CORVINUS
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Faculty of Food Science

USING INTEGRATED MEMBRANE PROCESSES FOR PRODUCING HEALTHY SEMIFINISH PRODUCTS

Thesis book

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PhD School/Program

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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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Introduction and goals

Nowadays consumer demands go towards natural material, healthy ingredients, and perfect quality products. These tendencies show changing of aspect of food industry and consumer. Numbers of bio-products manufacturers and bio-shops multiplied in the last few years. There are bio-shops in almost every Hungarian settlement. In folk therapy sea-buckthorn, which contains several important element, vitamins and antioxidants in higher concentration that other fruits, is discovered again. In East-Asia it has been used for 2000 years, as virtuous plant, and it is grown on 700 000 hectare.
Coffee is known as delight product, but it also has several positive physiological effects. Bio-coffee can be found in more and more bio-shops, also instant type. It is important that coffee saves its flavors during processing.
In food industry, as in other industry, energy consumption is high; same to equipment costs. Important to reduce these costs, so price of semifinished and finished products can be hold on low level. Alternative solution could be membrane processes, to take out vacuum-distillation. For these the quality of finished product can be increased, and conversion costs can be reduced.
Protection and sustainbility of environment is primary for everybody. Membrane methods are environmental.
My measurements were done in two main categories. One of my objectives was to find an alternative, economical method using nanofiltration and reverse osmosis to produce coffee concentration.
It was also my goal to concentrate sea-buckthorn juice. Valuable components of the juice were concentrated by membrane filtration. Concentration was carried out without and with prefiltration. Micro- and ultrafiltration was used for clarification, nanofiltration and reverse osmosis was used for preconcentration, and osmotic distillation for final concentration. Membrane methods are more economical than normally used vacuum-distillation.
My goal was to carry out mathematical modeling and also cost calculation of different processes.

Materials and methods

Experiments with coffee extract was done on nanofiltration membrane (64 % salt retention) and after that on reverse osmosis membrane (99,8 % salt retention), while permeate during nanofiltration contains aroma components. Active area of nanofiltration membrane was 0,047 m^2, while in case of reverse osmosis it was 0,3 m^2. Effect of different process parameters was under attention, such as temperature, transmembrane pressure difference, recirculation flow rate. Total solid content of samples was determined in oven and by refract meter.

At experiments with sea-buckthorn was carried out with heat treated juice and with juice pressed from fresh berries. Juices contained fibres, but not any other suspended materials (peel, seed). These were filtered out from the juice.
During my measurements microfiltration (0,45 µm pore size) and ultrafiltration (100 kDA) membrane was used for clarification. Precontentration of the juice was solved with nanofiltration (85 % salt retention) membrane and with reverse osmosis membrane (99,8 % salt retention). Experiment using fresh pressed juice was finished by osmotic distillation (0,2 µm pore size).
Following analytical assays were done: total solid content, viscosity, acid content, pH value, total phenol content, antioxidant capacity.

Results

Producing high quality products is important in food industry and in the market.
During the experiments my main objectives were to produce healthy semi finished products, concentrates in an economical way.
Nanofiltration (NF) and reverse osmosis (RO) were used for coffee experiments. It was established that both membrane procedure are able to use for coffee concentration, but based on cost calculation, nanofiltration was chosen.
Concentration of seabuckthorn with nanofiltration and reverse osmosis without using any type of prefiltration was not successful, because the membranes were fouled so fast, it was not able to reset the initial pure water flux of the membranes. It can be also told about 0,45 µm pore size microfiltration membrane, which was used for prefiltration. The juice was clear, and it could be used for further experiments, but cleaning of the membrane was so difficult.
Experiments were also carried out with juices squeezed from fresh and frozen berries. Based on these experiments it can be told, that juice from fresh berries is better for concentration.
At ultrafiltration (cut off 100 kDa) the permeate flux was low, but the membrane could be cleaned. The prefiltrated juice was concentrated with nanofiltration and reverse osmosis. Both methods were successful, so concentration was continued using osmotic distillation (OD) over 60 ref% total soluble solid content.

Total solid content of juice preconcentrated with RO after osmotic distillation was 65 ref %, that's why the complex system was carried out with these methods, and cost calculation was also done for this system.

Analytical experiments were also carried out for seabuckthorn. The total phenol content of the juice was nine time higher, while antioxidant capacity of the juice was 15 times higher after concentration, than the initial juice.

New scientific results

I. Experiments carried out for concentration of coffee extract

1. Both nanofiltration and reverse osmosis are able to concentrate coffee extratct.
   Flat sheet and spiral wound membrane were used for the experiments. NaCl retention of nanofiltration membrane was 64 %, while at reverse osmosis membrane it was 99,8 %. Both membrane increased total solid content of coffee; at it was NF 45 g/l, at RO it was 60 g/l at the end of concentration.

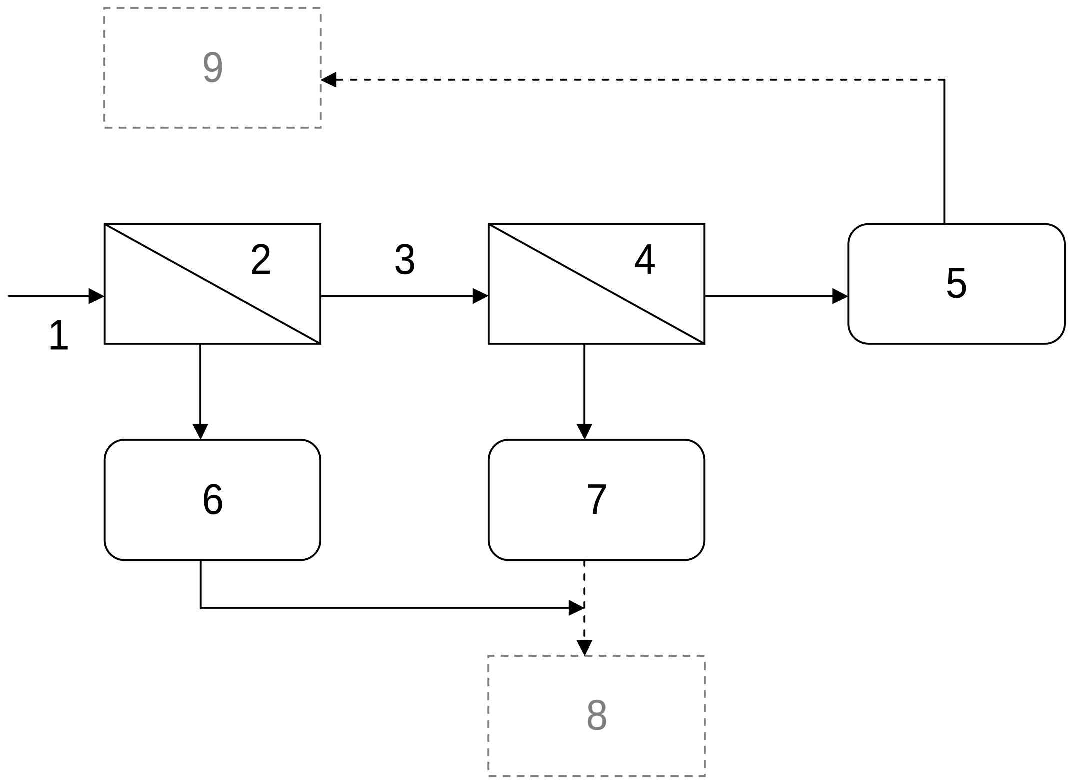
2. Based on cost calculation, it can be told, that total cost was 5 761 kHUF/year for NF, while in case of RO total cost of the system was 8 547 kHUF/year. Operation cost of reverse osmosis membrane is 10% higher than at nanofiltration.

II. Experiments carried out with sea-buckthorn

1. Without clarification sea-buckthorn is hard to be concentrated, but both with nanofiltration and reverse osmosis, total solid content was increased from 4 ref % to 16 ref%.
2. Clarification was carried out using frozen and heat treated juice and juice pressed from fresh berry with microfiltration. MF membrane was ceramic tube membrane with 0,45 µm pore size. Both type of juice fouled membrane rapidly, and it was not able to restore initial pure water flux of the membrane. With fresh pressed juice (40 $l/(m^2h)$) four times higher flux was reached, than with heat treated juice (10 $l/(m^2h)$).
3. Clarification was also done with ultrafiltration using juice pressed from fresh berries. UF membrane was a PAEK tube membrane with 100 kDa cut off. During these experiments clarified juice was reached, total solid content was 3,65 ref %.
4. After clarification prefiltration was done by nanofiltration (85 % NaCl retention, spiral wound membrane) and by reverse osmosis (99,8 % NaCl retention spiral wound membrane). Total solid content of the concentrate was 16 Brix°, of permeate was 3 Brix°, retention was

86% at nanofiltration. In case of RO, total solid content of retentate was 20,8 Brix°. Retention of RO membrane was 94,23 % for total solid content.

5. After preconcentration final concentration was carried out with osmotic distillation (0,2 µm capillary tube membrane). Concentration of nanofiltrated juice reached 62 ref%, while at RO final concentration was 64,3 ref%.
6. Based on analytical assays it can be told that total phenol content of the concentrated juice (UF-RO-OD) became nine times higher (2,5 mg/ml → 22,5 mg/ml), while antioxidant capacity was 15-times higher (20 mMAS/l →300 mMAS/l) than initial at the end of the process.
7. Based on experiments the following complex system was worked out for concentration of sea-buckthorn:



1. sea-buckthorn juice
2. MF
3. clarified juice
4. RO
5. permeate/water
6. suspended solids
7. concentrate
8. spray drying
9. wash

8. Based on cost calculation it can be told, that total cost of the system is 1 204 kHUF/year, where operation cost takes 28,6%, and installation cost takes 72,4%.

III. Mathematical model was established for coffee and sea-buckthorn experiments.

1. The van't Hoff equation was used to describe processes. Following equation was determined for calculated flux:

$$J_{számított} = \frac{\Delta p_{TM} - \Delta \pi_{számított}}{\eta \cdot R_T}$$

2. Using the model, membrane resistant was determined for both material. It was determined that total resistant is the higher at all membrane, and it is the lowest in case of clean membrane. Membrane resistant of nanofiltration membrane was always lower than reverse osmosis membrane.

Conclusion and suggestions

Membrane filtration is able to concentrate coffee extract. Based on cost calculation nanofiltration is more economical at proper flux rate. At nanofiltration 87,5 % yield can be reached. Costs are 44 % lower than reverse osmosis.

Sea-buckthorn can be concentrated with and without clarification. It is hard to concentrate the juice without prefiltration, membrane fouling was high at nanofiltration and reverse osmosis. Ultrafiltration is the best way for clarification. Further concentration (yield <80 %) can be solved with this juice. Using RO and OD combination, 65 ref % total solid content can be reached.

With these complex method valuable component (poliphenol content, antioxidant capacity) of sea-buckthorn can be increased to 9-15 times higher.

Total cost of above mentioned system is 1 204 kHUF/year, from which 60 % is installation cost, and 40 % is operation cost.

Coffee extract experiments can be carried on with osmotic distillation and spray drying. Sea-buckthorn experiments can be followed up by spray drying experiments.

Publication joins to my thesis

Articles with impact factors

[1] **I. Vincze**, Gy. Vatai (2004): Application of nanofiltration for coffee extract concentration; Desalination, 162, p. 287-294.

[2] **I. Vincze**, É. Stefanovits-Bányai, Gy. Vatai (2006): Concentration of sea-buckthorn (Hippophae rhamnoides L.) juice with membrane separation; Separation and Purification Technology. 57, p. 455–460. ISSN 1383-5866.

[3] **I. Vincze**, É. Stefanovits-Bányai, Gy. Vatai (2006): Using nanofiltration and reverse osmosis for the concentration of seabuckthorn (*Hippophae rhamnoides* L.) juice; Desalination, Volume 200, Issues 1-3, p 528-53

[4] Á. Kozák, Sz. Bánvölgyi, **I. Vincz**e, 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

Revised articles

[5] **Vincze I.**, Vatai Gy.(2005): Homoktövis (Hippophae rhamnoides L.) lé besűrítése membránszűréssel; Membrántechnika, 2005. október, 38-47. o.

[6] **Vincze I.**, Bányainé Stefanovits É., Vatai Gy. (2006): Homoktövis (*Hippophae rhamnoides* L.) lé sűrítmény előállítása membránszűréssel; Olaj, Szappan, Kozmetika, 2006. LV. Évfolyam, 3. szám; 2006. július-szeptember; p. 90-94. HU ISSN 0472-8602

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[7] **Vincze I.**, Vatai Gy.(2004): Kávéextraktum besűrítése nanoszűréssel: modellezés és gazdaságossági vizsgálatok; XII. Membrántechnikai Konferencia, Budapest, 2004. szeptember 2. 61-66. o. ISBN 963-9319-42-2

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[8] **I.** Vincze, É. Stefanovits-Bányai, Gy. Vatai (2005): Concentration of sea-buckthorn (Hippophae rhamnoides L.) juice with membrane separation; PERMEA, Lengyelország, Polanica Zdrój; (CDROM)

[9] **I.**Vincze, É. Stefanovits-Bányai, Gy. Vatai (2006): Element composition of seabuckthorn (*Hippophae rhamnoides* L.) juice concentrated by membrane filtration, 7 th International Symposium on Metal elements in enviroment, medicine and biology, 06-08. 11. 2006. Proceedings, p. 339-342. ISBN (13) 978-973-620-238-4

[10] **I. Vincze**, É. Bánfi, Á. Kozák, Gy. Vatai (2007): From the plantation to the table: using complex membrane process for the concentration of sea buckthorn (Hippophea rhamnodies L.) juice, PERMEA 2007, Membrane Science and Technology Conference of Visegrad Countries, Siófok, Magyarország, konferencia-kiadvány (CD) ISBN 978-963-9319-69-1