Research Paper

Concentration of Colourful Wild Berry Fruit Juices by Membrane Osmotic Distillation via Cascade Model Systems

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GRAPHICAL ABSTRACT

HIGHLIGHTS

• Concentration of fruit juices by membrane osmotic distillation (MOD).
• Cascade models with sucrose solutions to shorten duration of concentration processes.
• Effectiveness of cascade systems.

ABSTRACT

Concentration of juices is vacuum distillation, which is a quick and cheap process; however, it causes thermal degradation, a serious effect on valuable components [3]. Membrane based separation techniques, including membrane osmotic distillation (MOD) seem promising [4] due to their advantages: mild operation conditions, no hazardous waste formation, easy to insert and scale-up, module systems. In MOD two membrane separation techniques, osmotic distillation (OD) and membrane distillation (MD) are combined to eliminate water from aqueous solutions through capillary membranes. In both techniques, the driving force is the water vapour pressure difference between

1. Introduction

1.1. Concentration of fruit juices by MOD

The interest towards the consumption of soft drinks, juices and syrups is growing higher and higher nowadays, thus the concentration of juices is an important technology in the food industry and the producers intend to develop new, effective technologies. The relevance of innovative techniques considerably increased in the last decade [1, 2], highlighting the possibilities of higher efficiency. The most widespread industrial application for the concentration of juices is vacuum distillation, which is a quick and cheap process; however, it causes thermal degradation, a serious effect on valuable components [3].
the two sides of the membranes. In MD it is realised by different temperatures, while in OD, an osmotic agent: concentrated salt solution \([5]\) (e.g. \(\text{CaCl}_2\), with high osmotic pressure) is applied in the secondary side. Thus, water molecules in the vapour phase are forced to pass through the membrane.

Producing concentrate from juices by MOD could be a possible way for mild water withdrawal in industrial adaptation, preserving all the essentials, heat sensitive inner contents, but with an effective transport of water vapour \([6-8]\). OD is powered by the concentration gradient; meanwhile MD is carried out, driven by the temperature difference between the liquids on the two sides of the membrane. The technical implementation of the two membrane processes shows a number of identical features. The aim of the process is to increase the driving force by a cumulative way from the two separate procedures in one system. Only water vapour can pass through the hydrophobic capillary membrane pores, while all other components remain in the concentrate \([9-14]\).

For industrial usage of MOD, two difficulties should be solved: shortening the duration of the process and regeneration of the osmotic agent. A possibility to reduce the time of concentration is to enhance the driving force, e.g. to maintain the water vapour pressure differences. Cascade systems model the concentration process in cascade systems. The efficiency of the process shows a number of identical features. The aim of the process is to reduce the time of concentration by a cumulative way from the two separate procedures in one system. Only water vapour can pass through the membrane pores, while all other components remain in the concentrate.

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1.2. Types of wild berry fruits

For the experiments, fruits of cornelian cherry (\(\text{Cornus mas} \ L.\)), blackthorn (\(\text{Prunus spinosa} \ L.\)), common white beam (\(\text{Sorbus} \ L.\)) and elderberry (\(\text{Sambucus nigra} \ L.\)) were used. The fruits of the chosen plants are shown in Figures 1 and 2, and it can be seen that they are rich in colouring components, and they have deep red, blue and black colours. All the raw materials for the experiments were collected in the Transdanubian region of Hungary, where they are considered as native species, growing there for hundreds of years. Many traditional procedures are known regarding their usage and cultivation practices. Mostly jam, stewed fruit, marmalade, syrup, sweets, and several types of soft drinks are produced from the berries of these shrubs, as well as medicinal and cosmetic products \([15]\).

![Fig. 1. The fruits of cornelian cherry (\textit{Cornus mas} \ L.) (left image) and blackthorn (\textit{Prunus spinosa} \ L.) (right image).](image1)

![Fig. 2. The fruits of common white beam (\textit{Sorbus} \ L.) (left image) and elderberry (\textit{Sambucus nigra} \ L.) (right image).](image2)

These berries, used in the experiment, are not just tasty, but are also good sources of natural antioxidants. They contain many different radical scavenger components which have health benefits.

1.3. Theoretical description of water vapour transport

The driving force of MOD procedure comes from the vapour pressure difference between the two sides of the membrane. The main characteristic of the membrane is porosity and hydrophobia, therefore only water vapour is able to go through the membrane pores, thus direct contact between the solutions is avoided (see Figure 3) \([16]\). This way all water-soluble components (aroma, colour) remain in the concentrate during the process \([17-24]\).

![Fig. 3. Water vapour transport through the hydrophobic membrane pores.](image3)

Transport of gaseous materials through a membrane (flux, \(J_w\)) can be described in general by the following equation \([21]\):

\[
J_w = K \Delta P = K(P_{w1} - P_{w2}) \quad (1)
\]

where \(\Delta P\) is the pressure difference between the two sides of the membrane (bar) and \(K\) is the overall mass transfer coefficient \((\text{kg} \ \text{m}^{-2} \ \text{s}^{-1} \ \text{Pa}^{-1})\) \([17]\). In our case, there is water vapour transport occurring, and thus we can use water vapour pressure data:

\[
P_{w1} = a_{w1} \cdot P^*_{w1} \quad (2)
\]

where \(P_{w1}\) is equivalent with the product of water activity \((a_{w1})\) and the vapour pressure of pure water \((P^*_{w1})\). Thus, the flux can be written as shown below:

\[
J_w = K \cdot (P^*_{w1} - P^*_{w2}) = K \cdot a_{w1} - K \cdot a_{w2} \quad (3)
\]

i.e. the flux can be calculated as the difference of the water vapour pressure of the two main solutions of the sides of the membrane, taking the overall mass transport coefficient, \(K\) \((\text{kg} \ \text{m}^{-2} \ \text{s}^{-1} \ \text{Pa}^{-1})\).

Overall mass transfer coefficient \((K)\) can be calculated as it is indicated in this eq. \([25, 26]\):

\[
\frac{1}{K} = \frac{1}{k_1} + \frac{1}{k_2} + \frac{1}{k_m} \quad (4)
\]

where \(k_1\) and \(k_2\) are the mass transfer coefficients in the primary and the secondary sides of the membrane, respectively, and \(k_m\) is the mass transport coefficient of the membrane itself. When concentration polarization is negligible, only the membrane resistance should be taken into account, thus \(K\) becomes equal to \(k_m\).

Considering the equations above, the value of the overall mass transfer coefficient \((K)\) for the particular process can be determined if flux \((J_w)\) is measured experimentally and water vapour pressure and water activity data are known \([27]\).
2. Materials and methods

2.1. Wild berry fruit juices

The preparation of juices was carried out in the laboratory. At first, a sufficient amount of berries was collected in their yield period. Cornelian cherry and elderberry fruit were harvested in late summer, while beam fruits in autumn and finally blackthorn in winter. The berries were found on the sunny hills of Veszprém County, in Western Hungary. The harvested berries were washed and sorted. All four kinds of fruit and their seeds have different shapes and properties, so it was inevitable to work out individual mashing and separation methods. After removing the seeds, the liquid was pressed out from the fruit pulp by a hydraulic press. The juices were filtered via 45 µm pore diameter filters and pre-treated with centrifuges by 1500 rpm, for 15 minutes. To prevent contamination, 0.5 g sodium-benzoate was added to the juices (1 dm$^3$).

2.2. Membrane module and its operation

The experiments were carried out in a hollow fibre membrane module (Microdyn), which contained 34 fibres with a length of 60 mm. The membrane material was hydrophobic polypropylene. The characteristics of the module are shown in Table 1. The scheme of the module is depicted in Figure 4.

Table 1

<table>
<thead>
<tr>
<th>Membrane module Configuration</th>
<th>Capillary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane type [producer]</td>
<td>PP [Microdyn]</td>
</tr>
<tr>
<td>Pore size (µm)</td>
<td>0.2</td>
</tr>
<tr>
<td>Wall thickness (mm)</td>
<td>0.1</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>70</td>
</tr>
<tr>
<td>Inner diameter of capillary membrane tube (mm)</td>
<td>0.8</td>
</tr>
<tr>
<td>Material of the outer cover</td>
<td>glass</td>
</tr>
<tr>
<td>Length (mm)</td>
<td>60</td>
</tr>
<tr>
<td>Number of capillary tubes</td>
<td>34</td>
</tr>
<tr>
<td>Inner diameter of the module (mm)</td>
<td>15</td>
</tr>
<tr>
<td>Membrane surface area (cm$^2$)</td>
<td>68</td>
</tr>
</tbody>
</table>

The scheme of the experimental set-up is presented in Figure 5. The membrane module itself was located in the centre of the installation. The solutions (2 and 3) were circulated by a peristaltic pump (4) through the membrane module (1). Meanwhile, the temperature and weight were measured with the help of thermometers ($T_1$, $T_2$, $T_3$, and $T_4$) and balances (8), respectively. During the procedure, the conductivity of the juice and osmotic agent were continuously measured (5) for the purpose of membrane leaking prevention.

2.3. Concentration of various fruit juices

Concentrates were prepared from one litre of each fruit juice by the MOD procedure. The primary side of the membrane was continuously heated, at 38°C, while the osmotic side was cooled to 18°C. The liquids were circulated by a peristaltic pump, through the membrane tubes and the shell side, respectively, on a counter-current way, with a flow rate of 10 l/h. Due to the water vapour transport, the weight of the juices decreased gradually, while the volume of CaCl$_2$ solution increased. As the concentration reached the demanded 50-60°Brix, the process was stopped.

2.4. Experiments with model sucrose solutions for determination of K values

The basic idea of the cascade system is to divide the separation into stages, according to the concentration gradients and to choose the best concentrate pairs, in order to reach optimal driving force. Thus, to gain basic information about the behaviour of mass transport, planned experiments were carried out with model solutions, where sucrose concentrations were in the range of 0.05-0.50 M, against 2, 4 and 6 M CaCl$_2$ of osmotic agent solutions. All five different sugar solutions were concentrated by 6 M osmotic agent, and all three types of osmotic solutions were tested by the 0.20 M model solution. The parameters of the different adjustments are illustrated in Table 2.

Table 2

<table>
<thead>
<tr>
<th>Sucrose solution (M)</th>
<th>CaCl$_2$ osmotic agent (M)</th>
<th>$T_{w}$ (°C)</th>
<th>$T_{o}$ (°C)</th>
<th>Flow rate (l/h min$^{-1}$)</th>
<th>Active membrane surface area (m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05; 0.2; 0.3; 0.4; 0.5</td>
<td>6</td>
<td>35</td>
<td>18</td>
<td>40</td>
<td>0.068</td>
</tr>
<tr>
<td>0.20</td>
<td>4</td>
<td>35</td>
<td>18</td>
<td>40</td>
<td>0.068</td>
</tr>
</tbody>
</table>

From the weight loss of sucrose solutions (amount of water transported) during the concentration process, the initial transmembrane flux was possible to be determined as the duration $t$ (min) of the procedure and the membrane surface area $A$ (m$^2$) were known. Thereafter, the initial water vapour pressure and water activity values were calculated for both solutions, and finally the overall water transport coefficients were determined for each case.

2.5. Cascade model

The stages of the cascade system were determined, considering that the concentration of the model solution would increase gradually, while the osmotic agent would be diluted. Moreover, the system should work without regeneration. In the beginning, a two-stage cascade model was set up, where the starting sucrose solution was recirculated against 4 M osmotic agent. When the concentration of CaCl$_2$ decreased to 2 M, it was replaced by a 6 M agent to increase driving force. The following stages (3 and 4) of cascade systems are summarized in Table 3, where the different levels of changes in concentration are shown as well.

The cascade systems were studied theoretically by using the overall water transport coefficients determined earlier in various initial concentrations of sucrose solutions and osmotic agents. The Gauss-Newton method was used in the calculations, which is an applied mathematical technique to solve differential equations. In our case we had to solve the following differential
\[
\frac{dV}{dt} = A \times k_n \times (P_{w1} - P_{w2}) \Delta t
\]

\[
\Delta V = A \times k_n \times (P_{w1} - P_{w2}) \Delta t
\]

where \( \Delta t \) was adjusted to 5 seconds, as an infinite step, which seemed an appropriately short time period to avoid miscalculations. Thus, a flux was calculated, which – as the process started – resulted in concentration and volume changes in both solutions, as well as in the value of \( K \). After 5 min (chosen intentionally), the time of process \( K \) value was recalculated, and a new flux was obtained for the next 5 min. The whole process was modelled in this way, step by step for all the particular stages, and finally the concentration range of sucrose solution in various cascade systems was described.

The experiments of the cascade systems were performed with 200 mL sucrose solution and 2 L of osmotic agent, and both liquids were recirculated with a 40 mL/min flow rate. The temperature of the solutions was constantly kept at the same value (35-18 °C) by heating and cooling systems. After the concentration processes of each adjustment were finished, the flux values were obtained from the weight loss of sucrose solutions, and concentration of the particular sucrose solution was determined.

### 3. Results and discussion

#### 3.1. The concentration of juices by MOD

Four types of colourful wild berry juices were concentrated by the MOD procedure, which had not been investigated so far by membrane technology. The results of the MOD process are shown in Figure 6, where the volume of the juices and the concentrations are presented as a function of time. 50-60 °Brix concentration was achieved. It can be seen that each juice has its characteristics, thus the processes can differ in time and mass transport rate. The results are depicted in Figure 6 (left, the concentration of blackthorn and white beam, while in the right diagram, concentration of cornelian cherry and elderberry juices can be seen).

Initially, 20% Brix concentration of the blackthorn and white beam juices were increased up to 50 and 60% within 270 hours, respectively. In cases of cornelian cherry and elderberry juices, the required 50 °Brix was reached within 120 hours due to the higher flux, although the initial Brix concentrations were only around 10%. In each case, the final concentrations were above the required level. As it can be seen, the procedures take quite a long time. The cascade system could be a possibility to shorten the duration of the process.

#### 3.2. Model experiments with sucrose solutions, determination of \( K \)

Experiments with sucrose solutions were performed using the parameters summarized in Table 2. The volume changes of the different sucrose solutions as a function of time are presented in Figure 7. The flux values were determined from the slope of the initial, linear part of the curve, and with the known water vapour pressure and activity data, the values of the overall water transport coefficient (\( K \)) (ms\(^{-1}\)Pa\(^{-1}\)) for each adjustment were calculated (summarized in Table 4).
3.3. Cascade system for concentration of sucrose model solution

The cascade system designed (see Table 4) was studied theoretically as well as experimentally. Theoretically it was calculated by using the water transport coefficients determined and the Gauss-Newton method, described in subchapter 2.5. While for the experiments, sucrose model solutions were used in various adjustments in the cascade systems. In both cases, the concentration was investigated from 0.05 M up to 0.5 M. Table 5 presents the results of the theoretical and the real models.

As it can be seen, the given flux value was decreasing during the operation within the particular stage, then in the next step it started (against an osmotic agent with higher concentration) from a higher level (due to the higher driving force), resulting in more effective concentration. The results obtained in the theoretical and experimental cascade models are quite similar. There is no significant deviation between the flux and concentration values.

3.4. Cascade system for juice concentration

To simulate the concentration process of fruit juices in similar cascade systems, the time courses of the one-step MOD concentration were initially studied. A water transport equation (curve) was fitted to the experimental concentration data for each juice. The fitted equation was specified in which theoretical sucrose concentration is (more or less) equivalent to the particular fruit juice (from the model point of view). The model was fitted very well on the measured data ($R^2$ was 0.999), hence sucrose solutions seemed a good model substance for fruit juices. Then the concentration of the particular sucrose solution was modelled in the cascade systems with 2, 3 and 4 stages and the flux data were calculated. Moreover, the time courses of each cascade were calculated. The changes in the juice itself (volume decrease of the juice and the concentration) for the case of blackthorn juice are presented in Figure 8, while the changes in the driving force (water vapour pressure difference between the two sides of the membrane) are shown in Figure 9.

In Figure 8, it can be seen that shorter time is necessary to achieve the same concentration level by using the cascade system compared to the traditional one-step process. Thus, time is saved during the concentration processes. Figure 10 shows the final results of theoretical cascade systems on fruit juice concentration. In the diagram, the duration of the concentration processes for the four types of juices are presented. It is observed that compared to the traditional method, the cascade systems are always more efficient. In case of cornelian cherry concentration, time can be shortened by 52 hours, which is 20 % of the whole procedure. Meanwhile, in case of the other berries, the process can be decreased up to 22, 22 and 24 hours, that is also significant, and 15-21 % change compared to the time of the total concentration, respectively.

### Table 4
The matrix for water transport coefficient ($k_w$) determined.

<table>
<thead>
<tr>
<th>CaCl$_2$ / Sucrose solutions (M)</th>
<th>0.05 M</th>
<th>0.2 M</th>
<th>0.3 M</th>
<th>0.4 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 M</td>
<td>0.75I</td>
<td>0.501</td>
<td>0.334</td>
<td>0.223</td>
</tr>
<tr>
<td>4 M</td>
<td>0.490</td>
<td>0.327</td>
<td>0.218</td>
<td>0.145</td>
</tr>
<tr>
<td>6 M</td>
<td>0.475</td>
<td>0.317</td>
<td>0.211</td>
<td>0.141</td>
</tr>
</tbody>
</table>

### Table 5
Comparison of theoretical and real cascade models.

<table>
<thead>
<tr>
<th>Sucrose concentration (M)</th>
<th>Theoretical cascade model</th>
<th>Real cascade model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2-stage</td>
<td>3-stage</td>
</tr>
<tr>
<td>0.05 - 0.154</td>
<td>0.05 - 0.11</td>
<td>0.05 - 0.09</td>
</tr>
<tr>
<td>0.154 - 0.500</td>
<td>0.11 - 0.22</td>
<td>0.09 - 0.15</td>
</tr>
<tr>
<td>0.22 - 0.50</td>
<td>0.15 - 0.26</td>
<td>0.15 - 0.26</td>
</tr>
<tr>
<td></td>
<td>0.26 - 0.50</td>
<td></td>
</tr>
<tr>
<td>6.06 - 2.79</td>
<td>5.44 - 3.17</td>
<td>5.06 - 3.32</td>
</tr>
<tr>
<td>5.60 - 0.78</td>
<td>5.77 - 3.37</td>
<td>5.55 - 3.91</td>
</tr>
<tr>
<td></td>
<td>4.55 - 0.87</td>
<td>5.31 - 3.40</td>
</tr>
<tr>
<td></td>
<td>4.04 - 0.89</td>
<td></td>
</tr>
<tr>
<td>4.04 - 0.89</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 8. The concentration of blackthorn juices by cascade and traditional MOD systems.

Fig. 9. The changes of osmotic pressure difference during blackthorn (Bt.) juice concentration.
4. Conclusion

In this work the concentration process of four colourful, berry juices was studied by MOD procedure, which is a mild membrane process preserving the valuable, heat sensitive inner components of the juices. The technology proved its ability for concentration, but it seems to be too long for industrial usage. It is important to find possibilities to reduce the time of concentration. One of the options is the cascade system, which was studied in this work by using sucrose model solutions and a simplified simulation model. It has turned out that the length of the process is possible to shorten by 15-21 % applying 2, 3 and 4 stage cascades, which means a more effective concentration. Moreover, it seems that the concentration processes can be easily modelled theoretically by this method. There is no need to carry out many measurements, yet we can easily estimate how much benefits the cascade system provides, how much the operation time is shortened, and finally, how the cascade system can be designed more reliably.

5. References


