Deodorization of Fish Sauce by Continuous-Flow Extraction with Microbubbles of Supercritical Carbon Dioxide

M. SHIMODA, Y. YAMAMOTO, J. CUCUNUBA-CASTELLANOS, T. YOSHIMURA, M. MIYAKE, H. ISHIKAWA, AND Y. OSAJIMA

ABSTRACT: Volatiles were removed from fish sauce by continuous-flow extraction with microbubbles of supercritical carbon dioxide. The extraction was done at 35 °C and CO2/sample flow ratio of 0.14 and 0.29 under pressures of 10 to 30 MPa. After the treatment at a CO2/sample flow ratio, 0.29 at 10 MPa, remaining percentage ((the concentration in treated sample/that in untreated one) × 100) was 5.2% trimethylamine, 8.0% S-methyl ethanethioate, 30% dimethyldisulfide, 55 to 61% aliphatic aldehydes, and 25 to 42% carboxylic acids. The increase in CO2 flow rate improved the extraction efficiency significantly, but no effect of pressure was observed. The odor intensities of treated samples were between 1/4 and 1/8 of the untreated fish sauce.

Key Words: continuous extraction, deodorization, fish sauce, volatiles, supercritical carbon dioxide

Introduction

A PPLICATIONS OF SUPERCRITICAL CARBON DIOXIDE (SC-CO2) for the extraction of lipophilic organic compounds have been described by many authors. Huber and others (1996) and Bradley (1989) studied the SC-CO2 extraction for removal of cholesterol from anhydrous milk fat. Zabolotsky and others (1995) accomplished the SC-CO2 extraction of androstenedone and skatole from pork fat. Spanos and others (1993) reported the SC-CO2 extraction of β-carotene from sweet potatoes. SC-CO2 fluid has been applied for the extraction of vegetable oil (Taniguchi and others 1984; Aral and Saito 1986; Zhao and others 1987; Temelli 1992) as well as the separation of highly unsaturated fatty acids from fish oil (Suzuki and others 1989, 1990). In addition, the SC-CO2 extraction of hops (Daoud and Kusinski 1986), caffeine from coffee (Kurzhals 1982), and peel oil (Coppella and Barton 1987; Kalra and others 1987; Shin and others 1992) have been reported. As noted above, extractions with SC-CO2 have been applied to many kinds of natural products, which were dehydrated or low-moisture materials. The SC-CO2 extractions of lipids from materials with relatively high moisture contents (about 20%) have been described by some authors (Snyder and others 1984; Stahl and Gerard 1985; Dunford and Temelli 1997). Moisture at high-moisture content (>50%) is considered to act as a barrier for permeation of CO2 into a sample matrix, thus reducing the contact of the SC-CO2 phase with the sample solution (Dunford and Temelli 1997). To date, there have been few studies on the extraction of volatile compounds from an aqueous solution with the exception of our previous work (Shimoda and others 1994). It was found that bringing microbubbles of SC-CO2 into contact with the aqueous solution enabled the extraction of volatiles with high efficiency.

Fish sauce is a hydrolyzed product of fish and salt (3:1), which is allowed to ferment from 6 to 12 mo. People from Southeast Asia are familiar with its characteristic smell and are more concerned with the good taste it provides when blended with some local food preparations or when simply used as a sauce. However, in areas such as Japan, the United States, and Europe, people have not developed tolerance to its characteristic odor; thus, fish sauce has not become as popular as soy sauce. Deodorization of fish sauce is essential to improve its acceptability in areas outside Southeast Asia. We have reported a column treatment using aromatic porous polymer beads to remove odorants in fish sauce (Shimoda and others 1997).

The objective of this study is to remove the undesirable odorants from fish sauce using an apparatus for continuous-flow extraction with microbubbles of SC-CO2.

Materials and Methods

Continuous-flow extraction with microbubbles of SC-CO2

Continuous-flow extraction with microbubbles using SC-CO2 is accomplished with equipment shown schematically in Fig. 1. Liquid CO2 (commercial grade) and the liquid sample were both compressed with their respective plunger-type variable-speed compressors and pumped through the extraction vessel (8.0 cm i.d. × 115 cm long; 5.8 L). Liquid CO2 reached a supercritical state when the microbubbles of CO2 came out into the fish sauce.

Fig. 1—Continuous extraction system with microbubbles of supercritical carbon dioxide
Deodorization of Fish Sauce by SCFE . . .

thermo-controlled above its critical temperature from a stainless mesh fabric (pore size, about 10 μm) attached to the bottom of the extraction vessel. The dia of microbubbles of SC-CO₂ was estimated at about 220 to 400 μm, according to the density of SC-CO₂ by the following equation:

\[ \frac{4}{3}\pi R^3 \left( \rho_1 - \rho_2 \right) g = 2\pi \gamma \]

where \( R \) = radius of microbubble, \( \rho_1 \) = density of sample solution, \( \rho_2 \) = density of SC-CO₂, \( g \) = gravitational acceleration, \( r \) = radius of mesh pore, and \( \gamma \) = surface tension of sample solution. This equation represents a balance of the buoyancy of a SC-CO₂ bubble and the resultant surface tension. A photograph of microbubbles of SC-CO₂ rising in water is shown in Fig. 2. The size of SC-CO₂ bubbles were almost the same size as that calculated for the condition of 10 MPa and 35 °C. The microbubbles migrate upward in the sample while extracting volatiles. The SC-CO₂ including volatile compounds was withdrawn via a pressure-flow rate control valve and delivered to a knockout drum being maintained at 5.0 MPa. The treated sample was withdrawn via a pressure-flow rate control valve, and the dissolved CO₂ released in the CO₂ separator. The pressure and flow rate were controlled by these 2 control valves automatically. The sample was preheated to the treatment temperature using a heat exchanger placed between the sample tank and the sample pump. Furthermore, the extraction vessel was maintained at a constant temperature by circulating warmed water according to the treatment temperature.

In the present treatment, at first, fish sauce was loaded to 80% of the volume of the extraction vessel, and CO₂ was brought to the fixed pressure. Then, sample and CO₂ were both supplied at constant flow rates, respectively, while temperature, pressure, and the liquid level in the extraction vessel were maintained at fixed levels. The treatment conditions were as follows: pressure, 10, 20, and 30 MPa; CO₂ flow rate, 2.0 and 4.0 kg/h; sample flow rate, 14 kg/h; treatment temperature, 35 °C. The extraction was done once for each set of conditions. The average residence time of sample was about 20 min.

Materials

Commercial fish sauce, produced in Vietnam and held in an 18-L plastic container, was obtained from Takara Shuzo Co., LTD., Kyoto, Japan. The fish sauce had 42.0 brix soluble solids, and pH = 5.14.

Headspace gas analysis

Headspace volatiles were analyzed by a previously reported technique (Shimoda and others 1996). A 100-mL sample of fish sauce in a 300-mL Erlenmeyer flask with stopper, to which 5 μL of 1% cyclohexanol had been added as internal standard, was incubated at 40 °C for 20 min with stirring. About 100 mL of headspace gas was withdrawn with a large syringe through a column (3 mm i.d. × 10 cm) packed with 70 mg of Tenax TA resin to adsorb the headspace volatiles. For gas chromatography (GC) and GC-mass spectrometry (MS) analyses of headspace volatiles, the flow of carrier gas was stopped, and then the Tenax TA column was inserted into the GC injection port while simultaneously cryofocusing the GC column with liquid nitrogen for about 1 min. Headspace gas analysis was replicated 3 times for every sample.

GC and GC-MS analysis

Separation was achieved on a Shimadzu model GC 14A gas chromatograph equipped with a 60 m × 0.25 mm i.d. DB-Wax film (0.25 μm thick) fused silica capillary column (J & W Scientific, Folsom, Calif.) and a flame ionization detector (FID). The oven temperature was programmed from 50 to 230 °C at 3 °C/min. Injector and detector temperatures were set at 200 °C and 250 °C, respectively. A JEOL AUTO MASS 50 GC-MS programmed under the same conditions as above was used for identification of the volatile compounds (Shimoda and others 1996). Mass spectral data and retention times were compared with authentic compounds and literature data.

Sensory evaluation procedures

Subjects were asked to sniff the series of standard samples and the treated sample. The treated samples were interpolated with the standards on the basis of their odor intensities. The standard samples were prepared by stepwise double dilutions of the untreated fish sauce with saturated NaCl solution because the fish sauce has been saturated with NaCl. The odor intensities of subjective equality were estimated by a panel of 8 judges recruited among the graduate students in the laboratory of food analysis at Kyushu University.

Results and Discussion

Effect of CO₂ flow rate

The compositions of headspace volatiles before and after microbubble SC-CO₂ treatment are listed in Table 1. The microbubble SC-CO₂ treatments were carried out by the conditions of CO₂ flow rate 2.0 and 4.0 kg/h at 10 MPa to make clear the effects of CO₂ flow rate on the extraction of volatiles from fish sauce. The volatile composition of the untreated sample (control) is shown as peak-area percentages, and the figures in the columns of treated samples refer to the remaining percentages of volatiles in fish sauce, which were calculated on the basis of peak-area ratios to internal standard.

The remaining ratios of volatiles ranged from 5.2% to 73%, depending on their chemical types. Trimethylamine was extracted more than 90% of its amount because of its high volatility. Such a high removal of trimethylamine could be responsible for reducing the fishy odor of the treated fish sauce. S-Methyl ethanethiolate was extracted with high efficiency to reduce it to less than 15%. Dimethyl disulfide was also reduced to 30% to 37%. The removal of these sulfur compounds could contribute to weakening the unpleasant odor of fish sauce. Limited percentages of 2-methylpropanal and 3-methylbutanal were extracted and 55% to 73% of them remained in the treated samples. On the other hand, alkanones such as 2-butanone, 3-methyl-2-butanone, and 2-pentanone were extracted effectively, and only 12% to 40% of them were retained. Short-chain carboxylic acids such as propanoic, 2-methylpropanoic, and butanoic acid were retained to the extent of 25% to 57%, according to their hydrophobicities. The above aldehydes, ketones, and carboxylic acid acids are considered to cause unpleasant oxidation flavors (Heath and Reineccius 1986).
Sensory evaluation of deodorization

Sensory data on the odor intensity of treated fish-sauce samples are listed in Table 2. It was shown that the odor intensities of all 6 samples were weakened to less than 1/4 of the original odor intensity (P<0.05). Development of off-flavor and any change in the taste by present SC-CO₂ treatment were not observed.

Conclusions

THE CONTINUOUS-FLOW EQUIPMENT WITH MICROBUBBLES of SC-CO₂ removed the odors from fish sauce. The increase in CO₂ flow rate improved the removal efficiency, but the effect of pressure was not observed. The removal ratio of total volatiles was 56% to 59% at a CO₂/samplo ratio 0.14 and 69% at the ratio of 0.29.

References