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Oxygen Content and Oxidation in Frying Oil

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Abstract: The relation between oxygen content and oxidation was investigated in frying oils. When canola oil, a canola-soybean oil blend or a trioctanoylglycerol (glycerol tricaprate) sample were heated with stirring, their dissolved oxygen content decreased abruptly at about 120℃ and the carbonyl values (CV) increased gradually with heating and reached values of 6-7 at 180℃ in the blended and canola oils, while the CV of trioctanoylglycerol was zero up to 150℃. Probably this abrupt decrease in oxygen content above 120℃ can be attributed to the solubility of oxygen in oil rather than because of oxidative reactions.
The oxygen content of oil that has been stripped of part of its oxygen, increased at temperatures between 25 and 120℃. In oils that have lost their oxygen by being heated to 180℃, standing at room temperature will slowly restore their oxygen content as the oil cools. Intermittent simple heating of oil promoted oxygen absorbance during cooling periods and standing times, and it resulted in an elevated content of polar compounds (PC). Domestic deep-frying conditions also favor the presence of oxygen in oil below 120℃ and during the oil's long standing at room temperature. The oxygen content in oil was low during deep-frying, but oxidation was active at the oil/air interface of bubbles generated by foods being fried. Repeated use of oil at temperatures between 25-180℃ resulted in oil with low oxygen values.

Key words: oxygen content, frying oil, intermittent frying, polar compound, carbonyl value, autoxidation

1 INTRODUCTION

Clearly triacylglycerols containing unsaturated fatty acids are subject to oxidation and the greater their unsaturation the more they oxidize. In a previous paper[1)], we investigated the oxidation of frying oil used intermittently for a few hours at a time in hospital kitchens. The polar compound content (PC) and carbonyl values (CV) were obviously higher, compared with their Gardner color values, in used soybean oil than in blends of soybean and canola oil. But frying oil used continuously in commercial establishments[2)] for more than 8 h per day, and which had their oil partially replenished, did not have high PCs and CVs compared with their color values. When the relation between Gardner color value and the PC, CV, or acid values (AV) of the oils were investigated, well-correlated logarithmic regression curves were obtained from all oils and treatments except those used in hospital kitchens. Variables such as kitchen practice, kinds of fryers, types of vegetable oils, fryer temperatures, and amounts and kinds of fried foods did not greatly influence the relationships between Gardner color and PCs or CVs. Thus, oxidation of frying oils in which the frying frequency was overwhelmingly less than that in commercial establishments, such as hospital kitchen oil, occurred while standing between uses. Antioxidants in the oils easily lose their effectiveness with heating, especially at frying temperatures[3)]. The frying pattern of domestically used oils is similar to the frying pattern of hospital kitchen oils, and oil color cannot be used to predict the extent of oxidation. It is possible that oil consumed domestically may be more oxidized than that of hospital kitchen.

Gerde *et al.*[4)] measured oxygen content of heated soybean and olive oils with an YSI Model 53 Biological Oxygen Monitor equipped with a polarographic electrode, and found that oils showed an abrupt decrease in oxygen content at 120℃ and a very low amount of oxygen at 180℃. In a previous paper[1)] we confirmed that canola and soybean oils showed the same change in oxygen content measured using the same oxygen monitor as above, and found that the change was repeated in intermittent heating. However, it was not clear whether this phenomenon was caused by the physical properties of the oils or by oxygen consumption at high temperatures. The relation between oil oxidation and the oxygen content of oil during deep-frying and the changes in oxygen content of oil during repeated frying have not been known previously. In this paper, these questions are investigated using experimental models and typical deep-frying conditions.

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2 EXPERIMENTAL

2.1 Materials

Canola and blended oils were products of Nisshin Oilio, Tokyo, Japan. Trioctanoylglycerol was purchased from Sigma-Aldrich, St. Louis, US and methyl oleate, from Wako Pure Chemical Industries, Ltd., Osaka, Japan. Methyl linoleate was bought from Nacalai Tesque, Kyoto, Japan. Fatty acid compositions of fresh commercial oils were determined[5] using gas chromatography and are shown in Table 1. All solvents and reagents were purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan.

2.2 Methods for oil analyses

CVs were measured according to the standard methods of the Japan Oil Chemists' Society for analysis of fats, oils, and related materials[6]. PC values were determined with a CapSens 5000®, ALPHA M.O.S.(Tokyo, Japan). Because the oil samples from deep-frying were turbid with dregs and scum, they were subjected to centrifugation or filtration with filter paper before analyses.

2.3 Oxygen content of methyl oleate and methyl linoleate under heating

Methyl oleate, 1000 g, was poured into a 2-L four-necked separable round-bottomed flask fitted with a stirring bar, thermometer, and air pump delivering 110 mL/min of air into the flask. One neck of the flask was left open as an outlet for the pump. Methyl oleate was used immediately upon opening to prevent air absorption before the experiment. Under stirring at 85 rpm, the ester was heated from room temperature to 180℃ in 80 min: the surface to volume ratio was 0.15. When the ester temperature reached 25, 60, 100, 120, 150, and 180℃, a sample was removed by pipetting through the open neck of the flask, filling a 50-mL brown vial completely. The vial was closed with a cap lined with heat-stable sealant so that the upper part of the vial contained no air. When the bottled ester was cooled down to 25℃, its oxygen content was determined using a DO/O_2/Temp. Meter(UC-12-SOL; Central Science, Tokyo, Japan)equipped with a polarographic electrode[4]. The oxygen content reading of blended oil saturated with oxygen, by bubbling air, at 25℃ was set as 100%. After the oxygen content determination, a CV was measured. The same experiment was also carried out with methyl linoleate.

Table 1 Fatty acid compositions of frying oil.

Fresh oil	Blended oil	Canola oil
C14:0	0.1	0.1
C16:0	8.7	4.4
C16:1	0.1	0.2
C18:0	3.6	2.5
C18:1	36.4	60.9
C18:2	40.8	20.2
α-C18:3	6.5	7.9
Others	3.8	3.8

C14:0 myristic acid, C16:0 palmitic acid, C16:1 palmitoleic acid, C18:0 stearic acid, C18:1 oleic acid, C18:2 linoleic acid, α-C18:3 α-linolenic acid.

2.4 Oxygen content of oils under heating

The same experiment as in 2.3 was performed with very fresh canola and blended oils obtained from newly opened bottles and trioctanoylglycerol to determine changes in oxygen content in triacylglycerols under heating.

2.5 Oxygen content of oil heated continuously or intermittently

Very fresh blended oil, 1000 g, was heated at 180℃ in a 2-L four-necked round-bottomed flask for 4 h as in section 2.3: the surface to volume ratio was 0.15. Every hour the oil was sampled and its oxygen content and the PC values were determined. Also, very fresh blended oil, 1000 g, was heated at 180℃ in a 2-L four-necked flask for 1 h as in section 2.3 and its oxygen content and PC values were determined. The residual oil was kept in the flask at room temperature for 48 h with the covers removed, and its oxygen content and PC values were determined. This process was repeated three more times. The overall heating time was 4 h.

2.6 Oxygen content of oil under deep-frying

Fresh blended oil, 1000 g, was placed in an electric fryer (EP-D692; Twinbird, Niigata, Japan. The pan was 14 cm × 22 cm × 11 cm deep)and it was heated at 180℃ to deep-fry consecutively 4 potions of 125 g of potatoes cut into eight pieces. Each portion was fried for 5 min. After each frying, the oil was sampled and its oxygen content and PC values were determined after centrifuging the oil at 3000 rpm (1000 ×g)for 30 min. After four replications of deep-frying, the residual oil was left standing in the fryer for 24 h. The next day, the same deep-frying procedure was repeated.

2.7 Oxygen content of oil repeatedly used for deep-frying

Fresh blended oil, 1000 g, was put in the electric fryer used in section 2.6 and heated to 180℃ to deep-fry the foods listed in Table 2. This procedure was continued for 10 days without fresh oil replenishment: the used oil was exposed to the air for 2 days from the end of last deep-frying to the heating experiment described above. After the fifth deep-frying the residual oil was subjected to filtration with filter paper(No. 2; Advantec, Tokyo, Japan)to remove

Table 2 Frying program with blended oil.

Deep-fried foods	Fried amounts	Frying duration (min)	Day
Fried mushroom	300 g	9	1
Fried chicken	380 g	30	3
Breaded chicken cutlet	90 g × 4	19	5
Breaded pork cutlet	100 g × 4	21	7
Smelt	15 g × 20	19	10

dregs, and the filtered oil, 450 g, was heated in a 2-L four-necked round-bottomed flask to 180℃ as in section 2.3, and oxygen contents were determined at 25, 80, 120, 150, and 180℃. Fresh blended oil exposed to the air, was also heated as above to compare oxygen content with that of the repeatedly used oil.

2.8 The experimental design

In order to identify the reason why the abrupt decrease of oxygen content occurs at 120℃ in the heated oils, oxygen content changes in trioctanoylglycerol (hardly oxidized due to no double bond), canola oil and blended oil were traced with the measurement of CV (2.4), while the changes in oleic and linoleic acids, major compositional fatty acids of the oils, were also confirmed (2.3). In addition, the relation between oxygen contents and oxidation in intermittently heated oils (2.5 and 2.6) was investigated. The effect of thermal deterioration of oil on oxygen content was also found in 2.7.

2.9 Statistical analyses

All values obtained for oxygen content, CV, and PC are revealed as mean ± SD and were analyzed using one-way analysis of variance with Dunnett's multiple comparison post hoc test or Student's *t* test. Results were considered significant at $p < 0.05$.

3 RESULTS

3.1 Oxygen content of methyl oleate and methyl linoleate under heating

The oxygen content of methyl oleate decreased between 60-100℃ and displayed low values up to 180℃ (Fig. 1A). But the oxygen content of methyl linoleate decreased gradually from 60℃ to 150℃, and at 150℃ showed similar oxygen levels to those of methyl oleate. The CVs of methyl linoleate were significantly lower than those of methyl oleate at a range of 25-120℃; however, over 150℃, the CVs of both esters increased but the order was reversed because of their respective oxidizabilities (Fig. 1B).

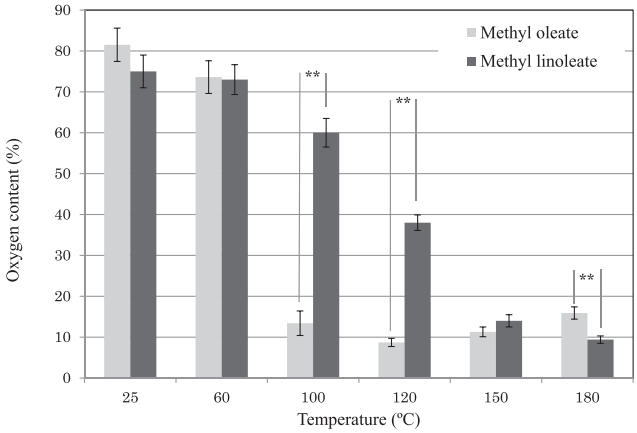

Fig. 1A The effect of temperature on the oxygen content of methyl esters. Values are expressed as mean±SD. ** $p < 0.01$ significantly different by Student's t test.

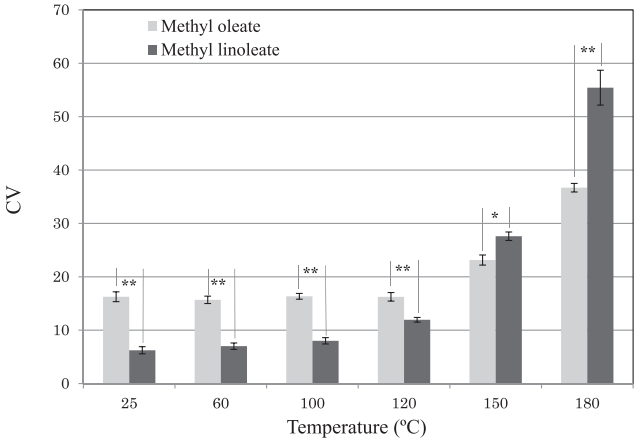

Fig. 1B The effect of temperature on the CV of methyl esters. CV stands for carbonyl value. Values are expressed as mean±SD. * $p < 0.05$, ** $p < 0.01$ significantly different by Student's t test.

3.2 Oxygen content of oil under heating

Blended oil, canola oil and trioctanoylglycerol (mp 8-8.3℃) had high oxygen contents at 100-120℃, but their oxygen contents decreased abruptly at 120℃ and higher. At 120℃ and 180℃ the rank order of their oxygen content

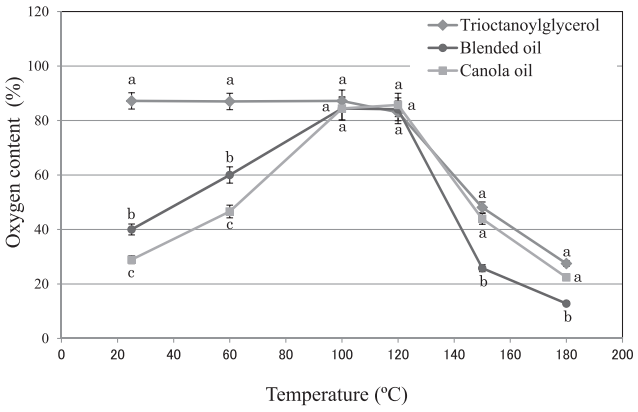

Fig. 2A The effect of temperature on the oxygen content of triacylglycerols. Values are expressed as mean±SD. The point with the non-common superscript letter differs significantly ($p < 0.05$) by Dunnett's multiple comparison post hoc test.

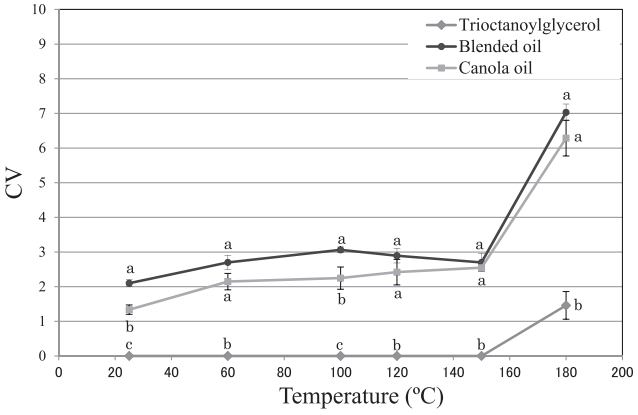

Fig. 2B The effect of temperature on the CV of triacylglycerols. CV stands for carbonyl value. Values are expressed as mean±SD. The point with the non-common superscript letter differs significantly ($p < 0.05$) by Dunnett's multiple comparison post hoc test.

was trioctanoylglycerol≒canola oil > blended oil (Fig. 2A). The CVs were similar in blended oil and canola oil when observed as slopes up to 150℃, but they increased sharply at 180℃ (Fig. 2B). While trioctanoylglycerol did not show increases in their CVs up to 150℃, there were slight increases at 180℃.

3.3 Oxygen content of oil heated continuously or intermittently

When oil was heated continuously, the oxygen content decreased and the PC value increased with heating time (Fig. 3A and 3B). Oil heated intermittently (Fig. 3A) had higher oxygen content before heating and had similar oxygen contents after heating for 1-h periods compared

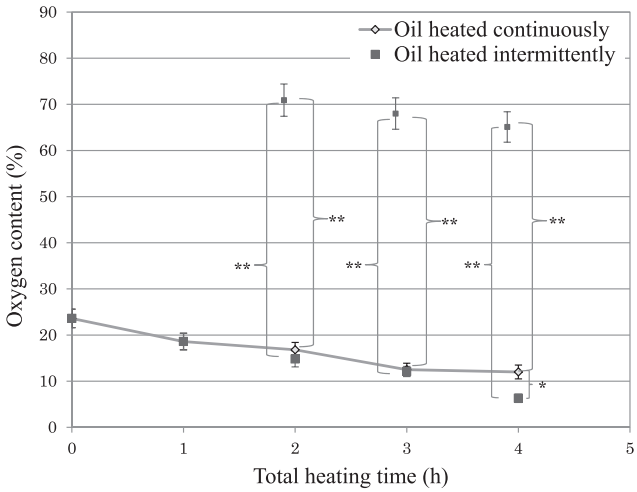

Fig. 3A Oxygen content of blended oil heated continuously and intermittently. Small square symbols show values before each 1-h heating. Values are expressed as mean±SD. * $p < 0.05$, ** $p < 0.01$ significantly different by Student's t test.

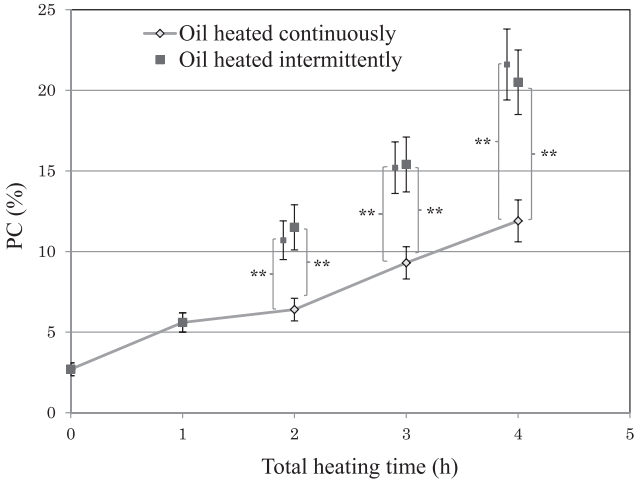

Fig. 3B PC of blended oil heated continuously and intermittently. Small square symbols show values before each 1-h heating. PC stands for polar compound content. Values are expressed as mean±SD. ** $p < 0.01$ significantly different by Student's t test.

with oil heated continuously for the same period: at 4 h of heating oxygen content was significantly lower than that of oil heated continuously for 4 h. As intermittent heating was repeated, the oxygen content before and after heating, respectively, continued to decrease. The PC value of intermittently heated oil was remarkably higher than those of the corresponding oils that had been continuously heated, and increased with the number of times heated (Fig. 3B).

3.4 Oxygen content of oil under deep-frying

During deep-frying, the oxygen content of the oil remained low (Fig. 4). The bubbles generated by the foods being fried were full of water vapor, but PC increased from 4.7% to 14% on the first day (frying time 30 min in total) and to 17.5% on the second day (frying time 22 min in total). Cooling from 180℃ to room temperature increased the oxygen content in a short period, and the level increased slightly until the next deep-frying. The next day, the decrease in oxygen content was again observed during frying.

3.5 Oxygen content of oil repeatedly used for deep-frying

Oil repeatedly used for deep-frying (Table 2) showed remarkably low oxygen contents during heating compared to fresh oil: the decrease started at 80℃ and the content was very low at 180℃ (Fig. 5).

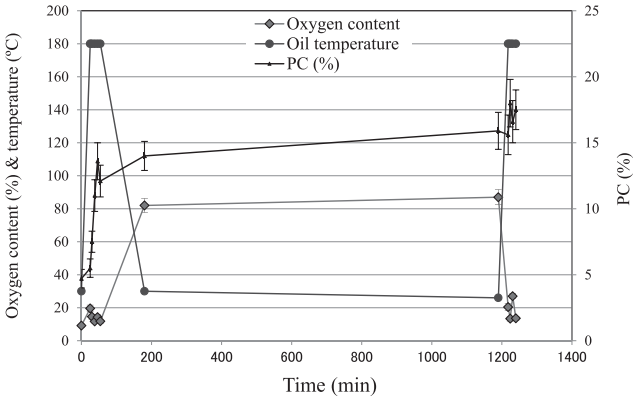

Fig. 4 Oxygen content, temperature & PC of blended oil under deep-frying. PC stands for polar compound content. Values are expressed as mean±SD.

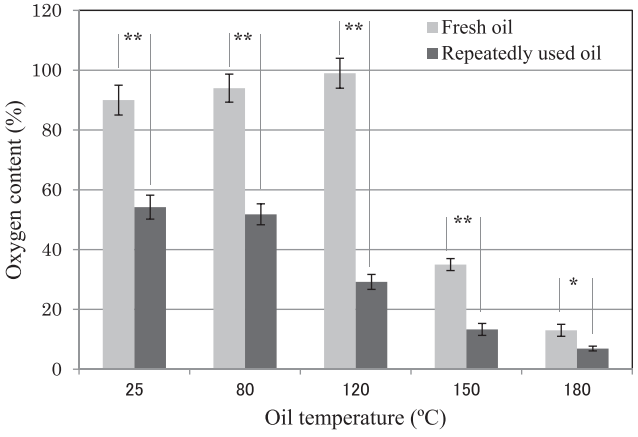

Fig. 5 Oxygen content in blended oil repeatedly used for deep-frying. Values are expressed as mean±SD. * $p < 0.05$, ** $p < 0.01$ significantly different by Student's t test.

4 DISCUSSION

A full investigation of oil oxidation from the viewpoint of oil oxygen content has not been reported to the best of our knowledge, although the relation between atmospheric oxygen level and oxidation has been studied[7]. One of our previous papers[1, 4] reported that the oxygen content in oil decreased abruptly at 120℃ during heating from room temperature to 180℃, and the oxygen content returned to a high level while the oil was allowed to stand at room temperature. In the present study, we first investigated oil oxygen content using methyl oleate and methyl linoleate, major constituent fatty acids of canola and blended oils, to determine whether the abrupt decrease at 120℃ was caused by oil oxidation or the physical properties of the oil. As shown in Fig. 1A, both esters showed high oxygen contents at 25℃; however, both decreased with heating. This suggests that large amounts of oxygen cannot remain in oil at high temperatures. While the oxygen content in methyl stearate (mp 39.1℃) is of interest, its determination for solid materials is not possible with the oxygen monitor employed. The oxygen content between 100-120℃ was higher in methyl linoleate than for methyl oleate. The CVs of both esters were almost constant up to 120℃ (Fig. 1B), suggesting that active oxidation had not occurred despite drastic decreases in oxygen content. However, it is possible that there is a time lag between generation of carbonyl compounds and other oxidation products that probably occurs. The initial high oxygen content of methyl oleate could be caused by the bottling procedure of the supplier. Methyl linoleate had a higher CV at temperature values over 150℃ than methyl oleate, so the oxygen content decreases may be partly attributable to the consumption of oxygen via oxidation.

Figure 2A shows that trioctanoylglycerol had a high oxygen content up to a temperature of 120℃, which decreased suddenly as the temperature rose. Oil composed of medium chain fatty acids as the constituent fatty acids, a product of Nisshin Oilio, showed similar changes with heating (data not shown). Blended and canola oils had a low oxygen content at 25℃ and 60℃, probably because the supplier filled their containers with nitrogen before capping them. The oxygen content of both oils increased with heating, but dropped suddenly at 120℃, just like trioctanoylglycerol. The oxygen contents of blended oil at 120℃ and 180℃ were lower than those of trioctanoylglycerol and canola oil. As shown in Fig. 2B, the CVs of both oils increased gradually up to 150℃ and then increased more strongly with further heating. The CVs of trioctanoylglycerol, which contained no double bonds, were zero during heating, but increased slightly by 180℃. The PC values of both oils show the same trend to their CVs (data not shown). The abrupt decrease in oxygen content at 120℃ can be attributed mainly to the physical properties of triacylglycerols, although Gerde *et al.*[4] suggested that

this phenomenon was due to oxidation at high temperatures. A comparison of Figs 1A and 2A suggests that triacylglycerols held more oxygen at 100-150℃ than fatty acid esters.

The oxygen content of oils depends on their chemical structure, the oxygen content around them, the temperature, their reaction rate with oxygen and the time allowed for equilibrium. The oxygen content of oil at the beginning of heating reflects their initial oxygen level (Figs. 1A, 2A).

When oil was heated intermittently, oxidative changes in the oil became greater than that of continuously heated oil (Fig. 3B). Large amounts of oxygen penetrated into the oil during cooling and standing time (Fig. 3A), and this accelerated autoxidation. Oxygen absorbed in oil should react with unsaturated fatty acids more directly than oxygen existing at the oil/air interface. Note that intermittent heating resulted in large PC increases during standing time, but there were small differences in the PC values before and after heating for 1 h. So in the present heating pattern, standing time was equally influential in allowing oxidation of the oil to heating time, and PC did not apparently increase during heating. Furthermore, in oil intermittently heated for 4 h in total, the PC values after 1 h heating were lower than those before 1 h of heating. The reasons for these results were thought to be caused by the loss by evaporation of low-molecular polar compounds during heating[8].

Our experimental model of domestic deep-frying did not employ replenishment of fresh oil containing intact antioxidants[3]. Romero *et al.*[9] reported that frequent replenishment of monoenoic oil with fresh oil permits one to fry sets of fresh potatoes very high number occasions. In addition to polymerization, oxidation of oil with low oxygen content was active during deep-frying (Fig. 4), where foods continuously produce innumerable bubbles composed mostly of steam and some air under high temperatures. The PC values increased mainly due to oxidation at the oil/air interface of bubbles.

When hot oil was left standing and cool, it absorbed oxygen very quickly, resulting in autoxidation. It was reported[4] that 100 ppb of polydimethylsiloxane (PDMS) formed a continuous monolayer on the surface of oil and prevents thermal oxidation, although PDMS is added primarily to inhibit foaming. If so, use of an oxygen barrier produced by PDMS should enable the maintenance of low oxygen content during the cooling of hot oil. In Japan, frying oil for domestic use does not contain PDMS, while that for commercial use does. Dueik *et al.*[10] and Nunes *et al.*[11] proposed a deep-frying procedure under reduced pressure to prevent oil oxidation. However, their proposal appears difficult to apply in domestic kitchens.

When repeatedly used frying oil was heated to 180℃, the oxygen content was lower than that of fresh oil in the temperature range investigated (Fig. 5). Recovered oil[12], used at food manufacturing industries and discarded, showed the same low oxygen content and low PC values (data not shown). Methyl oleate and methyl linoleate showed different oxygen content changes from those of fresh oil. The relationship between oxygen content and chemical structure is of significant interest for further study. Moreover, minor components in food oils, such as diacylglycerols, monoacylglycerols, free fatty acids, phospholipids, water, and minerals have an influence on their physical and chemical properties[13, 14].

Sanchez-Muniz *et al.*[15–17] suggested that triacylglycerol oligomer contents gave more precise information about the alteration of frying oil and its potential toxicity than PC values. However, dissolved oxygen triggers oxidation of the unsaturated fatty acid moiety and causes the oligomerization of triacylglycerol. Thus, the determination of oxygen content in oil is very important.

In conclusion, the abrupt decrease in the oxygen content of oil at 120℃ was attributed mainly to the physical properties of triacylglycerol. The contribution of oxidation to this decrease was relatively small. When frying oil was heated at 180℃ and then cooled, the oxygen content increased quickly. Domestic deep-frying conditions favor the presence of oxygen in oil below 120℃ and during the oil's long standing at room temperature. The oxygen content in oil was low during deep-frying but oxidation was active at the oil/air interface of bubbles generated by foods being fried. Repeated use of oil at temperatures between 25-180℃ resulted in oil with low oxygen values.

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