CORVINUS UNIVERSITY of BUDAPEST

Faculty of Food Science

INVESTIGATION OF GENTLE CONCENTRATION OF BERRY JUICES

PhD thesis

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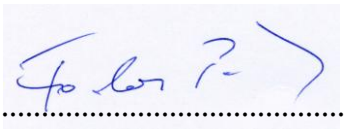
The applicant met the requirement of the PhD regulation of the Corvinus University of Budapest and the thesis is accepted for the defence process.



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INTRODUCTION

From the second half of the 19th century the dietetic habits of mankind underwent significant changes. In the monotonous, mostly cereal and meat based diet a whole range of fruit and vegetables rich in vitamins and minerals appeared. Recognizing the physiological advantages provided by their consumption, their need and demand kept growing. Not only the demand for quantity, but also the demand for the types mostly known and consumed in the countryside increased. Thanks to this, in the past 30 years the various berries pushed forward in an increasing pace, owing to their high vitamin and antioxidant content, which – as confirmed by research – have a beneficiary effect on cardiovascular diseases and cancerous growths.

The seasonality of ripening is an important and non-negligible aspect of fruit consumption that makes whole-year-round continuous supply difficult. In order to eliminate this, various preservation procedures have been developed. It was recognized already at the beginning of the 20th century that the shelf-life of fruit with high (85-90%) water content can be extended by removing part of the water content. By removing part of the water content of fruits not only their shelf-life can be increased, but also their transportation and storage becomes easier, thanks to the considerably smaller volume. By adding good quality concentrates, even poorer quality juices can be improved, thus increasing their nutritional value. Today the most widely used fruit juice preservation process is multi-stage evaporation. By the application of this preservation process the concentrates can be stored long without refrigeration. The disadvantage of evaporation concentration is that often the quality of the newly reconstituted fruit juice is not adequate due to thermal damages suffered during the concentration technology.

The increasing crowdedness of the market and growing consumer demand requires manufacturing products that are gently processed, therefore of higher original valuable material content. It appears today that in order to preserve the pleasure value and positive physiological properties of raw fruit various membrane technology processes are the most suitable procedures. Traditional membrane filtration procedures have long been in the centre of attention as alternative preservation methods, but their usability is limited by the driving force applied during the procedures, thus these procedures can only be used for raw juice clarification and pre-concentration on an industrial scale. In contrast, there are various mass transfer membrane operations that are not limited by the applied transmembrane pressure difference and the osmotic pressure of the concentrate. However, their industrial scale spread is limited by the relatively low flux values observed in both laboratory and pilot scale.

It is a fortunate situation that in Hungary there are several berries with health benefits, however their processing and gentle preserving is not always resolved. Therefore during the experiments the concentration potential of such popular berries as currants, raspberry and elderberry, to a high dry matter content was examined using an alternative membrane technology in both laboratory and pilot scale, so with the help of the obtained results the principles of an industrial scale procedure can be worked out.

OBJECTIVES

The primary goal of the experiments was to examine the flux values and attainable dry matter content observed during membrane distillation (MD) and osmotic distillation (MD) of black and red currant, raspberry and black elderberry. Using model solutions the effects of the operation parameters and the comparability of the operations were examined. Various analytical and sensory examinations were carried out in order to compare the physical and chemical attributes of the original and the concentrated juices.

During modelling mainly the comparability of the two operations and the effects of the operational parameters were examined by using test plan measurements. Economical examination of both operations was regarded as an important goal.

In the experiments the following sub-goals were set:

a) The effect of operation parameters in case of MD and OD – with model solutions
   - examination of the concentration ability of model solutions with various concentrations
   - examination of the effect of operation parameters with the help of a test plan

b) Experiments with fruit juices
   - juice concentration of all four berries with membrane and osmotic distillation
   - examination of physical and chemical properties of the fruit juices, and of the effect of the operation parameters on the flux and on the achievable dry matter content

c) Pilot scale concentrating experiments with fruit juices
   - examination of pilot scale feasibility
   - examination of fluxes and concentrations during scale increase

d) Mathematical modelling of MD and OD
   - modelling and characterization of the permeate flux observed during the concentration experiments with the help of time constants
   - modelling of juice concentration
   - regression model setup in order to describe the effects of the operation parameters

e) Economic analysis
   - economic analysis of membrane and osmotic distillation concentration of the examined berry juices, factory scale implementation cost estimates

MATERAILS AND METHODS

During the experiments measurements were made with laboratory and pilot size devices. In laboratory size the concentration potentials of model solutions and four different berry juices were examined. The examined berries were black currant (*Titania*), red currant (*Jonkheer van Tets*), raspberry (*Glen Ample*), and black elderberry (*Haschberg*).

The purpose of the model solution experiments was to examine the applicability of the used device, in particular the applicability of the membrane module for the concentration of aqueous solution containing non-volatile components to high dry matter content. The final dry matter content attainable during the concentration of the model solution was examined. Then the effect of three different operation parameters on the permeate flux in case of both the membrane distillation (MD) and the osmotic distillation (OD) was analysed.

The same hollow fibre membrane module was used for both operations. In the module there was a MYCRODYN 020 CP 2N hydrophobic microfilter membrane with a 0.1 m^2 effective surface area.

A 2^p type test plan was prepared to examine the effects of the different operation parameters with the use of a model solution in order to analyse their results with statistical methods as well. The examined parameters for both operations were the recirculation flow rate (Q_{rec}), feed concentration (C_B), and in case of the MD the applied temperature difference (ΔT), in case of OD the operating temperature (T).

After the model solution experiments measurements were taken with berry fruit juices. The operation parameter values applied here were determined based on the results of the model solution experiments. The tests were run in laboratory and pilot scale as well. The pilot scale measurements were made at the Tolcsva site of Fitomark ’94 Ltd. on a device designed by the department of Food Engineering produced by Hidrofilt Ltd. that is suitable for both mass transfer operations. The applied MYCRODIN hydrophobic microfilter membrane had a 10 m^2 effective surface area.

Before and after the experiments analytical tests were run in order to examine the effect that concentration has on the physical and nutritional factors, and on their quantitative changes. The examined parameters were the following: water-soluble dry matter content, titratable acidity, anthocyanin content, total phenol content, sugar content, organic acid content. Furthermore sensory analysis was made to compare the sensory qualities of the commercially available, raw, and reconstituted black currant juice from pre-concentrate and from the final concentrate.

NEW SCIENTIFIC RESULTS

I. The effect of the operation parameters on the permeate flux was examined with laboratory membrane distillation experiments with the help of sugar solutions. The examined parameters were:

the applied temperature difference (ΔT), the recirculation flow rate (Q_{rec}), and feed concentration (C_B).

Based on the results within the examined intervals the following objective function was set up:

$$J_{MD} = a'_{0_{MD}} + a'_{1_{MD}} \Delta T + a'_{2_{MD}} Q_{rec} + a'_{3_{MD}} \Delta T Q_{rec} + a'_{4_{MD}} Q_{rec} C_B \text{ , kg/(m}^2\text{h)}$$

where $a'_{0_{MD}} = 0{,}593$, $a'_{1_{MD}} = 0{,}106$, $a'_{2_{MD}} = 0{,}007$, $a'_{3_{MD}} = -0{,}002$ és $a'_{4_{MD}} = -0{,}0004$

$$10 \le \Delta T \le 20\ ^\circ C, \qquad 20 \le Q_{rec} \le 40\ L/h$$

under which it was determined that in case of MD both the applied temperature difference, and the recirculation flow rate had a significant effect, and the influence of the feed concentration was very slight.

II. The effect of three operation parameters on the permeate flux within the given interval with laboratory osmotic distillation experiments was examined, using sugar solutions as model solutions. The examined parameters were: the applied temperature difference (ΔT), the recirculation flow rate (Q_{rec}), and feed concentration (C_B).

In case of osmotic distillation the following objective function arose:

$$J_{OD} = a'_{0_{OD}} + a'_{1_{OD}} T \text{ , kg/(m}^2\text{h)}$$

where $a'_{0_{OD}} = -0{,}334$, $a'_{1_{OD}} = 0{,}067$

$$20 \le T \le 40\ ^\circ C$$

under which it was determined that in case of OD only the applied operating temperature has a significant effect on the permeate flux.

III. Running the MD and OD tests with sugar model solutions and four different berry juices on a laboratory scale device it was established that

a.) in case of membrane distillation within the examined intervals the fruit species practically have no effect on the permeate flux and its values do not differ from the flux of the model solution at a given dry matter content.

The maximum final concentrations achieved under the circumstances of the experiments were as follows:

- Black currant: 66.3 °Brix
- Red currant: 65.7 °Brix
- Raspberry: 69.5 °Brix
- Black elderberry: 61.1 °Brix

b.) in case of osmotic distillation the fluxes of each berry juices show a significant difference compared to the model solution flux, and the following sequence was established between them:

$J_{\text{model solution}} > J_{\text{red currant}} > J_{\text{raspberry}} > J_{\text{black currant}} > J_{\text{black elderberry}}$

During the experiments the following end concentrations were reached:

- Black currant: 65.7 °Brix
- Red currant: 68.4 °Brix
- Raspberry: 71.8 °Brix
- Black elderberry: 68.7 °Brix

Based on the final concentrations it was determined that both mass transfer membrane operations are suitable for concentrating the examined berry juices.

IV. Comparing the results of black currant concentration with OD under pilot scale circumstances with the flux values obtained under laboratory scale circumstances it was determined that a higher flux value was achieved at laboratory scale. The reason for the lower pilot scale flux was the smaller driving force, which is the result of the purity of the used salt. While at laboratory scale $CaCl_2$ of analytical purity was used for preparing the osmotic solution, which thus was in each case of 65-70 °Brix concentration, at pilot scale in turn the saline solution was prepared from industrial $CaCl_2$ of 77-80% purity, of which the initial concentration was 60.7 °Brix. Thanks to this the obtained pilot scale results converge more with the industrial scale realization.
Despite the lower flux during the pilot scale tests concentration of the black currant juice to a 63.2 °Brix concentration was successful, which corresponds to the results obtained during the laboratory scale experiments. Thus from the pilot scale results it was determined that the scale increase was successful, the operation is suitable for concentration of berry juices.

V. By the analytical examination of several nutritional parameters of the produced concentrates it was determined that under the applied operation parameters both mass transfer membrane operations retain acids, sugars, anthocyanins and other phenolic compounds.
Based on the results of the anthocyanin content examination it was determined that in the concentration capacity sequence of the analysed fruit juices obtained during OD concentration the anthocyanin content of the fruits plays a role. It was also established that high anthocyanin content has an effect on the attainable final dry matter content in case of both membrane operations.
Based on the results of the sensory profile analysis it was established that black current juice prepared by reconstituting a concentrate made by osmotic distillation according to judges proved to

be better for taste, colour intensity and overall impression than a fruit juice made of a commercial concentrate produced by evaporation.

VI. Based on laboratory and pilot scale tests the time constants of the flux of the fruit juice concentration by the two analysed membrane operations was established, and a mathematical model was applied on them:

$$\frac{J - J_0}{J_{SS} - J_0} = 1 - e^{-\frac{t}{T_i}}$$

$$T_{i_{MD}} = 3{,}36 \cdot \left(\frac{\Delta T}{\Delta T_0}\right)^{-1{,}01} \cdot \left(\frac{Q_{rec}}{Q_{rec_0}}\right)^{-0{,}685}$$

$$T_{i_{OD}} = 1{,}02 \cdot \left(\frac{T}{T_0}\right)^{-0{,}815} \cdot \left(\frac{Q_{rec}}{Q_{rec_0}}\right)^{-0{,}214}$$

where J – J_{MD}, or J_{OD}, kg/(m^2h)
J_0– initial flux, kg/(m^2h)
J_{SS} – steady state flux, kg/(m^2h)
t – time, h
T_i – time constant, h

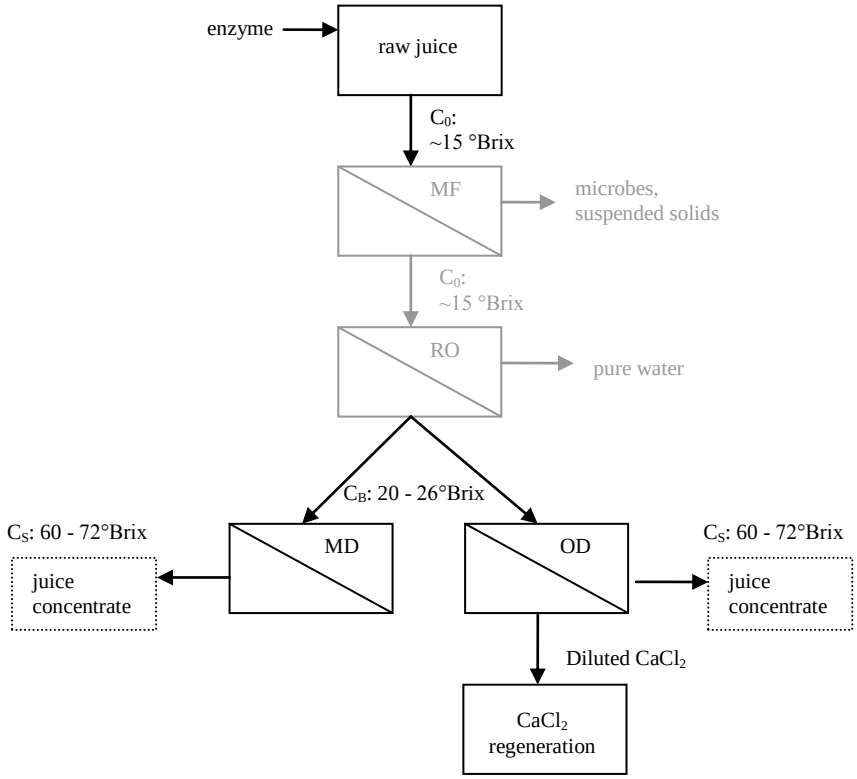
parameters: $10 \le \Delta T \le 20\ °C$ and $\Delta T_0 = 10\ °C$
$20 \le Q_{rec} \le 40\ L/h$ and $Q_{rec_0} = 20\ L/h$
$20 \le T \le 40\ °C$ and $T_0 = 20\ °C$

To determine the expected concentrate concentration (C_s) a cited (literary) mathematical model was used, and based on the laboratory test results the model parameters were determined, as a function of the concentration time (t) and the initial concentration (C_0):

$$C_s = a'' \cdot t^{b''} + C_0$$

VII. End concentration operations were developed that can be integrated into a complex membrane technology process, allowing berry juices to be concentrated to a high dry matter content (60 – 70 °Brix) gently, under low heat stress. The essence of the complex procedure is the following: the raw juice undergoes an enzymatic pectin degradation followed by a pre-treatment consisting of membrane filtration operations, then the juices can be concentrated either by MD or OD.

An economic analysis and cost estimates were prepared in order to compare the applicability of MD and OD, in case of OD also considering the costs of regenerating the osmotic solution. As a result it was determined that the production cost of 1 m^3 fruit juice concentrate in case of MD is 53.000, - HUF, in case of OD is 65.000, - HUF.



CONCLUSIONS AND SUGGESTIONS

During the research the concentration capacity of four berry juices was tested using two mass transfer membrane operations.

1. Based on the results of the laboratory experiments it was established that the analysed fruit juices behave similarly during the concentration with both methods. Nearly the same concentrate concentration with more or less difference can be obtained in the case of all four fruit juices.

2. By analysing the operation parameters it was determined that in case of MD the applied temperature difference, then the recirculation flow rate had the largest effect on the developed permeate flux. In case of OD the effect of the operating temperature is so significant that it suppresses the effect of the other two operation parameters.

3. From the sensory qualification results it was concluded that the volatile components other than water, such some of as the fragrances passes through to the permeate side. However, it can be determined from the overall impression of the judges, that a good quality, valuable product can be produced with the analysed concentration methods.

4. Based on the cost estimate results the production cost of the fruit juice concentrate production is acceptable, the sensory and nutritional quality of the manufactured product was excellent, it contains a significant quantity of antioxidant components.

Further objectives

1. In case of MD it would be worthwhile to run the pilot scale concentration tests, providing the propulsion applied at the laboratory scale analysis.
2. Further chemical analysis for other valuable nutrients is necessary to determine undoubtedly the "gentle" nature of the two operations.
3. In case of OD, beside the $CaCl_2$ it would be worthwhile to run further concentration tests with alternative salts and other soluble compounds.

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