Retardation of Volatile Aldehyde Formation in the Exhaust of Frying Oil by Heating Under Low Oxygen Atmospheres

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ABSTRACT: Volatile aldehydes were generated in the exhaust of high-oleic safflower oil during heating at 180°C by spraying water into atmospheres with four levels of oxygen concentrations (2, 4, 10, and 20%). These aldehydes were quantitatively analyzed by HPLC after the conversion to 2,4-dinitrophenyl hydrazones. Ten alkanals (C_2 through C_{10}), eight 2-alkenals (C_3 through C_{10}) and three 2,4-alkadienals (C_7, C_9, and C_{10}) were found. These aldehyde levels were found to be positively correlated with both the heating time and the atmospheric oxygen concentration. The total amounts of aldehydes were the lowest in the oil heated in an atmosphere with 2% O_2, and corresponded to 1/10 of those in the atmosphere with 20% O_2. Acrolein was not found in oils heated in the atmosphere with 2% oxygen. These results suggest that frying in atmospheres with low oxygen levels can effectively decrease the generation of volatile aldehydes in the exhaust.

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KEY WORDS: Acrolein, deep-fat frying, high-oleic safflower oil, oxidation, oxygen atmosphere, unsaturated fatty acid, volatile aldehyde.

Prolonged deep-fat frying results in poor acceptability and nutritive value owing to the thermal and oxidative reactions in the frying oil. Together with the generation of long-lived bubbles and an increase in viscocity, frying oil begins to generate a noticeable odor attributable to the various volatile decomposition products of the thermally oxidized oil. Although some of the volatiles in fried foods, formed mostly by reactions among the food components, are attractive volatile compounds from oxidized oil, they often damage the flavor of deep-fat fried foods (1). Volatile compounds formed in frying oil include aldehydes, ketones, hydrocarbons, alcohols, acids, esters, and aromatic compounds (1). Among these decomposition products, aldehydes are the most important because they are the most abundant (2) and their thresholds are lower than those of other secondary products that characterize the flavor of fried foods and oils. For instance, octanal and nonanal derived from oleic acid have a fruity and floral odor, whereas hexanal and 2-hexenal derived from linoleic and linolenic acids have an unpleasant grassy odor (3). In contrast, 2,4-decadienal derived from linoleic acid gives a desirable odor to fried foods (4). The acceptability of these aldehydes is also known to depend on their concentrations. Volatile aldehydes are known to contribute to the odor in a room where frying is taking place.

That these aldehydes are highly reactive and toxic in higher concentration has been established (5–11). In general, unsaturated aldehydes such as alkenals and alkadienals show much more severe toxicity than alkanals (5,6). Alkenals and hydroxyalkenals are known to reduce the enzymatic activity and cause hemolysis in mice (12). Some of these aldehydes are highly reactive and may be considered as secondary toxic messengers that disseminate and augment the initial free radical events (9). A number of reactive lipid aldehydes, such as 4-hydroxy-2-alkenals and malondialdehyde, have been implicated in the cytotoxic processes initiated by the exposure of biologic systems to oxidizing agents (10). Acrolein, which is produced by the thermal decomposition of fats (13), is a typical irritative volatile compound and is reported to cause repressed respirated, reducted heartbeat, and elevated blood pressure in rabbits (14). Because these volatile aldehydes are scattered in the air during deep-frying, they may have some harmful effects on the health of cooks.

Previously, we assessed the effects of atmospheric oxygen concentration on the oxidative deterioration of heated oil with (15) and without (16) water spray. The former system is commonly used as a model simulating deep-fat frying in Japan (17). We found that the deterioration of heated oil progressed nearly proportionally to the atmospheric oxygen concentration. Deep-fat frying under a low oxygen atmosphere is expected to retard not only the oxidative deterioration of frying oil but also the generation of harmful volatile aldehydes in the exhaust.

In this study, we assessed the effects of atmospheric oxygen concentration on the generation of volatile aldehydes from heated oils sprayed with water. High-oleic safflower oil was water-sprayed and heated at 180°C in atmospheres with different oxygen concentrations and modified with nitrogen (N_2) gas. The volatile aldehydes generated from heated oils were trapped in a solution of 2,4-dinitrophenylhydrazine (DNP) in 2 N HCl. The dinitrophenyl hydrazone (DNPH) of aldehydes was quantitatively analyzed by HPLC.

MATERIALS AND METHODS

Materials. Refined, bleached, and deodorized high-oleic safflower oil (PV <0.1 meq/kg; acid value, 0.04 meq/kg) with 75% oleic acid and 16% linoleic acid was provided by

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Ajinomoto Co. (Tokyo, Japan). Aldehydes were purchased from Tokyo Kasei (Tokyo, Japan), Wako (Osaka, Japan), and Aldrich (Milwaukee, WI).

Water-spraying and heating of oil. Two hundred grams of high-oleic safflower oil was placed in a 500-mL Erlenmeyer flask, water-sprayed (0.3 mL/min), and heated at 180°C for 30 h on a block heater under a blowing mixture of air and N_2 (3 L/min) as described previously (12). The oxygen concentration in the atmosphere was adjusted to 2, 4, 10, and 20%. During heating, an aliquot of oil (50 g) was periodically (6, 20, and 30 h) pipetted from the Erlenmeyer flask. Oxygen concentration in the head space of the Erlenmeyer flask was monitored by TCD-GC as described previously (12,13).

Derivatization and extraction of volatile aldehydes. Volatile aldehydes were trapped in a 2 N HCl solution that had been saturated with DNP at room temperature. The 2,4-DNP–HCl solution was replaced after 6 and 20 h. The solutions containing volatile aldehydes were allowed to stand overnight at room temperature and were then washed with distilled water. The precipitated DNPH derivatives of aldehydes were extracted with ethyl acetate. The ethyl acetate extracts were evaporated to dryness under reduced pressure and redissolved in 20 mL of ethyl acetate. The solution was diluted 20× in ethanol and filtered with a membrane filter (Chromatodisk, 45 μm; GL Sciences, Tokyo, Japan); 20 μL of the filtrate was then injected onto an HPLC column.

HPLC analysis. DNPH were analyzed on a Grand pack ODS-5NK column (4.6 × 250 mm; MASIS, Aomori, Japan) with a mixture of water and acetonitrile (80:25, vol/vol) as a mobile phase at 1.3 mL/min. The column temperature was 50°C. The DNPH were detected at 365 nm with a JASCO MD-910 photodiode array detector (Tokyo, Japan). Aldehydes were identified by the comparison of retention times and UV spectra with authentic specimens, and were quantitated using the external standard method. The recoveries of authentic aldehydes from the trap were >80%.

RESULTS

Alkanals. Figure 1 shows the changes in alkanals produced from high-oleic safflower oil during heating at 180°C with water-spray in atmospheres with four different levels of oxygen concentration. As a result, nine alkanals with 2 through 10 carbons were found. The total content of alkanals increased almost linearly with both heating time and oxygen concentration (Fig. 1). In the atmospheres with 2 and 4% O_2, acetaldehyde was dominant, whereas in the atmospheres with 10 and 20% O_2, hexanal and nonanal were dominant. They occupied approximately 55% of total alkanals in the air.

Alkenals. Figure 2 shows similar changes in the alkenals. Eight 2-alkenals with carbons 3 to 11 were found. Decenal, undecenal, acrolein, and heptenal were the main components and occupied around 80% of total alkenals in the oils heated in atmospheres of 10 and 20% O_2. Acrolein was the major component in the atmosphere with 4% O_2. Alkenals were scarcely formed in the atmosphere with 2% O_2.

Alkadienals. Figure 3 shows the changes in 2,4-alkadienals. Decadienal with a trace amount of heptadienal and nonadienal

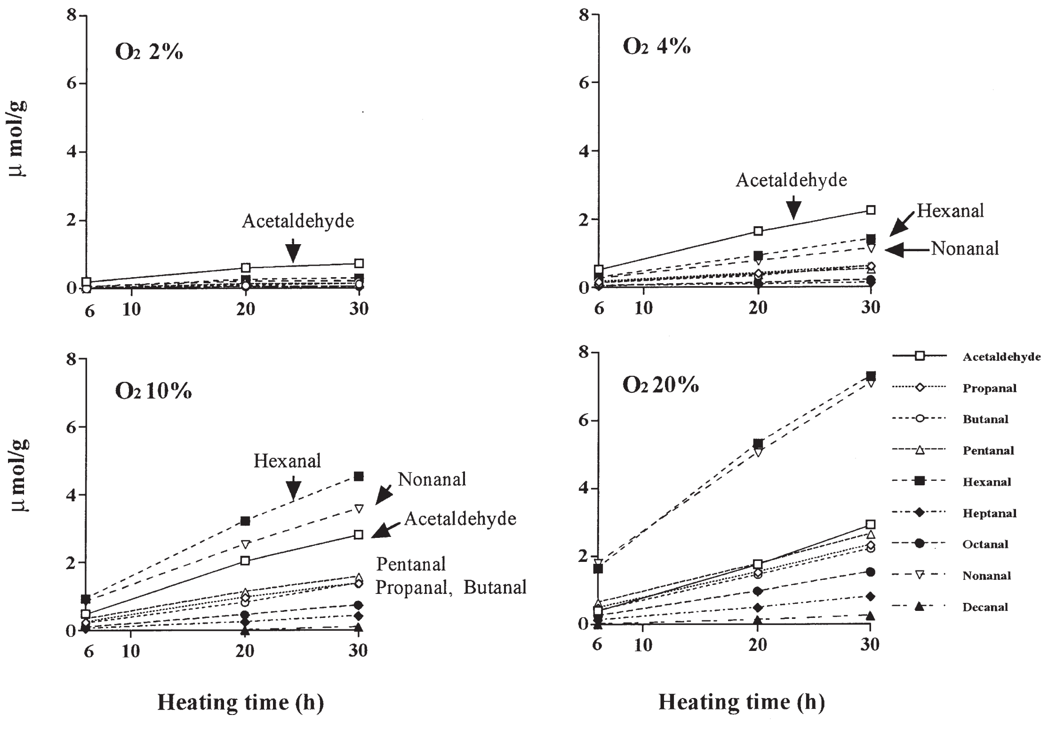

FIG. 1. Alkanals generated in the exhaust of high-oleic safflower oil heated and water-sprayed for 30 h at 180°C in atmospheres with different oxygen levels.

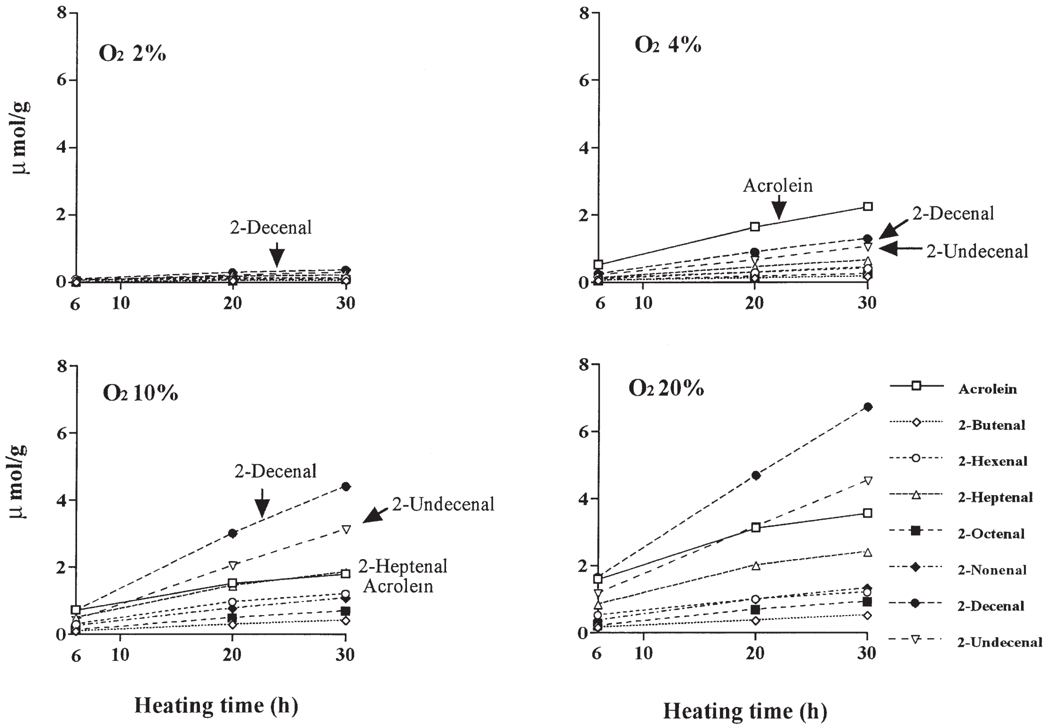

FIG. 2. Alkenals generated in the exhaust of high-oleic safflower oil heated and water-sprayed for 30 h at 180°C in atmospheres with different oxygen levels.

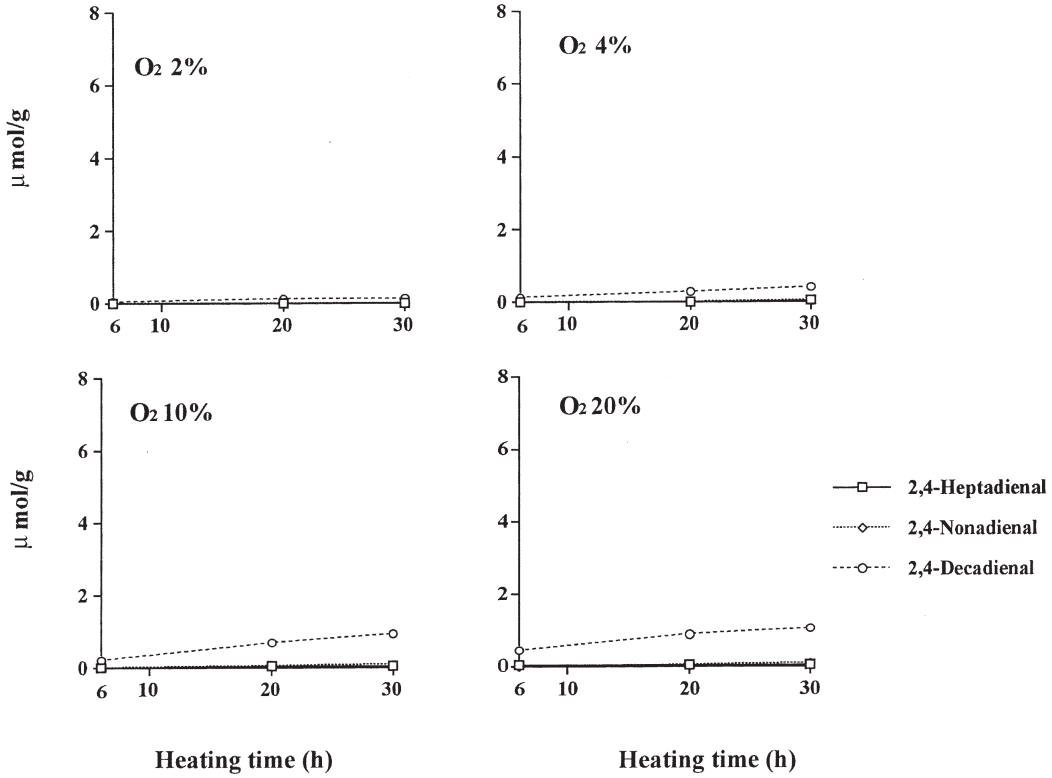

FIG. 3. Alkadienals generated in the exhaust of high-oleic safflower oil heated and water-sprayed for 30 h at 180°C in atmospheres with different oxygen levels.

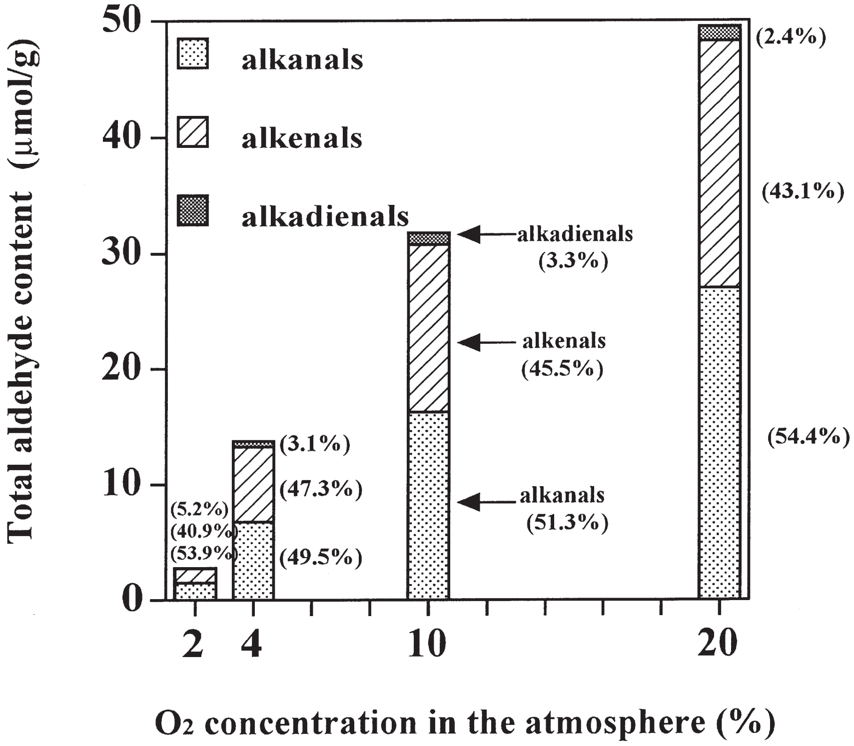

FIG. 4. Total aldehydes generated in the exhaust of high-oleic safflower oil heated for 30 h and water-sprayed at 180°C in atmospheres with different oxygen levels. Values in parentheses show the percentage of each aldehyde class.

was found in this class. Decadienal increased with heating time and oxygen concentration; however, there was far less than the amount of alkanals and alkenals. The amount of 2,4-decadienal formed after heating for 30 h in the atmosphere with 20% O_2 was 1 μmol/g.

Total amount of aldehydes. Figure 4 shows the sum of three types of aldehydes in high-oleic safflower oil during heating at 180°C for 30 h in atmospheres with different levels of oxygen. The total amounts of aldehydes increased linearly with oxygen concentration, in accordance with the changes in carbonyl value, acid value, and the content of polar materials in heated oil as reported previously (15,16). On the other hand, the percentages of each aldehyde class were almost all consistent, independent of the oxygen concentration in the atmosphere. Alkanals and alkenals were the main components, making up 95% of all aldehydes. Furthermore, the total amount of volatile aldehydes was about one-fifth that of carbonyl compounds in the frying oil. Oxygen concentration had a definite effect on the retardation of volatile aldehyde formation.

Suggested origin of volatile aldehydes. Volatile aldehydes are generated mainly from frying oil *via* β-scission of alkoxy radicals formed by the homolytic cleavage of FA hydroperoxides (2). The major aldehydes identified in the exhaust of heated high-oleic safflower oil were grouped according to their origin (oleic acid, linoleic acid, or glycerol) as shown in Figure 5. Among the alkanals, octanal, nonanal, and decanal are derived from oleic acid, whereas acetaldehyde, pentanal, and hexanal are derived from linoleic acid (2,18). As for unsaturated aldehydes, 2-decenal and 2-undecenal are derived from oleic acids, whereas 2-heptenal, 2-octenal, 2-nonenal, and 2,4-decadienal are derived from linoleic acid (2,18). In the atmosphere with 20% O_2, the sum of aldehydes derived from oleic acid (octanal, nonanal, decanal, 2-decenal, and 2-undecenal) were comparable to those from linoleic acid (acetaldehyde, pentanal, hexanal, 2-heptenal, 2-octenal, 2-nonenal, and 2,4-decadienal). On the other hand, in the atmosphere with 4% O_2, the total amounts of aldehydes derived from linoleic acid were greater than those derived from oleic acid.

The ratio of oleic acid (75%) in high-oleic safflower oil was much higher than that of linoleic acid (16%). The patterns of aldehydes generated from high-oleic safflower oil during heating at 180°C at different oxygen concentrations illustrate the importance of linoleic acid as a precursor of volatile aldehydes, especially in atmospheres with low oxygen concentrations. The selective decrease of linoleic acid in heated high-oleic safflower oil has been described previously (16) and is in accord with these observations.

Among the major aldehydes, only the origin of acrolein is arguable. The thermolysis of glycerol at a higher temperature (230°C) was suggested by Nawar (13). In the present study this is not the case because no acrolein was formed in the atmosphere with 2% oxygen. The formation from linolenate (18) could not be determined from the FA composition of high-oleic safflower oil. Acrolein was formed from trilinolein

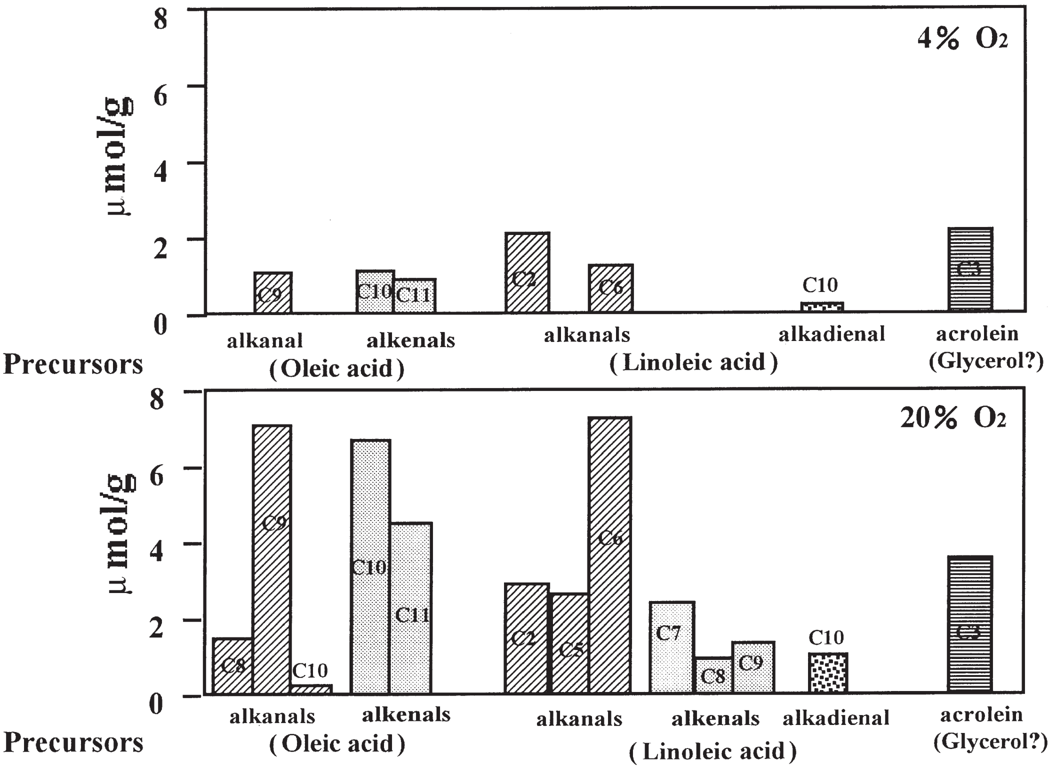

FIG. 5. Grouping of volatile aldehydes by origin generated from high-oleic safflower oil during heating and water-spraying for 30 h at 180°C in atmospheres with 4 and 20% O_2.

but not from methyl linoleate, which (18) may suggest its formation from a glycerol moiety by oxidation under frying conditions. The amount of acrolein from the high-oleic safflower oil heated in the atmosphere with 4% O_2 was 2.0 μmol/g. In the atmosphere with 20% O_2, acrolein increased to 3.7 μmol/g, but the increase was not significant compared with other aldehydes derived from oleate or linoleate oxidation. These observations suggest that the mechanism for acrolein formation may be different from other aldehydes derived from the oxidation of unsaturated FA. The hydrolysis of TAG is suggested to accelerate the formation of acrolein in frying oils (19). In conclusion, heating oil in atmospheres with low oxygen concentrations retards the generation of volatile aldehydes in the exhaust. Because these aldehydes (especially acrolein) are highly toxic (5,7,8,14), frying under a low oxygen concentrations can retard aldehyde formation in addition to the deterioration of the frying oil.

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