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Concentration of Cornelian cherry fruit juice by membrane osmotic distillation

Katalin Bélafi-Bakó*, András Boór

University of Pannonia, Research Institute on Bioengineering, Membrane Technologies and Energetics, Egyetem u. 10, 8200 Veszprém, Hungary
Tel. +36-88-624726; Fax: +36-88-624038; email: bako@almos.uni-pannon.hu

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ABSTRACT

The application of membrane technologies for food and beverage processing has considerably increased recently. Emerging technologies are in the status of breakthrough. To avoid degradation of certain natural antioxidant components, loss of amino acids and discoloration in the final product, an alternative membrane procedure – reverse osmosis (RO) – succeeded against the traditional multi-stage vacuum evaporation. Due to the development and improvements, a higher feed concentration can be reached by membrane distillation (MD) and osmotic evaporation (OE). These methods are developed for concentrated fruit juice production to improve quality and reduce energy consumption. This research introduces a coupled operation of MD and OE (membrane osmotic distillation, MOD) for an effective, but still mild concentration of valuable fruit juices. Fruit juice from Cornelian cherry (*Cc*) was investigated, with special regard to the preservation of valuable compounds. To make sure that the process is able to preserve the fruit's high dietary value, antioxidant activity of the juice produced was determined and compared in each consecutive operational step. Cornelian fruits are good sources of natural antioxidants, containing many different radical scavenger components that provide protection against harmful-free radicals and, therefore, associate with lower incidence and mortality rates of cancer and heart diseases in addition to a number of other health benefits.

Keywords: Coupled membrane process; Antioxidant capacity

1. Introduction

Consumption of fruits and fruit juices is more and more important in the every-day diet of majority of the world's population. Fruit juices are often available in concentrated form which is traditionally carried out by multi-stage vacuum evaporation. Membrane separation processes offer a mild alternative for the concentration. Firstly reverse osmosis was applied but it has a significant barrier to reach higher concentrations because of osmotic pressure limitations [1,2]. Coupling osmotic evaporation and membrane distillation shows a potential to overcome the limitations, moreover enhanced product quality might be achieved [3–8].

The aim of the present paper is to apply a coupled operation of MD and OE (referred to as membrane osmotic distillation, MOD) for an effective, but still mild concentration of valuable fruit juices [9,10]. Red fruits were studied earlier, this time fruit juice from Cornelian cherry was investigated, with special regard to preservation of valuable compounds [11]. To check the ability of the proposed process to preserve the fruit's high dietary value, antioxidant activity, total phenol and anthocyanin content of the juice were determined and compared.

*Corresponding author.

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Table 1
Composition of Cornelian cherry

Values	Unit of measurement
43.78–76.75	mg/100 g vitamin C
2.215–4.690	% total acidity (as malic acid)
3.024–7.168	% TSS/acid ratio
4.220–9.960	% sugar
2.024–5.664	% reducing sugar

Fig. 1. Fruits of Cornelian cherry [17].

Cornelian cherry (*Cornus mas* L.) ranges from a deciduous shrub to a 5–7 m high tree, native to Southern Europe and Southwest Asia. It has a tiny, yellow blossom, which blooms in early spring; its fruit is red, 1–2 cm long, elongated and edible drupe, containing a single seed and ripens in the end of August [12,13]. The fruit of Cornelian cherry contains a great amount of vitamins, glucose, fructose, organic acid, tannin, pectin, fragrance- and painting materials and carotenoids [13]. Table 1 contains Cornelian cherry compounds according to Güleryüz studies [14].

The fruits can be consumed fresh and they are also used to produce jam, stewed fruit, marmalade pestil, syrup, sweets and several types of soft drinks. They are used for medicinal and cosmetic purposes as well [14–17]. Cornelian fruits are good sources of natural antioxidants, containing many different radical scavenger components that provide protection against harmful-free radicals and therefore associated with lower incidence and mortality rates of cancer and heart diseases in addition to a number of other health benefits [16]. Among natural compounds, phenolics and in particular flavonoids were found to be an important part of human diet and are considered as active principles in many medicinal plants.

2. Materials and methods

2.1. Filtration and concentration of fruit juice

The fresh, raw fruit juice from Cornelian cherry – provided by Fitomark '94 Ltd. (Tolcsva, Hungary) – was ultrafiltered by a 3DTA (Uwatech) test equipment for the clarification. The UF cell was supplied with a 0.9 l feed tank and a cylindrical-shaped membrane module, equipped with flat-sheet membrane (type polyethersulfone, nominal molecular weight cut-off 45 kDa, active membrane surface area 150 cm²), operated in a cross-flow mode at 1.2–1.5 bar and room temperature, with 10 l/h axial flow rate.

For the MOD experiments 6 M aqueous osmotic solution was prepared from calcium chloride dihydrate (Spektrum 3D) and was used in five-fold initial volume excess to prevent dilution. The membrane contactor used contained 34 polypropylene capillary membranes (Microdyn) with a total effective internal area of 68 cm², nominal pore size of 0.2 μm, 70% porosity, 0.8 mm outer and 0.6 mm inner diameter, thickness of 0.2 mm, and a length of 80 mm (Fig. 2). The solutions were pumped through the shell side (osmotic circle) and the lumen of fibers (product circle) in a counter-current mode, using peristaltic pumps at 3.0 l/h flow rate. Constant bulk temperature was maintained employing a heat exchanger on each side: 35°C and 22°C in the feed and osmotic side, respectively. The set-up can be seen in Fig. 2.

In order to quantify the water flux through the membrane, the mass loss of the reservoir comprising diluted solution was acquired over time. The content of solid matter in fruit juices was determined on the basis of the amount of total soluble solid (TSS).

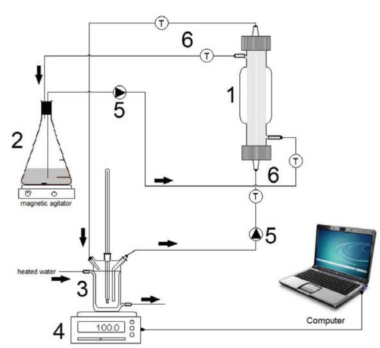

Fig. 2. The experimental set-up, (1) membrane contactor, (2) $CaCl_2$ osmotic solution, (3) Cornelian cherry juice, (4) balance, (5) pump and (6) heat exchanger.

2.2. Antioxidant activity, total phenol and anthocyanin content determination

Benzie and Strain's spectrophotometric method was used for determination of the antioxidant capacity in the samples [18]. The FRAP assay was developed to measure the ferric reducing ability of plasma (FRAP) at low pH by using 2,4,6-tripyridyl-s-triazine and $FeCl_3$ reagents in acetate buffer (pH 3.6). The absorbance was measured at 593 nm using a calibration curve for ascorbic acid (AA) and the results were expressed as mg AA/L.

The total poly-phenol content is determined by the Singleton and Rossi spectrophotometric method, with the help of Folin-Ciocalteu reagent. The base of the determination is complex making reaction between the hydroxide group of poly-phenols and the reagent. The absorbance of the blue coloured solution is proportional to the poly-phenol content of the extract. The total poly-phenol content is referred to Gallic acid [19].

The anthocyanin content is measured with a method developed by Giusti, M.M. and Wrolstad, R.E. [20]. The procedure is based on pH difference; there are two divergent buffer solutions in which the samples are dissolved. The absorbance is investigated also in two values: 520 nm and 700 nm, then the demanded content can be figured out with the help of the following equations:

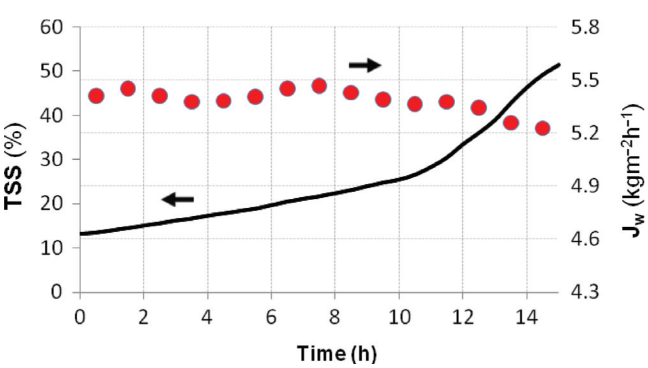

Fig. 3. Time course of concentration of Cornelian cherry fruit juice.

The absorbance of the diluted sample (A):

$$A = (A520 - A700)\,\text{pH}1.0 - (A520 - A700)\,\text{pH}\ 4.5$$

The total anthocyanin pigment concentration in the original sample (TA):

$$\text{TA}\ (\text{mg/l}) = (A \times \text{MW} \times \text{DF} \times 1000)\,/\,(\varepsilon/1)$$

3. Results

Fresh Cornelian cherry fruit juice with an initial TSS of 13.14% was clarified by ultrafiltration. A recovery factor of 78% was reached in an operation time of 2.15 h. The initial flux was 36.0 kg/m^2/h and about 44% flux reduction was observed. Final product of the UF process step was a clarified juice with a TSS of 12.59% and it was concentrated in a hollow fiber membrane module. The concentration process i.e., TSS and the variation of MOD evaporation flux as a function of time in a total recycle mode of operation is presented in Fig. 3.

The final TSS concentration, 51.45% was reached in an operation time of 15 h. Average water flux of 5.33 ± 0.12 kg/m$^{2/}$h was calculated. A slight decrease of the water flux could be observed due to the monotonous increase of the feed solution's concentration, resulting in decreasing driving force of the process. In the final part of the concentration experiments, after reaching feed TSS concentration of about 35%, rapid increase of the feed viscosity caused lower flux values.

The antioxidant capacity values, the total phenol and anthocyanin content of the samples were determined and compared. After rediluting the concentrated juices to the same TSS concentration of the fresh juice (allowing direct comparison between the samples), the analytical properties of the samples of fresh juice, UF permeate and MOD retentate were measured. The values of antioxidant capacity expressed in mg AA/L concentration, the total phenol and anthocyanin content are given in Table 2.

Although the total effective internal membrane area was only 68 cm^2, thus quite long operation time was

Table 2
Antioxidant capacity, total phenol and anthocyanin content of the samples

Sample	TSS (%)	Antioxidant capacity (mg AA/l ± SD)	Total phenol content (mg GAE/l ± SD)	Anthocyanin content (mg/l ± SD)
Fresh juice	13.14	12.77 ± 1.23	11.80 ± 1.56	139.44 ± 7.34
UF permeate	12.59	12.33 ± 1.82	11.67 ± 1.87	143.63 ± 5.29
MOD retentate	51.45 (concentrated)	11.35 ± 1.41 (rediluted)	12.38 ± 1.45 (rediluted)	163.65 ± 8.27 (rediluted)

necessary to reach high concentration level, we found that the valuable antioxidant capacity, the total phenol and anthocyanin content of the juice was preserved and thermal degradation was avoided.

4. Conclusion

Fresh juice obtained from Cornelian cherry can be considered as a valuable, highly nutritive beverage, and is characterized by high level of vitamins and antioxidant capacity. These beneficial characteristics may be preserved if mild membrane processes are applied for the concentration of the fresh juice. In this work membrane osmotic distillation (MOD) was used to concentrate the juice, where a hollow-fibre membrane contactor was the module, maintaining different bulk temperatures on each side of the hydrophobic membrane and using an osmotic salt solution as the receiving phase. The total antioxidant activity – determined by the FRAP assay – of the fresh juice, the UF permeate and final concentrates confirmed the assumptions, that the membrane technique is suitable not only for producing over 50 % TSS concentrate, but for preserving the valuable compounds of the juice as well.

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