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APPLICATION AND MODELLING OF COMPLEX MEMBRANE TECHNIQUES FOR PROCEEDING OF APRICOT JUICE

Thesis of PhD dissertation

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Introduction and objectives of the work

There is an increasing demand on the consumption of fruits which is the consequence of changes in the dietary habits worldwide. Fruits are the sources of vitamins and mineral substances which play an essential role in the health of the human body. Beside the quick-frozen products the so-called fruit product such as the fruit juices and fruit concentrates also provide possibilities to satisfy these demands which was produced by the application of modern technologies that keeps the original characteristics of the raw material.

The research group of the Department of Food Engineering at the Corvinus University of Budapest follows several investigations and experiments for production of different fruit concentrates from different origin (e.g. from raspberry, black currant, red currant, grapes, sour cherry, elder-berry and apricot). According to the results from these experiments it could be established that the behaviour of the fruits under the same concentration treatment is different. For this reason the necessity for studying all the raw materials separately emerged.

In this study my investigations were based on the apricot which belongs to the stone fruits. The apricot has distinct characteristics from several aspects. From this point of view it is different from the previously listed berries. It has a remarkably favourable physiological effect for the human health as well as this is one of the most delicious and popularly consumed processed fruit. The self-life of the fresh apricot is quite short. It could be stored not more than few weeks which depends on the species. The reason of that is the fast ripening and softening. To prolong its shelf-life, it is necessary to work out an alternative preservation method that retains the valuable components of the fruit.

Main objectives of my work:

- To produce an apricot juice concentrate possessing good quality with the application of combined membrane techniques at low temperature in which the loss of the valuable components would be minimized as much as possible. At the same time the high total antioxidant capacity (FRAP), total polyphenol- (FCR), total acid- and vitamin C contents would be kept and maximized.
- To determine the composition of the most effective technological set-up that provides economical production of the previously mentioned product. The correct selection of the operation parameters such as transmembrane pressure difference (Δp_{TM}), recirculation flow rate (Q_R) and temperature (T) play a role in the determination.

Materials and methods

For the laboratory and pilot scale experiments the Hungarian apricot of Gönc was used as raw material. The effectiveness of different pectin-degrading enzymes on the apricot was tested.

The most effective liquid recovery and the favourable enzyme treatment parameters were reached by the application of Pectinex YieldMASH enzyme which was used further on for the juice extraction.

Diverse membrane processes was tested in eight different complex connections. The most valuable product was provided by the following process line:

The enzyme treated fruit juice was clarified by micro- (SCHUMASIV, 0,45 μm) and ultrafiltration (37.03 I8, 100 kDa). The pre-filtered and clarified apricot juice was concentrated by nanofiltration (TS80, R_{NaCl}=80%) and reverse osmosis (ACM2, R_{NaCl}=93%) membrane to 20-25 °Brix total soluble solid (TSS) content. It was followed by the final concentration with the application of osmotic distillation and membrane distillation (MD020CP2N, hydrophobic) which gave the final 60-65 °Brix total soluble solid (TSS) content.

In each operational phase the effect of operating parameters such as transmembrane pressure difference, temperature, and recirculation flow rate were investigated.

According to my results from the preliminary experiments a cooling system was designed for eliminating the fluctuation of the temperature.

The most favourable operational parameters were chosen based on the laboratory measurements. In parallel with the determination of the most suitable order of connections and parameters experiments were also performed in pilot scale.

The composition of all samples was determined by the application of analytical assays. The following parameters were measured in the retentates and permeates: total solid content, total phenol-, vitamin C, total acid content and total antioxidant capacity.

New scientific results

The apricot fruit and the apricot juice is the source of different valuable components which are well known from their several positive physiological effects. The traditional evaporation process as the alternative possibility of the concentration destroys these valuable components in the apricot juice. At the same time the combination of membrane techniques could be applicable at low temperature as well as it is a mild concentration method.

1. Based on my experiments I worked out the base of a three step technology for the concentration of the pectin-degrading apricot juice in which the microfiltration (MF, reverse osmosis (RO) and the osmotic distillation (OD) were connected together. As a result 20-25 °Brix total soluble solid (TSS) content could be reached in case of the semi- concentrated product while 60-65 °Brix TSS content could be obtained for the final concentrated product. The final concentrate contains vitamin

C and different sugars. The antioxidant capacity and the polyphenol content are also several times higher in the final concentrate than in the original juice. It could be consumed in concentrated or in a water-diluted form as well as in a fibre-mixed form or just as the base of different fruit products.

2. Pectin-degrading enzyme treatment is essential because of the pectin content of the fresh apricot. Based on my researching work the Pectinex YieldMASH is the most effectively applicable enzyme for the enzymatic treatment of the apricot juice.

3. Laboratory experiments were performed for testing the previously chosen membrane processes in eight different connections as well as comparing their connection efficiency (Figure 18.).

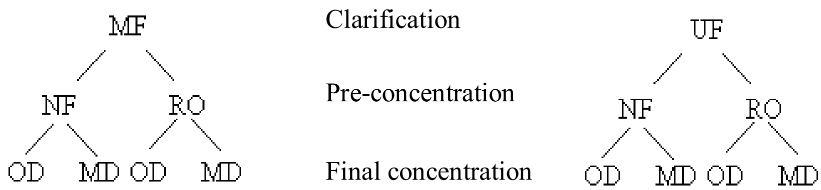

Figure 18.: Possibilities of the connections

3.1. Clarification: Microfiltration (MF) membrane (pore size: 0,45 µm, Pall) and ultrafiltration (UF) membrane (molecular weight cut off: 100 kDa, Berghof) were applied for the the clarification of the apricot juice. The flux values of the microfiltration were higher than in case of the ultrafiltration and the valuable component losses were also minimal. As a consequence the application of microfiltration is advisable.

The initial flux values were the followings in case of microfiltration at different temperatures: at 25°C the flux value was 26 L/(m^2h), at 30°C it was 38 L/(m^2h) while at 35°C the initial flux value was 65 L/(m^2h). When the flow rate increased (from 300 L/h to 500 L/h) the initial flux at 35°C increased from 19 L/(m^2h) to 65 L/(m^2h), at 30°C it increased from 13,5 L/(m^2h) to 38 L/(m^2h) while at 25°C that flux increased from15 L/(m^2h) to 26 L/(m^2h). When the flow rate was between 100 and 300 L/h there was no significant changes in the fluxes at the three temperatures.

In case of ultrafiltration the initial flux values were as followings: between 25-30°C the flux changed from 9,5 L/(m^2h) to 12 L/(m^2h) while in the temperature range between 30-35°C it increased from 12 L/(m^2h) to 16,5 L/(m^2h). When the flow rate was increased the flux showed 140% higher value.

3.2. Pre-concentration: Nanofiltration (NF) membranes and reverse osmosis (RO) membranes were applied in the pre-concentration step. 20-25 ° Brix total soluble solid (TSS) content (NaCl retention: 93%, Trisep) was reached by RO membrane while with the application of NF membrane this value was 14-18 °Brix (NaCl retention: 80%, Trisep). In case of the reverse osmosis and nanofiltration the operational parameters had no significant effects on the flux of the permeate.

3.3. Final concentration: Osmotic distillation (OD) and a membrane distillation (MD) were compared in the final concentration step. In case of osmotic distillation the operating parameters had no remarkable effect on the procedure. The initial flux increased from 0,7 kg/(m^2h) to 1,5 kg/(m^2h) comparing the membrane distillation tube module and osmotic distillation tube module.
At the final concentration step the osmotic distillation is advisable because higher flux values can be reached beside lower operation costs.

3.4. Complex system: For the production of apricot juice concentrate the complex system of microfiltration (MF) – reverse osmosis (RO) and the osmotic distillation (OD) is effectively applicable.

4. Pilot experiments were performed with the application of microfiltration (pore size: 0,45 µm pore size, Microdyn), reverse osmosis (NaCl retention: 97%, MFT Köln) and osmotic distillation (hydrophobic, pore size: 0,2 µm, Microdyn).
Pilot tests also verified the accuracy of the developed technology. Quite close retention values as well as the same flux values were measured at the same operational parameters.

5. On the basis of the mathematical modelling and simulation based on the results of the laboratory experiments using apricot juice the followings were established:

5.1. The flux of apricot juice could be described with the dynamics model in case of microfiltration and ultrafiltration. I determined the time constants of the processes based on the knowledge of the temperature and the flow rate. When the Re numbers were the same at 35°C the time constant of the filtration was T_i=0,76 h in case of microfiltration while in case of ultrafiltration this time constant was T_i=0,97 h.

5.2. For modelling of ultra- and microfiltration the resistance-in-series model was applied. In case of ultrafiltration the membrane resistance was constant ($2,94\cdot10^{12}$ 1/m) and increasing the flow rate (from 1m^3/h to 2 m^3/h) the gel-layer resistance decreased with 15 %. When the temperature increased with 5°C, the gel-layer resistance decreased with 55%.
In case of microfiltration at consant membrane resistance value ($3,18\cdot10^{11}$ 1/m) the increase of the flow rate (from 300 L/h to500 L/h) has decreased the gel-layer resistance with 90% at 35°C.

5.3. Based on the experiments I demonstrated that the van't Hoff's rule and the equations derived from that rule are suitable for the calculation of **osmotic pressure of the apricot juice**. According to the models the following parameters were calculated at 25°C for sacharose: the osmosis pressure differences were 11,6 bar at 240 L/h and 9,9 bar at 400 L/h while this value was 11,2 bar at 600 L/h. Using the save operating parameters on the basis of the experimental data the filtrate was gained at about 10 bar pressure difference which was determined from the flux curves.

5.4. The mass transfer coefficients calculated according to the Sherwood criterial equation change between $1{,}95 \cdot 10^{-5}$ and $2{,}45 \cdot 10^{-5}$ m/s while these mass transfer coefficients change between $0{,}8 \cdot 10^{-5}$ and $1{,}08 \cdot 10^{-5}$ m/s derived from the experimental results of the laboratory reverse osmosis ACM2 TRISEP membrane.
These mass transfer coefficients are in the range of the mass transfer coefficient values which could be calculated by the criterial equation found in the literature ($2{,}08 \cdot 10^{-6} – 4{,}39 \cdot 10^{-5}$ m/s).

6. Optimization: The data collection of SuperPro Designer programme was uploaded with up-to-date economical data. Calculations were also made for establishment of a plant with 1000 tons (60 days, 5 h/day) of final concentrated apricot juice. According to my calculations the plant investment will be refunded in 5 years.

Conclusions

During this research I worked out the basic of a complex process for the concentration of apricot juice.

1. Two methods: ultra- and microfiltration were used for the clarification of the apricot juice. The microfilter membrane with 0,45 μm pore size was a suitable for the pre-filtration of the apricot juice based on the operational parameters and analytical measurements.

2. As the first step of the concentration nanofiltration and reverse osmosis were applied. Approximately 20 °Brix TSS content could be gained with nanofiltration but the permeate also contained valuable components based on the analytical measurements. In case of reverse osmosis the valuable component retention of the tested membrane was above 99% and the TSS content was 25 °Brix. Membrane distillation and osmotic distillation were used for the final concentration step which gave 60-65 °Brix TSS content concentrate. According to the operating parameters and the economical calculations the application of osmotic distillation can be recommended.

3. Microfiltration, reverse osmosis and osmotic distillation were applied in pilot scale tests based on the laboratory experiments. In pilot scale the results were proper and the fluxes showed similar values as previously in case of the laboratory experiments.

4. I also realized the recycling of the by-products derived from the apricot juice production. The Hungarian Hungaricum called 'pálinka' could be produced with good quality as well as fruit jam production mixed with or without fresh fruit is also another alternative. Pasteurized or dried forms could also be used as a source of fibre.

5. Different flux values and operating parameters as well as membrane technical connections are required in case of concentration of other fruits (e.g.: black currant, red currant, sea buckthorn, elder-berry) than in case of the apricot which was the raw material of my studies. This establishment is based on the comparison of operating parameters of my membrane process measurements and the results of other research projects of the department.

6. The reverse osmosis is also suitable for the re-concentration of the dry-matter content of the ice crystals (because of its high TTS content) after cryoconcentration. These experiments were also performed but my dissertation does not contain these results.

Suggestions

1. To perform further investigations in pilot scale to eliminate problems derived from scaling up. To test the retention of the valuable components in pilot scale. To prepare an osmotic solution with the application of osmotic distillation which is easy to re-concentrate or as a diluted solution it could be utilized further on as fertilizer.

2. It may be useful for testing the shelf-life of the concentrates further on using microbiological and chemical measurements.

3. From my point of view it is essential to reduce the TTS content of the concentrates. Hereby more relishable product could be gained as well as further sweetening step would not be necessary because of the high TSS content.

4. It could be useful for making detailed analysis from the comparative study referring the concentration of different fruits which processing step is similar and could found in the literature.

Publications joined to my thesis

Articles with impact factor

1. **Fogarassy E.,** Galambos I., Bekassy-Molnar E., Vatai Gy. (2009): Treatment of high arsenic content wastewater by membrane filtration, Desalination, 240,p. 270-273. ISSN 0011-9164. (IF = 2,034)

2. **Csiszár E.,** Galambos I., Békássy-Molnár E., Vatai Gy. (2006): Ultrafiltration of humic acid containing well-water in pilot scale: new mass transfer model for transient flow regime, Desalination 199, p. 512-514. ISSN 0011-9164 (IF = 0,917)

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3. Mora Molina J., Vatai Gy., **Fogarassy E.**, Bekassy-Molnar E. (2008): Application of Membrane Filtration to Wastewater Desalination, Progress in Agricultural Engineering Sciences, A Journal of Agricultural, Environmental and Process Engineering, Vol. 4. p.: 77-92. DOI:10.1556/Progress.4.2008.5.

4. Galambos I., **Csiszár E.,** Békássy-Molnár E., Vatai Gy. (2005): Mass-transfer model for humic acid removal by ultrafiltration, Environment Protection Engineering, Vol. 31, No. 3-4., pp:145-152. ISSN 0324-8828

Full paper in international conference books:

5. **Fogarassy E.** (2008): Kajszibarack lé tükrösítése membrántechnikával, Magyar Tudományos Akadémia Agrártudományok Osztálya, Agrárműszaki Bizottság Kutatási és fejlesztési tanácskozás
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6. **Fogarassy E**., Békássyné Molnár E., Vatai Gy. (2007): Biological vinegar concentration by membrane technology, 5th International Congress on Food Technology, Thessaloniki, (poszter) Proceedings volume 2. p.: 89-93. ISBN 978-960-88557-3-1

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8. **Fogarassy E**., Kozák A., Békássy-Molnár E., Vatai Gy. (2009): Influence of the operation parameters on the concentration of apricot juice. EUROMEMBRANE International Conference. Montpellier, France. Proceedings: p.: 322

9. Kozák A., **Fogarassy E**., Rácz G., Békássy-Molnár E., Vatai Gy. (2009): Concentration and and modeling of sucrose solution and apricot juice by mass transfer processes. EUROMEMBRANE International Conference. Montpellier, France. Proceedings: p.: 345

10. Nagy Á., **Fogarassy E**., Békássyné Molnár E., Hegedüs A., Stefanovits-Bányai É., Vatai Gy. (2009): Különböző technológiai eljárások hatása kajszi sűrítmények értékes anyagaira. Lippay-Ormos-Vas Tudományos Ülésszak, Budapest. Konferencia kiadvány: p.: 192-193. ISBN 978-963-503-397-3

11. Nagy Á., **Fogarassy E**., Stefanovits-Bányai É., Hegedűs A.(2009): Miként befolyásolja a kajszibarack sűrítmények antioxidáns kapacitását a membrántechnika.16th Symposium on Analytical and Environmental Problems, SZAB, Szeged p.: 122-125. ISBN 978-963-482-975-1