Ψ – constans [-],

$Q_{M,i}$ – mass transfer coeffient of membrane of „i” component in case of difference of partial vapour pressure [mol/(m^{2}Pas)],

$Q_{M,j}$ – mass transfer coeffient of membrane of „j” component in case of difference of partial vapour pressure [mol/(m^{2}Pas)],

γ_i – „i” component activity coefficient [-],

γ_j – „j” component activity coefficient [-],

P_i^0 – „i” component saturated pressure at given temperature [Pa],

P_j^0 – „j” component saturated pressure at given temperature [Pa].

M_i – „i” component molecular mass [kmol/kg],

M_j – „j” component molecular mass [kmol/kg],

CONLUSIONS AND SUGGETIONS

According to the examination of wine separation membrane phenomena, the analysis of the literature, the development of mathematical models and the design connections, we can assume that the recommended complex wine alcohol reducing and dehydrating technology system has several benefits, which indicate the industrial achievement. The technology can be operated with very high environmental efficiency. There is no waste water during the operation, because the water from wine can be recirculated into the system or added to the final product.

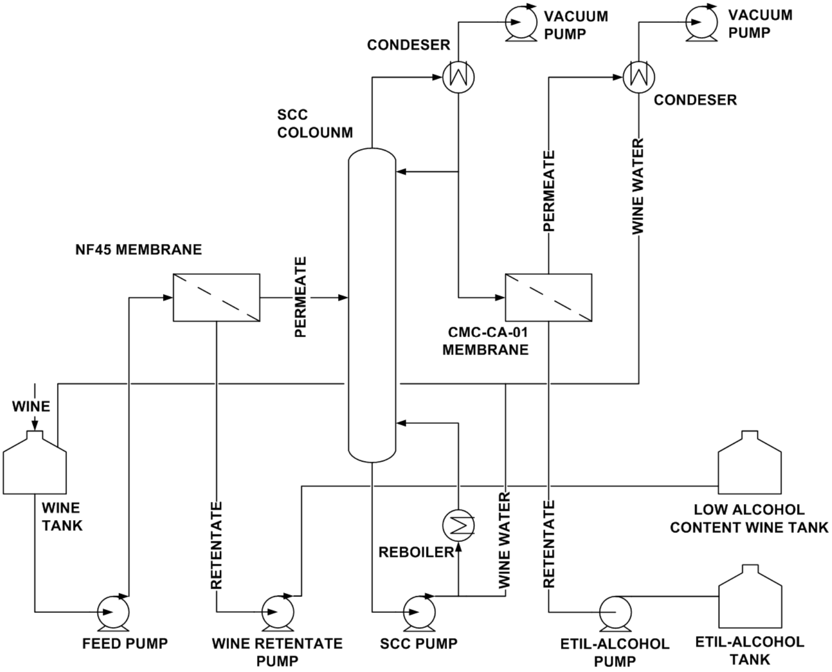

Figure 1. Alcohol removing of wine and wine alcohol dehydration system with diafiltration.

Therefore the productivity and quality of the wine increase at the same time. Regarding all that, this appropriated process for the technological requirements of 21st century can have a very important role in the quality evolution of low alcohol content and alcohol-free wines.

PUBLICATION JOINED TO THE THESIS

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- **LÁSZLÓ TAKÁCS,** GYULA VATAI, KORNÉL KORÁNY (2007): Production of alcohol free wine by pervaporation, J. Food Engineering 78, p. 118-125.
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