Original paper

Flavor Retention in Progressive Freeze-Concentration of Coffee Extract and Pear (La France) Juice Flavor Condensate

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Concentration of coffee extract and pear (La France) juice flavor condensate was carried out by progressive freeze-concentration (PFC) and the change in flavor profiles before and after concentration was analyzed. The results were compared with those by reverse osmosis (RO) and vacuum evaporation at 50°C (Evp). From GC/MS analysis, nine major flavor components, all heterocyclic, were detected for coffee flavors while twelve flavor components, mostly alcohols and esters, were detected for pear flavors. In Evp, almost all flavors were lost from the concentrate. In RO, some components, especially esters and alcohols, selectively permeated through the membrane so that the flavor distribution balance was changed for the reconstituted product after concentration. In PFC, the flavor distribution balance was almost unchanged for the reconstituted product after concentration although a loss was observed to some extent because of the incorporation of solutes into the ice phase. This incorporation of solutes into the ice phase was proved to be nonselective because the flavor balance in the ice phase was also unchanged from the original. This nonselective separation mechanism between the ice and the liquid phase seemed to explain the good retention of the flavor balance in PFC.

Keywords: flavor retention, progressive freeze-concentration, reverse osmosis, vacuum evaporation, coffee flavor, pear juice flavor

Introduction

There are three methods for the concentration of liquid food: evaporation, reverse osmosis, and freeze concentration. Among these three, the most widely used method is evaporation due to the low cost of the apparatus, however, the quality of the concentrated product is deteriorated in some cases because of the heat applied. By applying a vacuum, the boiling temperature can be reduced to improve the quality of the product. In this method, water is removed as vapor by boiling, thus, the energy cost makes this the most expensive among the three methods.

The second concentration method is reverse osmosis (RO). This is the more attractive option, since it operates at room temperature, causing minimal thermal damage to the product and consuming less

energy. In this method, water is removed through permeation of the membrane, which rejects the permeation of solutes. The main drawbacks of RO are the need for frequent replacement of the expensive membrane and the difficulty in cleaning it. Another drawback is the restricted concentration level (around 30 Brix) because of the limitation in applicable pressure. To improve this, osmotic evaporation has been proposed (Barbe *et al.*, 1998; Cassano *et al.*, 2003; Jiao *et al.*, 2004; Vaillant *et al.*, 2005; Cisse *et al.*, 2011; Aguiar *et al.*, 2012). In this method, the driving force is the transmembrane vapor pressure difference between the sample and the stripping solution, which causes the vapor transfer from the sample to be concentrated to the stripping solution through a membrane. For this purpose, a microporous hydrophobic membrane

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is used. Although a high concentration level is possible (up to 60 Brix) with this method, a substantial loss in flavor components has been reported (Cisse *et al.*, 2011; Aguiar *et al.*, 2012).

Among the methods of liquid food concentration, freeze concentration is reported to be the best method in terms of preserving the original characteristics of the liquid food (Deshpande *et al.*, 1982; Ramteke *et al.*, 1993). The only commercially available freeze concentration method to date is known as suspension crystallization. In this method, small ice crystals are formed in a scraped surface heat exchanger and transferred to a ripening vessel to allow the ice crystals to grow by Ostwald ripening mechanism (Huige and Thijssen, 1972). Finally, these crystals are separated from a concentrated mother solution in a washing column. This method, however, is not widely used in liquid food concentration due to the complexity of the system and the high initial capital cost, because this system is only applicable for large-scale continuous production.

As an alternative method, progressive freeze-concentration (PFC) has been proposed. In this method, only a single ice crystal is formed on a cooling surface to concentrate the solutes in a solution. A small test apparatus has been proposed with a cylindrical sample vessel in which an ice crystal grows vertically from bottom to top to concentrate the solution inside (Liu *et al.*, 1997). By using this test system, the effective partition coefficient of solutes between the ice and the liquid phases in PFC was theoretically analyzed based on the concentration polarization model (Miyawaki *et al.*, 1998; Gu *et al.*, 2005; Gunathilake *et al.*, 2013), and the importance of the operating conditions, such as ice crystal growth rate and mass transfer at the ice-liquid interface, was pointed out. As for the scale-up of PFC, the falling film system was proposed (Fleshland 1995; Hernandez *et al.*, 2009; Sanchez *et al.*, 2010; Sanchez *et al.*, 2011). In this system, an ice crystal grows on a vertically placed cooling plate on which the solution to be concentrated flows as a falling film. In spite of its simplicity, the limited liquid flow rate on the cooling surface results in poor mass transfer between the ice and the liquid phases, causing low separation efficiency, as was expected by the concentration polarization theory (Miyawaki *et al.*, 1998). In addition, the falling film system has an open air surface which leads to the loss of volatile compounds during operation.

As for a high-quality scale-up system for PFC, a closed tubular ice system with circulating flow has been developed (Miyawaki *et al.*, 2005). In this system, the high circulation flow rate and the closed system with no free surface are expected to give high separation efficiency and high-quality for concentrated products, especially in the retention of volatile compound like flavors. The major drawback of PFC involves the decreased yield with an increase in sample concentration because of the incorporation of solute into the ice phase. This could be successfully overcome by applying the partial ice-melting technique to improve the yield (Miyawaki *et al.*, 2012).

There are many liquid foods whose qualities are strongly characterized by flavors. Among those, coffee extract and pear (La

France) juice flavor condensate were chosen and their concentration was carried out in this paper. The flavor retention after concentration was compared among PFC, reverse osmosis (RO), and vacuum evaporation (Evp).

Materials and Methods

Materials Coffee extract was prepared by extracting 1 part coffee powder with 5 parts water at 90°C for 30 min and filtrated firstly with a 200 mesh filter and then by a paper filter. Pear (La France) juice flavor condensate was a by-product in vacuum concentration of pear juice and was gifted by Kakoh Fruits and Flavors, Tokyo.

Apparatus A small cylindrical test apparatus was used for the progressive freeze-concentration (Miyawaki *et al.*, 1998) of coffee extract. A stainless steel cylindrical sample vessel (96 mm in diameter, 270 mm in height) was used. The vessel was plunged into a cooling bath (NCB 3200, Tokyo Rikakikai, Tokyo) at a constant speed. The temperature of the cooling bath was kept at −15°C. The sample vessel was equipped with a 6-blade turbine type (8 cm in diameter) stirrer (SM-102, As One, Osaka) for stirring the solution at the ice liquid interface. A tubular ice system with circulating flow (MFC-10, Mayekawa, Tokyo) was used for the concentration of pear juice flavor condensate. This system was composed of two upright, jacketed cylindrical tubes (59.5 mm in diameter, 1800 mm in length) combined at the top and the bottom by tubing, circulation pump, and feed tank. A coolant, whose temperature was controlled by a controller and a refrigerator, was supplied to the jacket side of the tube to cool down the tube to form the ice layer inside.

A reverse osmosis test cell (C40B, Nitto Denko, Osaka) was used for reverse osmosis concentration. The membrane used was a flat sheet membrane (NTR 70 SWC (NaCl rejection, 99.6%), Nitto Denko, Osaka). The applied pressure was 3 MPa and the solution in the test cell was stirred near the membrane with a magnetic stirrer.

A rotary evaporator (RE 200, Yamato Scientific, Tokyo) was used with an aspirator (Gas-1, As One, Osaka) and a cooling unit (TRL 108H, Thomas Scientific, NJ, USA). The sample was kept at 50°C in a water bath (BM 200, Yamato Scientific, Tokyo).

The tentative concentration analysis for samples before concentration, concentrates, ice formed after PFC, permeate in RO, and condensates after Evp were carried out by a refractometer (APAL-1, As One, Osaka).

Flavor assay Solid phase micro extraction (SPME) was used for the flavor extraction. A 10 mL sample, mixed with 40 ppm methyl butanoate as an internal standard, was transferred into a 20 mL screw-cap vial and heated up to 45°C. Next, the SPME fiber (50/30 μ m, DVB/CAR/PDMS (Grey), Supelco Analytical, PA, USA) was inserted into the head space of the vial for the extraction and adsorption of flavor components to the SPME fiber for 15 min. Then, the SPME fiber was removed from the vial and inserted into the injection port of the gas chromatograph (GC) or gas chromatograph/mass spectroscopy (GC/MS).

Table 1. Concentration of coffee extract by progressive freeze-concentration (PFC), reverse osmosis (RO), and vacuum evaporation (Evp).

		PFC	RO	Evp
Original	Volume (mL)	700	300	300
	Conc. (Brix)	4.0	4.0	4.0
Concentrate	Volume (mL)	148	71	156
	Conc. (Brix)	12.1	19.4	10.3
Ice/Permeate/Condensate				
	Volume (mL)	545	221	118
	Conc. (Brix)	1.5	0	0.5
Conc. Ratio	Volume based	4.73	4.23	1.92
	Brix based	3.03	4.85	2.58

Flavor components of the samples were identified by GC/MS (Focus DSQ II, Thermo Scientific Japan, Yokohama) and quantified by GC (G3900, Hitachi, Tokyo). The same type of capillary column (InertCap Wax, GL Sciences, Tokyo) was used for both GC/MS and GC. The initial column temperature was 40°C, which was heated up to 220°C at a rate of 10°C/min. The GC detector was a flame ionization detector (FID) kept at 250°C.

Results and Discussion

Concentration of coffee extract Table 1 shows the results obtained for the concentration of coffee extracts using the three concentration methods. Volume-based concentration levels were 4.7, 4.2, and 1.9 fold, respectively, for PFC, RO, and Evp and accordingly, the Brix-based concentration increased from 4.0 Brix to 12.1, 19.4, and 10.3 Brix, respectively. The Brix-based concentration levels were 3.03, 4.85, and 2.58 fold, respectively, for PFC, RO, and Evp.

Flavor analysis in the concentration of coffee extract Figure 1 shows the GC chromatogram of head-space analysis for the original coffee extract, its concentrate by PFC, and the ice formed in PFC. Nine major peaks were observed for the coffee extract. The chemical components of the peaks were identified by GC/MS as listed in Table 2. Coffee flavor contained many heterocyclic compounds, which were generated in the roasting process. In PFC, the chromatograms show quite similar profiles before and after concentration. In this case, a similar profile was observed also for the ice phase. This incorporation of solute into the ice phase results in reduced yield; however, this does not appear to alter the flavor profile.

Figure 2 shows the GC chromatogram for RO concentration of coffee extract. In this case, the flavor profile in the concentrate did not appear much different from that of the original. In the chromatogram for permeate, small peaks were observed for the components that passed through the membrane. In Fig. 3, the GC chromatogram for Evp concentration of coffee is shown. In this case, most flavors were lost from the concentrate, except 2-furfuryl alcohol, and some were transferred to the condensate.

Fig. 1. GC chromatogram for original solution, concentrate, and ice in progressive freeze-concentration of coffee extract.**Table 2.** Identification of peaks in GC chromatogram of coffee extract in Fig. 1.

Peak No.	Flavor component	Retention time (min)
IS*	methyl butanoate	5.58
1	methyl pyrazine	12.44
2	2-ethyl-6-methyl pyrazine	14.43
3	2-ethyl-5-methyl pyrazine	14.56
4	2-ethyl-3-methyl pyrazine	14.79
5	furfural	15.79
6	2-furfuryl acetate	16.66
7	5-methyl-2-furaldehyde	17.43
8	2-furfuryl alcohol	18.43
9	1-furfurylpyrrole	20.63

*) Internal standard

Table 3 summarizes the relative concentration ratio of all flavor components compared with the original solution for the three concentration methods. Among the three, the concentration ratio was quite low for Evp, showing the poorest quality of the methods, although this was done at a reduced temperature of 50°C. Concentration ratios in RO differed greatly among components, while large differences were not observed among components in PFC.

As for the difference in flavor distributions among ice, permeate, and condensate, the majority of flavor components were lost or transferred into the condensate in Evp. In RO, permeation ratios differed greatly among components. In PFC, the loss of flavors into the ice phase was around 20% and was larger than RO; however, the flavor profile of the ice phase did not differ greatly from the original sample. This means that the incorporation of components into the ice phase in PFC is nonselective. This

Fig. 2. GC chromatogram for original solution, concentrate, and permeate in reverse osmosis concentration of coffee extract.

Fig. 3. GC chromatogram for original solution, concentrate, and condensate in vacuum evaporation of coffee extract at 50°C.

Table 3. Comparison of concentration ratios among the three methods in the concentration of coffee extract

Peak No.	Progressive freeze-conc. (PFC)			Reverse osmosis (RO)			Evaporation (Evp)		
	Conc.	Ice	Reconstitute	Conc.	Permeate	Reconst.	Conc.	Condensate	Reconst.
1	2.098	0.235	0.769	3.276	0.000	0.664	0.107	1.964	0.034
2	1.968	0.260	0.752	2.829	0.000	0.670	0.000	2.579	0.000
3	1.948	0.271	0.779	2.922	0.000	0.669	0.077	2.797	0.000
4	1.981	0.312	0.795	2.736	0.000	0.728	0.021	2.663	0.000
5	1.961	0.242	0.814	2.779	0.199	0.591	0.200	1.862	0.066
6	2.252	0.248	0.913	5.143	0.004	0.619	0.056	1.103	0.034
7	2.275	0.293	0.753	3.611	0.072	0.725	0.132	2.258	0.055
8	2.679	0.247	0.821	3.828	0.063	0.752	1.247	1.084	0.443
9	2.522	0.300	0.728	2.494	0.200	0.565	0.075	1.541	0.038

corresponds to the mechanism of solute incorporation into the ice phase, in which solutes are nonselectively incorporated into the space between the dendrite ice-crystal structures (Watanabe *et al.*, 2013). This nonselectivity in solute incorporation into the ice phase supports the effectiveness of the partial ice-melting technique to improve the yield in PFC (Miyawaki *et al.*, 2012). In this method, the incorporated components into the ice phase are recovered by the partial melting of ice, thereby improving the yield. The present result suggests that the quality of the recovered product by the partial ice-melting is expected to be quite similar to the original.

After concentration, the concentrates obtained were diluted with water for reconstitution based on the Brix-based concentration ratio. The flavor profiles are also shown for the reconstituted products in Table 3. Based on this, a radar chart was drawn (Fig. 4), clearly showing the difference in flavor profile balance among the three concentration methods. As compared with the original solution, PFC shows a better flavor-profile balance than RO, reflecting the

difference in the selectivity of the concentration mechanism, while Evp showed the poorest result.

Concentration of pear juice flavor condensate Table 4 shows the results obtained for the concentration of La France pear flavor condensate using the three concentration methods. Volume-based concentration levels were 3.67, 4.62, and 4.95 fold, respectively, for PFC, RO, and Evp. Accordingly, the Brix-based concentration increased from 1.0 to 2.7 Brix for PFC and to 3.5 Brix for RO, but this decreased to 0.8 for Evp. This suggests that the major components were lost from the concentrate in Evp.

Flavor analysis in the concentration of pear juice flavor condensate Figure 5 shows the GC chromatogram of head-space analysis for the original pear juice flavor condensate, its concentrate by PFC, and the ice formed in PFC. Twelve major peaks were observed for the pear juice flavor condensate, the chemical components of which were identified by GC/MS as listed in Table 5. The major components in pear condensate were low-

Fig. 4. Comparison of flavor profiles for the reconstituted product after concentration of coffee extract by progressive freeze-concentration (PFC), reverse osmosis (RO), and vacuum evaporation (Evp).

Table 4. Concentration of pear (La France) juice flavor condensate by progressive freeze-concentration (PFC), reverse osmosis (RO), and vacuum evaporation (Evp).

		PFC	RO	Evp
Original	Volume (mL)	12180	300	500
	Conc. (Brix)	1.0	1.0	1.0
Concentrate	Volume (mL)	3320	65	101
	Conc. (Brix)	2.7	3.5	0.8
Ice/Permeate/Condensate				
	Volume (mL)	8862	227	370
	Conc. (Brix)	0.4	0.5	1
Conc. Ratio	Volume based	3.67	4.62	4.95
	Brix based	2.7	3.5	-

molecular weight alcohols and esters, differing greatly from the coffee extract. In PFC, the chromatograms showed quite similar profiles before and after concentration. In this case, a similar profile was also observed for the ice phase. This incorporation of solute into the ice phase results in reduced yield; however, this loss can be recovered by applying the partial ice-melting technique.

Figure 6 shows the GC chromatogram for RO concentration of pear juice flavor condensate. In this case, the flavor profile in the concentrate differed greatly from that for the original. In the chromatogram for the permeate, small peaks were observed for the components that passed through the membrane. In Fig. 7, the GC chromatogram for Evp concentration of pear juice flavor condensate is shown. In this case, almost all of the flavors were lost from the concentrate, thus reconstitution of the concentrate was not carried out.

Table 6 summarizes the relative concentration ratio of all flavor components compared with the original solution for the three methods in the concentration of pear juice flavor condensate. Among the concentrates, the concentration ratio was quite low for Evp, showing that most of the components were lost. Concentration ratios in PFC and RO differed greatly among components because the flavor analysis by head-space SPME does not necessarily

Fig. 5. GC chromatogram for original solution, concentrate, and ice in progressive freeze-concentration of pear (La France) juice flavor condensate.

Table 5. Identification of peaks in GC chromatogram of pear (La France) juice flavor condensate in Fig. 5.

Peak No.	Flavor component	Retention time (min)
1	ethyl acetate	3.25
2	ethanol	4.32
IS*	methyl butanoate	5.28
3	butyl acetate	7.59
4	1-butanol	9.34
5	pentyl acetate	9.72
6	2-methyl-1-butanol	10.52
7	hexyl acetate	11.83
8	1-hexanol	13.20
9	3,4,5-trimethyl-4-heptanol	14.13
10	3,7-dimethyl-1,6-octadien-3-ol	15.96
11	1-octanol	16.13
12	allyl methyl sulfide	17.36

*) Internal standard

reflect the concentration distribution in the solution. As for the difference in distributions among the ice, permeate, and concentrate, a substantial part of the flavor components lost from the concentrate was trapped in the condensate in Evp. In RO, all the components, more or less, permeated through the membrane, although the permeation ratios differed among components.

In the literature, the permeation of apple aroma compounds (Alvarez, 1998), alcohols, esters, and aldehydes (Pozderovic, 2006ab; 2007) through RO membranes has been investigated, and lower molecular weight alcohols and esters were reported to permeate easily through RO membranes. In PFC, the loss of flavors into the ice phase, roughly 20%, was larger than RO; however, the flavor distribution in the ice phase was unchanged compared with

Fig. 6. GC chromatogram for original solution, concentrate, and permeate in concentration of pear (La France) juice flavor condensate by reverse osmosis.

Fig. 7. Chromatogram for original solution, concentrate, and condensate in vacuum evaporation of pear (La France) juice flavor condensate at 50°C.

Table 6. Comparison of concentration ratios among the three methods in the concentration of pear juice flavor condensate.

Peak No.	Progressive freeze-conc. (PFC)			Reverse osmosis (RO)			Evaporation (Evp)	
	Conc.	Ice	Reconstitute	Conc.	Permeate	Reconst.	Conc.	Condensate
1	3.614	0.199	0.968	1.882	0.179	0.395	0.000	0.037
2	5.939	0.204	1.353	2.632	0.410	1.713	0.005	0.853
3	2.374	0.226	1.096	1.010	0.071	0.292	0.000	0.027
4	5.406	0.203	1.171	3.006	0.095	1.285	0.001	0.784
5	1.635	0.208	0.932	0.580	0.049	0.203	0.000	0.000
6	3.916	0.205	1.098	2.116	0.018	1.014	0.000	0.573
7	1.201	0.199	1.068	0.381	0.065	0.191	0.000	0.000
8	2.276	0.239	0.933	1.001	0.077	0.751	0.001	0.837
9	1.059	0.128	0.824	0.462	0.024	0.481	0.005	0.309
10	0.954	0.266	0.654	0.512	0.022	0.453	0.000	0.821
11	1.092	0.316	0.792	0.562	0.100	0.516	0.000	0.834
12	1.490	0.212	0.946	1.378	0.106	1.119	0.018	0.956

the original sample, as was the case with the coffee extract. In the literature, good flavor retention was also reported in the concentration of Andes berry juice by PFC (Ramos *et al.*, 2005).

The flavor profiles for the reconstituted products after concentration and dilution are also shown for PFC and RO in Table 6. Based on this, a radar chart was drawn (Fig. 8), clearly showing the difference in the flavor profile balance between PFC and RO. In PFC, the flavor balance is closer to the original solution, whereas substantial losses were observed for some components in RO. These components are ethyl acetate, butyl acetate, pentyl acetate, and hexyl acetate, all of which are esters. Because of this, the flavor distribution balance was completely changed in RO. As the permeation ratios of these compounds through the membrane are not necessarily high (Table 6), these compounds might also have been lost by adsorption to the membrane and apparatus, in addition

Fig. 8. Comparison of flavor profiles for the reconstituted product after concentration of pear (La France) juice flavor condensate by progressive freeze-concentration (PFC) and reverse osmosis (RO).

to membrane permeation. In Table 6 and Fig. 8, concentrations of some components after reconstitution are apparently higher than those in the original solution. This might have occurred because of the large change in flavor profile balance, especially for RO, and the indirect nature of SPME analysis for solution analysis.

Conclusion

Concentration of coffee extract and pear (La France) juice flavor condensate was carried out by PFC, RO, and Evp, and the results were compared in terms of flavor retention. PFC showed the best quality after concentration and reconstitution, with the closest flavor distribution balance to the original solution before concentration. RO showed intermediate quality among the three methods. In this case, some of the low-molecular weight flavors were mainly lost via membrane permeation. Evp showed the poorest quality; most of the flavors were lost and some were transferred into the condensate, although it was operated at reduced pressure with a boiling point of 50°C. These differences seemed to originate from differences in the mechanism of separation of solute from the solution among the three methods. In PFC, separation and concentration are nonselective among the components, while these are highly selective in RO and Evp. Although the yield might be lower for PFC than RO, as a result of the incorporation of solutes into the ice phase, the loss is expected to be recovered by application of the partial ice-melting technique.

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