



**CONCENTRATION OF BLACKCURRANT JUICE AND
RED WINE BY INTEGRATED MEMBRANE
PROCESSES**

Thesis book

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Introduction and objectives

In the recent years – in our country as well – it can be observed that the consumers favour the high-quality food products, which are made from natural raw materials and are rich in valuable components. New eating habits appeared to the organization of health protection and the prevention of diet-related diseases. Increasingly, the high nutritional value and antioxidant effects of vegetables and fruits are in the focus of researches. For these reasons the blackcurrant and the popular red wine were chosen as raw materials for my experiments. One goal was the theoretical and experimental investigation of the mild concentration of blackcurrant juice using complex membrane process. The resulting healthy fruit juice concentrate has to be rich in valuable components and can be easily stored, and diluted. The other goal of my work was the production of a red wine concentrate rich in valuable compounds. During my work the theoretical and experimental feasibility of the concentration made by membrane technique was studied.

Materials and methods

The blackcurrant juice was made from two types of black currant (Titania and Otelo) by pressing and enzyme treating (Pektopol PT400). The resulted fruit juice was clarified by micro- (SCHUMASIV, 0,45 μm) and ultrafiltration (37.03 I8, 100 kDa). The prefiltered blackcurrant juice was concentrated by nanofiltration (R55A, $R_{\text{NaCl}}=70\%$ and XN45, $R_{\text{NaCl}}=80\%$) and reverse osmosis (ACM2, $R_{\text{NaCl}}=97\%$) membrane up to 25-30 °Brix total soluble solid (TSS) content. In each operational phases the operation

parameters, such as transmembrane pressure difference, temperature, and recirculation flow rate were varied and their influence on the retention of different valuable components and permeate flux was investigated. The flow sheet of the measuring equipment is shown in Figure 1. Analytical assays have been conducted to analyze the samples: the TSS-, monomer anthocyanin-, total phenol-, total acid content and antioxidant capacity were determined in the retentates and permeates.

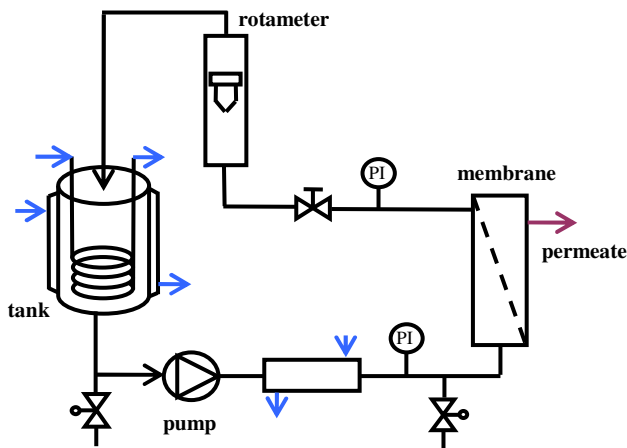


Figure 1. Flow sheet of the applied equipments

After the laboratory experiments some pilot tests was performed in the plant of Fitomark '94 Ltd, Tolcsva. The membrane used was agreed by the reverse osmosis membrane (ACM2, $R_{NaCl}=97\%$) used in the laboratory.

For the red wine (type Egri Cuvée) concentration experiments a nanofiltration membrane (XN45, $R_{NaCl}=80\%$) was used, that permeates the water and ethanol. The concentrations were carried out according to the 2^p type experimental design investigating the effects of two operating parameters (transmembrane pressure difference and temperature). The

retentates and permeates were analysed: the alcohol-, sugar-, total acid-, sulphonic acid-, extract-, volatiles-, monomer anthocyanin- and resveratrol content were determined. The utilization of by-product (permeate) carried out by distillation at Department of Brewing and Distilling.

Both the case of red wine and blackcurrant juice sensory analysis (profile analysis, MSZ ISO 11035:2001) was fulfilled to determine, whether the products meet the market expectations of consumers.

New scientific results

I. Experiments with blackcurrant juice [1], [2], [4], [5], [6], [7], [9], [10]

1. The blackcurrant berries and the juice made from the berries contain many valuable components that have many beneficial physiological effects. The traditional concentration by evaporation damages the valuable materials of the fruit juice, however concentration with membranes is a mild method. A wide range of membrane filtration has been studied and found that for production of blackcurrant juice concentrate the microfiltration (MF) - reverse osmosis (RO) complex system can be successfully used, while for the same purpose, the ultrafiltration (UF) - nanofiltration (NF) is not warranted. The 0.45 μm pore size microfiltration membrane opposed the 100 kDa ultrafiltration membrane left the valuable materials. At the concentration using reverse osmosis membrane 20-30% higher total soluble solid content (TSS) could be reached as nanofiltration membrane and the retentions were also 5-10% higher. On the base of the experimental results a two-stage technology (MF+RO) is worked out for concentration of enzyme-treated blackcurrant juice to 25-30 °Brix TSS content (Figure 2.).

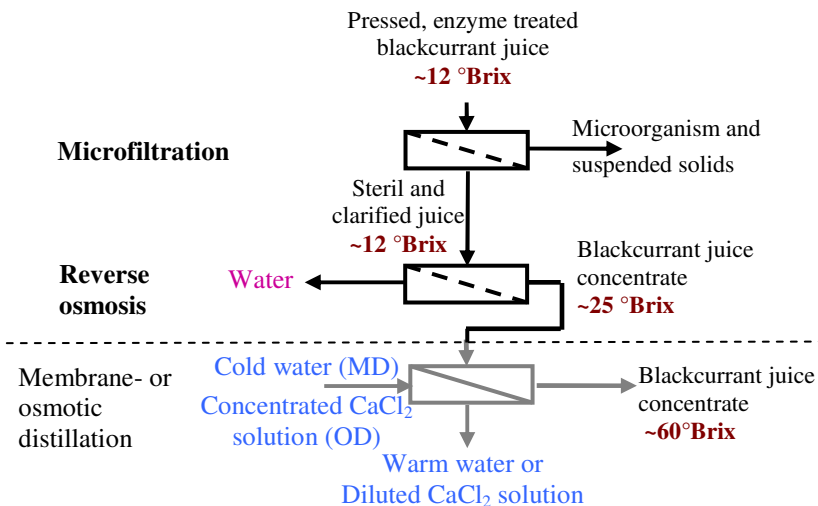


Figure 2. Technology of blackcurrant juice concentrate production

The product can be consumed in concentrated form, or diluted with water and sweetener. The product is spicy, fragrant, can be stored in refrigerator. It contains anthocyanins and phenolic compounds concentrated and its antioxidant capacity is two times higher than that of the original juice. (The final concentration of this juice concentrate over 60 °Brix can be carried out by membrane distillation (MD) or osmotic distillation (OD), through the latter's experiments are not the subjects of my dissertation.)

2. The suspended solids (TSS) has been removed from blackcurrant juice using microfiltration. During the clarification the influence of operating parameters was examined to the TSS content of blackcurrant juice and to the permeate flux. Applying one and a half times higher transmembrane

pressure the permeate flux increased 30-40% and the filtration's time decreased 12-15%. Increasing the flow rate with 200 L/h or the temperature with 5 °C resulted 1.3 times higher and 2.6 times higher permeate flux, respectively.

3. The clarified blackcurrant juice with 12 °Brix was concentrated to 25-30 °Brix by reverse osmosis. Raising the transmembrane pressure difference from 38.5 bar to 51 bar the permeate flux increased 10-15%. Increasing the temperature did not influence the TSS content of the concentrate.

4. Cost estimation was calculated for an MF-RO system: the plant processing was 112000 litre of fresh fruit juice (capacity of 5000 litre per day), daily 8-hour shift was planned. Found that despite the high investment cost (17100 Euro/year) the concentration using membranes is economic (67700 Euro/year). Concentration of one litre blackcurrant juice costs 0.76 Euro. Depending on the degree of dilution 2-3 litres blackcurrant juice can be prepared from the concentrate.

5. The mathematical modelling – based on experiments – resulted in the next establishment for blackcurrant juice:

- For modelling of microfiltration the resistance-in-series model can be applied. The membrane resistance was constant ($8.9 \cdot 10^{11}$ 1/m), increasing the flow rate (from 100 L/h to 500 L/h) the fouling resistance decreased 60% and the gel-layer resistance decreased 40%. It was established at the concentration of blackcurrant juice by reverse osmosis that the generated gel layer on membrane surface has the greatest resistance. In case of nanofiltration rising the transmembrane pressure

difference of 25% the fouling resistance can be reduced 12.5% and the gel-layer resistance of 4%. At reverse osmosis the percentage decline was greater, the fouling resistance decreased by 64% and the gel-layer resistance by 32.5%.

- On the basis of experiments it was proved that the van't Hoff law is applicable to the calculation of the blackcurrant juice's osmotic pressure. The fits of the osmotic pressure model was investigated to the results of concentrations (reverse osmosis and nanofiltration) and the values of permeability coefficient (signed B in the model) was determined for blackcurrant juice. This value was 0.7867 L/(m²hbar) in case of reverse osmosis and 1.0301 L/(m²hbar) in case of nanofiltration.

II. Red wine studies [3], [8], [11]

6. The red wine contains a number of components (eg. anthocyanins, resveratrol) which have a positive physiological effect. My goal was mild production of a red wine concentrate in which the valuable components are enriched. For this purpose a nanofiltration membrane with 80% salt rejection was used which retained 72-96% the valuable materials, in addition to the water with the alcohol passed through the membrane. The TSS and sugar retention of the nanofiltration membrane was over 80% of all measurements, while the membrane slightly retained the volatile acids (<18%). Diluting the red wine concentrate a delicious drink can be made with decreased alcohol content (< 4%) which contains the valuable compounds, such as anthocyanins, resveratrol that have beneficial effect to human body.

7. The effect of operational parameters, such as transmembrane pressure difference and temperature, was determined on the average permeate flux and the retention of certain components. Both parameters have significant effect on the average permeate flux and the retention of valuable components. In the products (retentate and permeate) the anthocyanin and resveratrol content was determined. Raising the temperature the retention of anthocyanin and trans-resveratrol also decreased of 20-30%, while rising the pressure it decreased of only 8%.

8. The mathematical modelling was based partly on newly developed equations, partly on literature formulas:

- The permeability coefficient in case of red wine concentration were determined: 0.896 L/(m²hbar) at 20 °C and 1.4335 L/(m²hbar) at 40 °C.
- 50% increase in temperature did not affect neither the gel-layer nor the fouling resistance. 50% increases in transmembrane pressure difference resulted 15% decreases in fouling resistance and 40% increase in gel-layer resistance.
- The relationship of osmotic pressure and retentate concentration was determined and the following equation was got: $\pi_R = 1,427 \cdot c_R^{1,074}$ where π_R (bar) and c_R (°Brix)
- Regression relationships were set up between the operational parameters (transmembrane pressure difference and temperature) and the retention of valuable components of red wine:

$$\text{Retention of anthocyanin (\%)} = 99,8350 - 0,0263 \cdot T + 0,0083 \cdot P$$

$$\text{Retention of total resveratrol (\%)} = 121,6195 - 2,0827 T - 1,4983 P + 0,0637 T \cdot P$$

$$20 \text{ } ^\circ \text{C} \leq T \leq 40 \text{ } ^\circ \text{C} \text{ and } 10 \text{ bar} \leq P \leq 20 \text{ bar}$$

9. For utilization of permeate, distillation procedure was applied (Figure 3.). The water, the ethanol and small part of the flavour, aroma compounds passed through the membrane pores so the permeate distillate was similar to the wine spirit. The sensory analysis showed that the assessors agreed with the overall pattern of the two samples (wine spirit and permeate distillate), the second distillate of permeate has also a good taste like wine spirit.

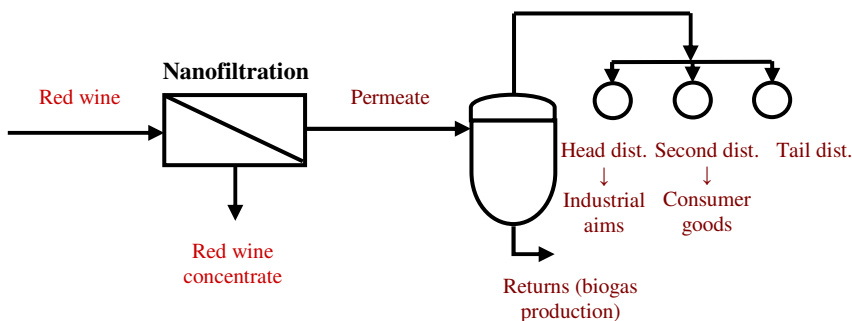


Figure 3. Production of red wine concentrate and utilization of the products

10. Cost estimation was done for wine processing by membrane separation and found that despite the high investment cost (20730 Euro/year) the system can be operated economically (46450 Euro/year). Concentration of one litre red wine costs 0.57 Euro from which 2.5 dl wine concentrate can be made. Neither in the literature nor in the market can not be found a similar wine concentrate, so there is not benchmark for comparison of the costs. The product, the wine concentrate is rich in resveratrol, in anthocyanin and its alcohol content is the same like the wine's. After dilution the drink with reduced alcohol content is similar to red wine, what can be consumed by sick, elder and vulnerable people.

Conclusions and suggestions

During the experiments I developed the basis of a complex process for red wine and blackcurrant juice concentration and the utilization of by-products.

For clarification of blackcurrant juice two methods were used: micro- and ultrafiltration. The analytical measurements showed that the 100 kDa MWCO ultrafiltration membrane retained the valuable components highly, for this reason it is not suitable for clarification of blackcurrant juice. In case of microfiltration membrane with 0.45 μm pore size the retention of valuable materials was less than 1% that's why it is proper method for the prefiltration. For the first step of the concentration nanofiltration and reverse osmosis were used. At nanofiltration 20 °Brix TSS content has been reached but the retention of valuable components was less than that of reverse osmosis. The nanofiltration permeate had pale pink colour so a little amount of valuable compounds passed through the membrane and the analytical assays proved this statement. The reverse osmosis permeate was colourless, the retention of the choosed membrane was over 99% in most cases. The reached TSS content was 25-30 °Brix. For final concentration membrane- or osmotic distillation can be used which is applicable to reach 60 °Brix TSS content.

Nanofiltration was suitable for the concentration of red wine. The valuable components (eg. anthocyanin, resveratrol) enriched in the concentrate, while the amounts of undesired components (alcohol, volatile acids) reduced. The by-product of red wine concentration (the permeate) can be utilized by distillation, its second distillate has similar character like the wine spirit.

More experiments are needed to reach the final concentration of blackcurrant juice by membrane- and osmotic distillation. A whole cost estimation is needed to calculate and compared with the evaporation, the traditional process in the industry.

It may be useful doing further examinations for the shelf-life of the concentrates (also blackcurrant juice and red wine) by microbiological and chemical methods.

Publications joined to my thesis

Articles with impact factor

- [1] **Sz. Bánvölgyi**, Sz. Horváth, É. Stefanovits-Bányai, E. Békássy-Molnár, Gy. Vatai (2009): Integrated membrane process for blackcurrant (*Ribes nigrum* L.) juice concentration, *Desalination* 241 281-287. p.
- [2] Á. Kozák, **Sz. Bánvölgyi**, I. Vincze, I. Kiss, E. Békássy Molnár, Gy. Vatai (2008): Comparison of integrated large-scale and laboratory-scale membrane processes for the production of black currant juice concentrate, *Chemical Engineering and Processing*, 47 1171-1177. p.
- [3] **Sz. Bánvölgyi**, I. Kiss, E. Békássy-Molnár, Gy. Vatai (2006): Concentration of red wine by nanofiltration, *Desalination* 198 8-15. p.
- [4] **Sz. Bánvölgyi**, Sz. Horváth, E. Békássy-Molnár, Gy. Vatai (2006): Concentration of blackcurrant (*Ribes nigrum* L.) juice with nanofiltration, *Desalination* 200 535-536. p.

Revised article

- [5] **Bánvölgyi Sz.**, Horváth Sz., Békássyné Molnár E., Vatai G. (2006): Feketeribiszke-lé (*Ribes nigrum* L.) koncentrációja nanoszűrővel, *Olaj, szappan, kozmetika* LV. Évf. 2. szám, pp 61-64. ISSN 0472-8602

Full paper in international conference book

- [6] **Sz. Bánvölgyi**, E. Békássy-Molnár, Gy. Vatai (2007): Combined Membrane Technology for Prefiltration and Preconcentration of Blackcurrant Juice. 5th International Congress on Food Technology. Proceedings addendum pp 674-680. 2007 Thessaloniki, Greece
- [7] **Sz. Bánvölgyi**, Sz. Horváth, E. Békássy-Molnár, Gy. Vatai (2007): Processing of blackcurrant (*Ribes nigrum* L.) juice by ultrafiltration and reverse osmosis. PERMEA 2007, Konferencia-kiadvány (CD), Siófok, Hungary
- [8] **Sz. Bánvölgyi**, E. Békássy-Molnár, G. Panyik, Gy. Vatai. (2005): Concentration of red wine with membrane technology, PERMEA 2005, (CDROM) Polanica Zdrój, Poland

Full paper in national conference book

- [9] Horváth Sz., Molnár Zs., **Bánvölgyi Sz.**, Békássyné Molnár E., Vatai Gy. (2008): Feketeribiszke-lé kíméletes koncentrációja membránműveletekkel, MTA-AMB 2008. évi XXXII. Kutatási és Fejlesztési Tanácskozása, konferencia-kiadvány 119-123. o., ISBN 978-963-611-445-9
- [10] **Bánvölgyi Sz.**, Békássyné Molnár E., Vatai Gy. (2007): Feketeribiszke-lé előszűrése és elősűrítése membrántechnikával, MTA-AMB 2007. évi XXXI. Kutatási és Fejlesztési Tanácskozása, konferencia-kiadvány 51-55. o., ISBN 978-963-611-445-9

TDK essay

- [11] Mosonyi Sz. (2004): Vörösbor értékes komponenseinek kísérleti besűrítése és modellezése, BKÁE

