The Effect of Oxygen Concentration on Oxidative Deterioration in Heated High-Oleic Safflower Oil

Mariko Fujisaki[a,*], Satoshi Mohri[b], Yasushi Endo[a], and Kenshiro Fujimoto[a]

[a]Graduate School of Agricultural Science, Tohoku University, Aoba, Sendai 981-8555, Japan,
and [b]Miyagi Prefectural Institute of Technology, Izumi, Sendai 981-3206, Japan

ABSTRACT: High-oleic safflower oil was heated at 180°C in atmospheres with four levels of oxygen concentrations (2, 4, 10, and 20%) modified with nitrogen gas, to assess the effects of atmospheric oxygen concentration on the oxidative deterioration of deep-frying oils. Acid value, carbonyl value, polar materials, linoleic acid, tocopherol contents, and oxidative stability were measured to evaluate the quality of heated oils . These values were found to be correlated with both heating time and oxygen concentration. Acid and carbonyl values and polar material content of oils heated at oxygen concentrations of 2 and 4% were lower than those at 10 or 20%. On the other hand, linoleic acid and tocopherols were hardly reduced in oils after heating for 30 h at 2% O_2, whereas they were decomposed according to the oxygen concentration and heating time. Oxidative stability was well maintained in oils heated at 2 and 4% O_2. These results suggest that the oxidative deterioration of heated high-oleic safflower oil depends on oxygen concentration.

Paper no. J9425 in *JAOCS 77*, 231–234 (March 2000).

KEY WORDS: Acid value, carbonyl value, deep-fat frying, high-oleic safflower oil, oxidation, polar material, tocopherol, unsaturated fatty acid.

Continual heating of fats and oils, such as by deep-fat frying, causes oxidative deterioration, which produces undesirable flavor and antinutritional changes. Changes occurring during deep-fat frying are rather complex because many compounds in foods such as water and lipophilic substances move to the fat layer to interact with fats (1) . However, the oxidative deterioration of fats is the most important reaction because fats are heated at high temperatures for a prolonged time in the presence of air. The oxidation of fats at higher temperatures proceeds in a fashion similar to autoxidation at room temperature by the free radical mechanism. However, there is a distinct discrepancy in that hydroperoxides, which are the primary oxidation products in autoxidized oils, do not accumulate in frying oils because of the instability of hydroperoxides at frying temperature. Although the occurrence of oxygen is essential for oxidative deterioration of fats and oils, the oxygen level is seldom a limiting factor in autoxidation of fats and oils at room temperature because the combination of an alkyl radical with atmospheric oxygen ($^3O_2$) causes a very rapid reaction (2,3). In order to retard autoxidation, the oxygen level is reported to be less than 2% (2,3). However, at frying temperature, hydroperoxides spontaneously decompose to form dimers and volatile products. The short-lived free radicals are involved in these reactions as intermediates. Therefore, oxygen concentration is suggested to be more important in regulating the oxidative deterioration of frying oil than autoxidation at room temperature. In this study, we assessed the effects of atmospheric oxygen concentration in heated fats and oils on oxidative deterioration. High-oleic safflower oil was heated at 180°C at different oxygen concentrations modified with nitrogen (N_2) gas. Deterioration was evaluated by measuring chemical characteristics, polar materials formation, residual fatty acids in triacylglycerols, tocopherol contents, and oxidative stability.

MATERIALS AND METHODS

Materials. Commercially refined, bleached, and deodorized high-oleic safflower oil [peroxide value < 0.1; acid value (AV), 0.04] with 77% oleic acid and 17% linoleic acid was provided by Ajinomoto Co. (Tokyo, Japan).

Heating of oil. Two hundred grams of high-oleic safflower oil was placed in a 500-mL Erlenmeyer flask and heated by blowing in a mixture of air and N_2 at 180°C for 30 h and using a block heater, as shown in Figure 1. 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, 30 h) pipetted from the Erlenmeyer flask and then immediately cooled for lipid analyses. Oxygen concentration in the head space of the Erlenmeyer flask was determined by a Shimadzu GC-4A gas chromatograph (Kyoto, Japan) equipped with a thermal conductivity detector (TCD) and a molecular sieve 5A-packed column (3.0 mm × 2 m). The column temperature was 80°C, and the injection and detector temperatures were 90 and 100°C, respectively. Heating under each condition was performed in triplicate and the results were shown in figures as averages with SD.

Analyses of heated oils. AV was determined by alkali titration according to the standard methods of the Japan Oil Chemists' Society (JOCS) (4). Carbonyl value (CV) was determined by the 2,4-dinitrophenylhydrazine method with triphenylphosphine pretreatment (5).

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*To whom correspondence should be addressed at the Graduate School of Agricultural Science, Tohoku University, 1-1 Tsutsumidori-Amamiyamachi, Aoba, Sendai 981-8555, Japan. E-mail: fujisaki@biochem.tohoku.ac.jp

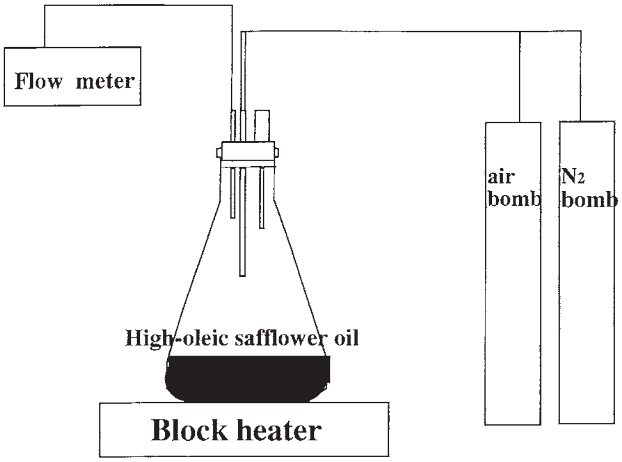

FIG. 1. Deep-fat frying simulation system.

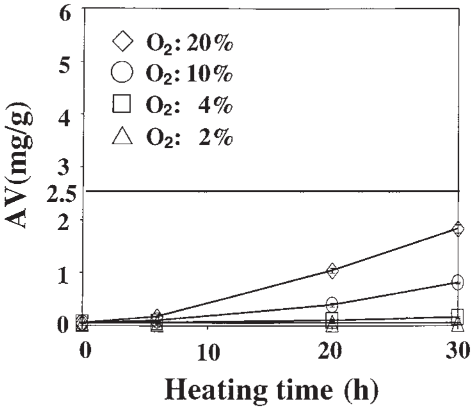

FIG. 2. Changes in acid value (AV) during heating of high-oleic safflower oil at 180°C in atmospheres with different oxygen levels. Error bar amplitude matches mean ± SD of three replicates.

Polar materials were quantitatively detected by thin-layer chromatography (TLC) with a hydrogen flame-ionization detector (FID) using an Iatroscan TH-10 (Iatron, Tokyo, Japan) with silica gel rods S-III (Iatron). A mixture of *n*-hexane/diethyl ether/formic acid (80:20:1, vol/vol/vol) was used as a mobile phase.

Residual linoleic acid (18:2) content in oils was monitored by gas chromatography (GC) after conversion to methyl esters with acetyl chloride (6). A GC-380 gas chromatograph (GL Sciences, Tokyo, Japan) equipped with a CP-Sil 88 capillary column (0.25 mm × 50 m, Chrompack, Middelburg, Netherlands) was used. FID and injection temperatures were 250°C and the column temperature was programmed from 170 to 225°C at 4°C/min.

The tocopherol contents in the heated oils were determined by normal-phase high-performance liquid chromatography (HPLC) detected with a fluorescence detector (excitation wavelength, 297 nm; emission wavelength, 327 nm) using a Finepak Sil column (4.6 mm × 25 cm, 5 μ, JASCO, Tokyo, Japan). The mobile phase was *n*-hexane/2-propanol (99.5:0.5, vol/vol) at a flow rate of 0.7 mL/min. 2,2,5,7,8-Pentamethyl-6-hydroxychroman was used as an internal standard.

The oxidative stability test. Aliquots of sample oils (200 mg) were put into 10-mL test tubes and then sealed with a W-type cap. They were stored at 60°C in the dark, and the head space gas was periodically analyzed by GC as previously described to determine the oxygen concentration. The induction period was designated as the days in which the oxygen concentration in the head space decreased to less than half of the original.

RESULTS AND DISCUSSION

AV and CV. Figure 2 shows the changes in AV of high-oleic safflower oil during heating at 180°C in atmospheres with four different levels of oxygen concentration. In general, AV of high-oleic safflower oil increased linearly with both heating time and oxygen concentration. That is, the increase during heating in an oxygen level of 20% was higher than those in 10 and 4% O_2, while heating in an atmosphere with 2% O_2, did not lead to a notable increase AV, even after heating for 30 h. The decrease of atmospheric oxygen was found to be effective to retard the generation of free fatty acids in heated oil.

Figure 3 shows the changes of CV during heating. Although CV increased gradually with heating time at any oxygen concentration, the CV of heated oils were positively correlated with atmospheric oxygen concentration. That is, the oil heated at an oxygen level of 20% showed the most remarkable increase in CV, followed by 10, 4, and 2% O_2, respectively. The CV after heating for 30 h in 20% O_2 reached 149.8 meq/kg. In Japan, the admissible limit of CV in frying oils is 50 meq/kg by the official specification concerning food establishments. The oils heated for 10 h in 20% O_2 and 30 h in 10% O_2 exceeded this value, whereas the CV of the oil heated in the atmosphere with 4% O_2 were smaller than this value. Most importantly, almost no increase in CV was observed by frying in the atmosphere with 2% O_2. CV is referred to as one of the major chemical characteristics that show oxidative deterioration of frying oil, because hydroperoxides are unstable under frying conditions and can decompose to yield carbonyl compounds.

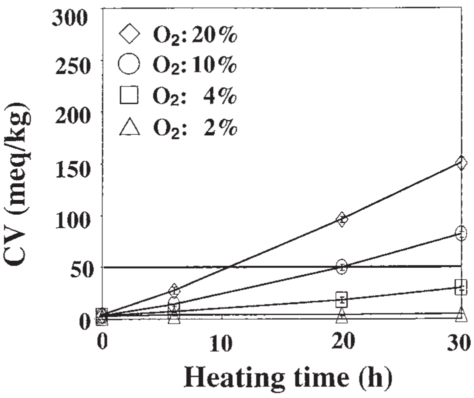

FIG. 3. Changes in carbonyl value (CV) during heating of high-oleic safflower oil at 180°C in atmospheres with different oxygen levels. Error bar amplitude matches mean ± SD of three replicates.

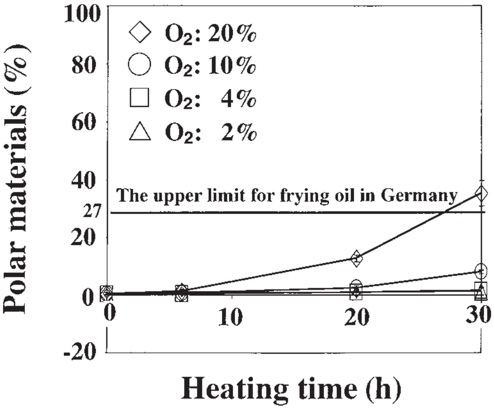

FIG. 4. Changes in content of polar materials produced during heating of high-oleic safflower oil at 180°C in atmospheres with different oxygen levels. Error bar amplitude matches mean ± SD of three replicates.

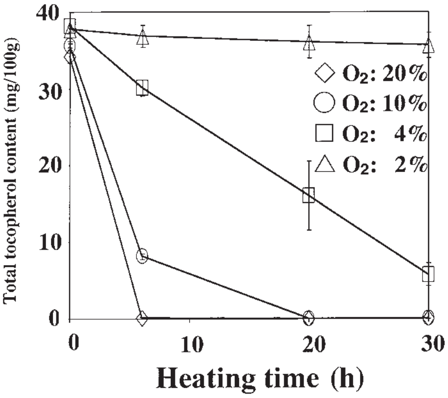

FIG. 6. Changes in total tocopherol content during heating of high-oleic safflower oil at 180°C in atmospheres with different oxygen levels. Error bar amplitude matches mean ± SD of three replicates.

Polar materials. Polar materials, mainly polymerized triacylglycerols with some polar groups, also are formed as major secondary oxidation products during deep-fat frying. Polar material contents also increased linearly with time and oxygen concentrations, similar to the chemical characteristics described above (Fig. 4). However, the formation of polar materials was effectively retarded in the atmosphere with 10% O_2. In the atmospheres with 4 or 2% O_2, the polar materials were negligible even after heating for 30 h. The decrease of oxygen concentration was effective in retarding the production of polar materials during heating of high-oleic safflower oil.

Linoleic acid. The contents of 18:1 and 18:2 as major unsaturated fatty acids in the original high-oleic safflower oil were 77.9 and 16.6%, respectively. During the initial heating for 6 h, the 18:2 contents decreased slightly to approximately 14% regardless of the atmospheric oxygen concentration (Fig. 5). However, after that period, the 18:2 contents decreased linearly with heating time in the atmospheres with 4–20% oxygen concentration. In the atmosphere with 2% oxygen, the decrease of 18:2 content was negligible, suggesting that the oxidative deterioration of heated high-oleic safflower oil was efficiently retarded. The decrease of linoleic acid was negatively correlated with the changes of carbonyl value and polar materials. These results suggest that linoleic acid is preferentially oxidized in heated high-oleic safflower oil to form polar materials with carbonyl moieties.

Tocopherols. The changes of tocopherols in heated high-oleic safflower oil in the atmospheres with four oxygen concentrations are shown in Figure 6. The initial total tocopherol content in the high-oleic safflower oil was 36.4 mg/100 g oil. Tocopherols decreased with time and atmospheric oxygen concentration. All tocopherols were lost after 6 h of heating at 20% O_2 or 20 h of heating at 10% O_2. Tocopherols were also decomposed gradually by heating in the atmosphere with 4% O_2, whereas almost no change was observed during heating in the atmosphere of 2% O_2.

The oxidative stability at 60°C. The induction periods of heated oils at 60°C are shown in Figure 7. Induction periods drastically decreased with heating time and atmospheric oxygen concentration. The result that the length of induction period showed a fairly good positive correlation with tocopherol

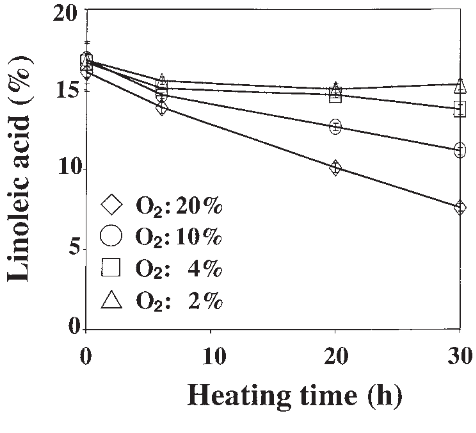

FIG. 5. Changes in linoleic acid content during heating of high-oleic safflower oil at 180°C in atmospheres with different oxygen levels. Error bar amplitude matches mean ± SD of three replicates.

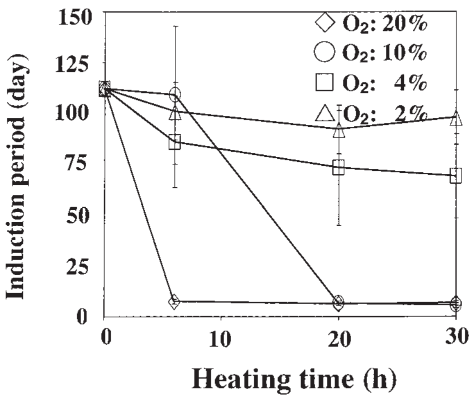

FIG. 7. Changes of induction period of heated high-oleic safflower oil at 180°C in atmospheres with different oxygen levels. Error bar amplitude matches mean ± SD of three replicates.

contents suggests that the major factor which affects the oxidative stability of heated oil is the content of tocopherols as antioxidants.

In case of autoxidation of packed fats and fatty foods at room temperature, the oxygen level should be decreased to less than 2% (7). Andersson and Lingnert reported that lipid oxidation in rapeseed oil at 50°C was only slightly influenced by oxygen concentration at 1.0%, and the influence was enhanced below 0.5% (8). Present studies showed that the decrease of atmospheric oxygen is effective to retard oxidative deterioration of heated oil at 180°C even if the atmospheric oxygen concentration decreases to 10%, and it is almost proportional to the atmospheric oxygen concentration. These results are in fair agreement with those of Kitamura (9) who assessed the oxidative deterioration of some heated oils by refractive index. From these results, frying in low oxygen atmospheres may be effective to retard oxidative deterioration, however, the effects of water and food ingredients which are present in frying systems should be examined.

ACKNOWLEDGMENT

We wish to thank the Oils and Fats Research Laboratories, Ajinomoto Co. for providing high-oleic safflower oil.

REFERENCES

1. Orthoefer, F.T., S. Gurkin, and K. Liu, Dynamics of Frying, in *Deep Frying*, edited by E.G. Perkins and M.D. Erickson, AOCS Press, Champaign, 1996, pp. 223.
2. Marcuse, R., and P.-O. Fredriksson, Fat Oxidation at Low Oxygen Pressure. I. Kinetic Studies on the Rate of Fat Oxidation in Emulsions, *J. Am. Oil Chem. Soc. 45*:400–407 (1968).
3. Goldblith, S.A., M. Karel., and G. Lusk, The Role of Food Science & Technology in the Freeze Dehydration of Foods, *Food Technol. 17*:139–144 (1963).
4. Japan Oil Chemists' Society, *Standard Methods for the Analysis of Fats, Oils and Related Materials*, Japan Oil Chemists' Society, Tokyo, Japan, 1996, method 2.3.1.
5. Chiba, T., M. Takazawa, and K. Fujimoto, A Simple Method for Estimating Carbonyl Content in Peroxide-Containing Oils, *J. Am. Oil Chem. Soc. 66*:1588–1592 (1989).
6. Lepage, G., and C.C. Roy, Direct Transesterification of All Classes of Lipids in a One-Step Reaction, *J. Lipid Res. 27*:114–120 (1986).
7. Deobald, H.J., and T.A. Mclemore, The Effect of Temperature, Antioxidant, and Oxygen on the Stability of Precooked Dehydrated Sweet Potato Flakes, *Food Technol. 18*:145–148 (1964).
8. Andersson, K., and H. Lingnert, Kinetic Studies of Oxygen Dependence During Initial Lipid Oxidation in Rapeseed Oil, *J. Food Sci. 64*:262–266 (1999).
9. Kitamura, K., Examination of Deterioration Rate on Deep-Fat Frying Oils by Refractometer. Heat Deterioration Law of Oils in Deep-Fat Frying, *J. Jpn. Oil Chem. Soc. 47*:609–614 (in Japanese) (1998).

[Received October 13, 1999; accepted December 1, 1999]