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COMPARATIVE STUDY ON CONCENTRATION OF JUICES FROM COLOURFUL WILD BERRY FRUITS BY MEMBRANE OSMOTIC DISTILLATION

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Concentration of fruit juices by membrane osmotic distillation (MOD) was studied. For the experiments, fresh juices were obtained from colourful wild berries: cornelian cherry, blackthorn, and whitebeam, which can be considered as valuable, highly nutritive beverages and characterized by high level of vitamins and antioxidant capacity. These beneficial properties may be preserved if mild but effective, environementally-safe membrane processes are applied for the concentration. MOD is a coupled operation of membrane distillation (MD) and osmotic evaporation (OE), where a hydrophobic membrane is used, while the osmotic agent was concentrated $CaCl_2$ solution. As a result of our experiments, we found that high concentration was possible to reach in the fruit juices studied, while the flux was between 0.3 and 2.4 $lm^{-2}h^{-1}$. Comparing the analytical results of the fresh and concentrated juices, it has turned out that the antioxidant capacities were almost completely preserved during the concentration process.

Keywords: membrane processes, antioxidant capacity, cornelian cherry, blackthorn, whitebeam

Introduction

Fruit juices have been traditionally concentrated by multi-stage vacuum evaporation, resulting in a loss of fresh juice flavors, color degradation and a ”cooked” taste due to the thermal effects. The promising membrane alternatives (membrane separation processes, [1, 2]) offer potential advantages over the evaporation technique, such as improved product quality, easy scale-up and lower energy consumption, however, they are generally limited by the low flux and fouling.

Reverse osmosis (RO) is one of the membrane processes suitable for concentration of juices [3], but it cannot reach concentrations more than 25–30 °Brix with a single-stage RO system due to high osmotic pressure limitation, which is quite below the value of 45–65 °Brix for standard products obtained by evaporation. Membrane osmotic distillation (MOD) is a relatively novel process, where membrane distillation and osmotic evaporation is coupled; thus, the water vapor pressure difference across the membrane is added and higher driving force is obtained.

In our earlier works, MOD was used to concentrate juices from various fruits (e.g. apple) [4, 5], then the research was focused on colourful fruits like raspberry, black currant, and elder berry due to their higher antioxidant capacity and other beneficial features (high level of vitamins, anthocyanins... etc.) [6]. Recently, the research work was extended to other colourful berries, which are mainly wild grown and can be found in the woods of Hungary.

In this work the following fruits were studied:

cornelian cherry *(Cornus mas, L.)*
blackthorn *(Prunus spinosa, L.)*
common whitebeam *(Sorbus aria)*.

The fruit of Cornelian cherry is red *(Figure 1)*, 1-2 cm long, elongated and edible drupe, containing a single seed and ripens in the end of August [7]. The berries contain a great amount of vitamins, glucose, fructose, organic acid, tannin, pectin, fragrance- and painting materials, and carotenoids.

Figure 1: Cornelian cherry

The fruit of blackthorn *(Figure 2)*, called a ”sloe”, is a drupe 10–12 millimeters (0.39–0.47 in) in diameter, black with a purple-blue waxy bloom, ripening in autumn [8], and harvested traditionally in October or

November after the first frosts. Sloes are thin-fleshed, with a very strongly astringent flavour when fresh.

Figure 2: Blackthorn

Common whitebeam *(Sorbus aria)* is a deciduous tree [8], the fruits are scarlet berries *(Figure 3)* similar to rowan berries, but less juicy, often eaten by birds.

Figure 3: Common whitebeam

All these fruits can be consumed fresh and often used to manufacture jam, marmalade, syrups, sweets, and soft drinks. All of them are rich source of natural antioxidants, phenolics, and flavonoids.

The goal of this work was to compare the juices of these fruits from the concentration by MOD point of view on one hand, and to study the preservation level of valuable compounds (antioxidant capacity and total polyphenol content) during the concentration process.

Materials and methods

Materials

Fresh raw fruits were collected in the forests of middle-west Hungary and were stored in a freezer.

Calcium chloride dihydrate was technical grade from *Spektrum 3D*, Hungary, all other chemicals were analytical grade and purchased from *Sigma-Aldrich*, Germany.

Experimental set-up

The fresh, raw fruit juices were obtained by a hand pressing process which was then ultra-filtered by a 3DTA *(Uwatech)* test equipment for 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 cm^2), 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 mol/dm^3 aqueous osmotic solution was prepared from calcium chloride dihydrate 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 cm^2, 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. 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 10.0 l/h flow rate. Constant bulk temperature was maintained employing a heat exchanger on each side: 30°C and 17°C in the feed and osmotic side, respectively [6].

During the process the mass loss of the reservoir comprising diluted solution was acquired over time.

Analytical methods

The experiments were followed mainly by measuring the total suspended solid (TSS) of the samples taken.

Benzie and *Strain*'s spectrophotometric method was used for determination of the antioxidant capacity in the samples [9]. 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 was determined by the *Singleton* and *Rossi* spectro-photometric method, with the help of *Folin-Ciocalteu* reagent. The base of the determination is a 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 [10].

Results and discussion

Concentration of fruit juices

The concentration experiments of the juices from the three fruits (cornelian cherry, blackthorn and common whitebeam) were carried out in the MOD apparatus. The TSS values of the three juices as a function of time are presented in *Figure 4*.

As it can be seen, the fastest process was found in case of blackthorn juice, probably due to its lower initial TSS value. The runs were quite long (100-250 hours) because of the relatively small membrane surface area.

High final concentration (around 60%) was achieved for all the three juices.

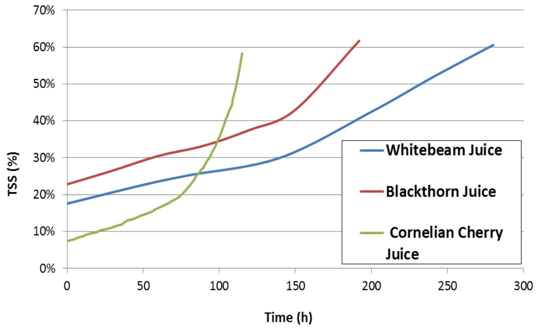

Figure 4: TSS values versus time

The flux data are summarized in *Figure 5*, where significant differences can be observed. Higher fluxes were found in case of cornelian cherry than the other two juices, which may be explained by the much lower initial TSS value in the beginning of the process.

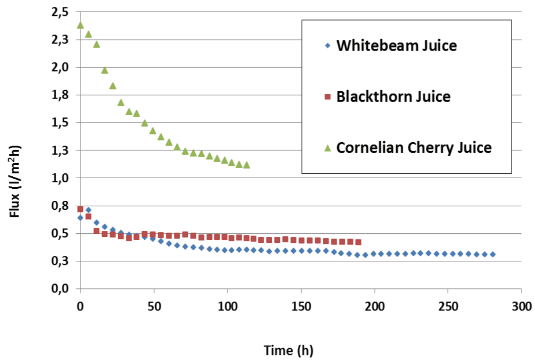

Figure 5: Flux values for the juices

The antioxidant capacity and the total phenol content of the fresh, concentrated, and rediluted juices were determined and shown in *Figure 6* and *7*.

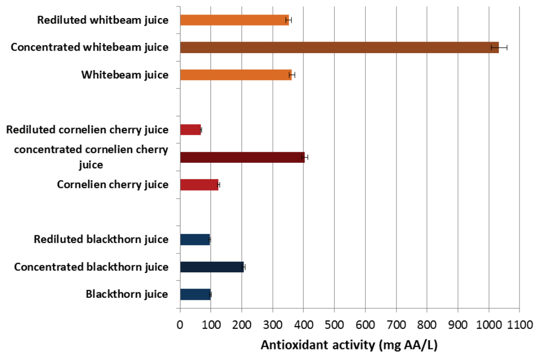

Figure 6: Antioxidant capacity of the juices

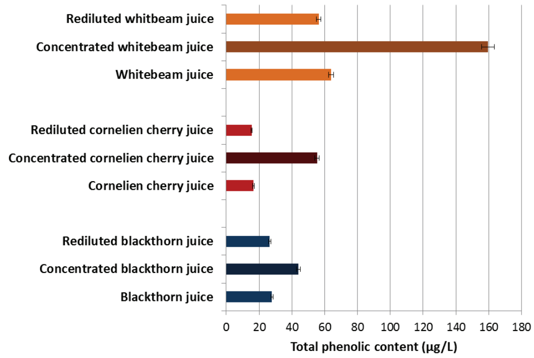

Figure 7: Total polyphenol content of the juices

It can be seen that both values for the fresh and rediluted juices were found similar, which means that it was possible to preserve majority of the valuable compounds in the juices and the concentration process can be considered mild enough.

Conclusion

In this work, concentration of three colourful juices by membrane osmotic distillation was studied. We found that around 60 TSS was achieved by the process and both the antioxidant capacity and the total polyphenol content were almost completely preserved confirming the advantages of the mild membrane process.

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