Inhibition of Frying Oil Oxidation by Carbon Dioxide Blanketing
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Abstract: The oxidation of oil starts, in general, from the penetration of atmospheric oxygen into oil. Inhibition of the vigorous oxidation of oil at deep-frying temperature under carbon dioxide flow, by disrupting the contact between oil and air, was first demonstrated using oil in a round bottom flask. Next, the minimum carbon dioxide flow rate necessary to blanket 4 L of frying oil in an electric fryer (surface area 690 cm²) installed with nonwoven fabric cover, was found to be 40 L/h. Then deep-frying of potato was done accordingly; immediately after deep-frying, an aluminum cover was placed on top of the nonwoven fabric cover to prevent the loss of carbon dioxide and the carbon dioxide flow was shut off. In conclusion, the oxidation of oil both at deep-frying temperature and during standing was remarkably inhibited by carbon dioxideblanketing at a practical flow rate and volume. Under the deep-frying conditions employed in this study, the increase in polar compound content was reduced to half of that of the control.

Key words: carbon dioxide, oxygen content, antioxidation, nonwoven fabric, intermittent deep-frying

1 INTRODUCTION
Because natural antioxidants, such as tocopherols, lose their effects after just a few hours of deep-frying\(^{1-3}\), this limits their applicability to large scale cooking. Recently pH-regulating agents were reported to be superior antioxidants to \(\alpha\)-tocopherol\(^5\). On the other hand, polydimethylsiloxane (PDMS) has been approved for use as an antifoamer by the Food Sanitation Act of Japan\(^6-11\), and is added at ppm amounts to oil for industrial purposes. PDMS also shows a far greater antioxidative effect than natural and synthetic antioxidants\(^6-8\). However, oil supplemented with ppm PDMS is easily perceived by the differences in touch, mouth feel and flavor compared to the original oil. Therefore, the use of PDMS as an antioxidant remains limited.

We have investigated oil oxidation during intermittent heating, focusing on the oxygen content of oil\(^5,8-10\). When oil is subjected to oxidation, the oxygen penetrating the oil from the air attacks the oil. Thus, the oxygen content of oil is closely related to the initial oxidation. When fresh frying oil is heated from room temperature, the dissolved oxygen content of oil rises, then decreases abruptly at 120 °C, and reaches ca. 15% at 180 °C. The change in the oxygen content is caused mainly by the physical property of the oil, and also by the consumption of oxygen due to the vigorous thermal oxidation of oil at high temperature. Because peroxides generated are not heat-stable, peroxide value readily decreases at deep-frying temperature while amounts of polar compounds increase gradually. When the oil is allowed to stand after heating, autoxidation proceeds in accordance with the increase in oxygen content, resulting in increases of peroxides, followed by polar compounds\(^8-10\).

Displacing the air covering the oil’s surface with carbon dioxide inhibits the supply of oxygen to the oil. Aladedunye \textit{et al.}\(^{11}\) heated 4 L of canola oil at 185 ± 5 °C blanketed by 150 L/h carbon dioxide flow and fried 8 batches of French fries per day for 7 days continuously, with the result that oxidation of the oil was remarkably reduced. While a hood is employed to exhaust the carbon dioxide-containing air during deep-frying, the amount of air-flow could pose a danger for the operator. In addition, the balance between carbon dioxide and oil costs requires consideration.

Aladedunye \textit{et al.}\(^{11}\) also fried frozen French fries at 9.7 kPa vacuum at 180 ± 2 °C using an industrial vacuum deep-fryer in comparison with deep-frying under carbon dioxide blanketing. A total of eight batches of French fries were fried daily for 7 consecutive days. The vacuum frying gave better results for polar compound content (PC), anisidine value, and contents of dimeric, polymeric and oxidized triglycerides compared to carbon dioxideblanketing. However, vacuum frying is rather designed for drying relatively large or industrial quantities of raw foods. For retail
frying, such as fast food outlets, carbon dioxide blanketing should be practical. On the other hand, a batch of oil is used only for a few hours in total in domestic deep-frying; thus, the health effects of oxidation are likely minimal.

In this study, the blanketing effects of carbon dioxide and nitrogen, both of which are reasonable in cost, availability and security to inhibit oil oxidation, were compared in a model experiment. Next, the minimum carbon dioxide flow rate was obtained for an electric fryer covered with nonwoven fabric. The flow of carbon dioxide was employed only during heating of oil, and the fryer was covered tightly with an aluminum plate over the nonwoven fabric during cooling, allowing for a maximum antioxidative effect with a minimum amount of carbon dioxide under the frying conditions assessed.

2 EXPERIMENTAL

2.1 Materials

Canola oil was a product of J-Oil Mills Ltd. (Tokyo, Japan), and was composed of 0.1% myristic acid, 3.3% palmitic acid, 0.2% palmitoleic acid, 2.1% stearic acid, 61.9% oleic acid, 20.8% linoleic acid, 9.2% α-linolenic acid, and 2.4% others. All solvents and reagents were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Kobe Sanso (Kobe, Japan) supplied the carbon dioxide and nitrogen gases.

2.2 Chemical properties

Peroxide value (PV) was determined according to the standard methods of the Japan Oil Chemists’ Society for analysis of fats, oils, and related materials. A 4 mL oil sample was placed in a 15 mL test tube and heated to 50 °C to determine the polar compound content (PC) with a digital edible oil tester (testo270; Testo Japan, Yokohama, Japan).

2.3 Instrumental analyses

The oxygen content of oil was determined using a DO/O₂/Temp Meter (UC-12-SOL; Central Science, Tokyo, Japan) equipped with a polarographic electrode. The oxygen content reading (relative oxygen content) of canola oil saturated with oxygen by bubbling air at 25 °C was set as 100%. Carbon dioxide was detected using a high concentration carbon dioxide detector (XP-3140; COSMOS, Osaka, Japan).

2.4 Heating and cooling of oil under air, carbon dioxide or nitrogen

Very fresh canola oil (1,100 g) was poured into a 2 L four-necked separable round-bottomed flask fitted with a stir 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. Under stirring at 85 rpm, the oil was heated from room temperature to 180 °C. The surface to volume ratio was 0.15 cm⁻¹. When the oil temperature reached 180 °C, stirring was maintained for 1 h, then the oil was allowed to stand and cool without stirring or aeration. At 25, 60, 100, 120, 150, and 180 °C, sufficient sample was removed by pipetting through the open neck of the flask to fill a 50 mL brown vial completely. The vial was closed with a cap lined with heat-stable sealant and ensuring that no air was trapped in the vial.

When oil samples were cooled to room temperature, relative oxygen contents, PVs, and PCs were determined.

The same thermal treatment was performed with carbon dioxide or nitrogen instead of air.

The flow rate of these gases was 60 mL/min. Before heating, the upper void volume of the flask was flushed with each gas for 15 min to eliminate the air, followed by plugging the open neck with cotton lightly. A continuous flow of gas was introduced until the oil temperature reached room temperature.

2.5 Heating of oil under air or carbon dioxide, followed by standing for 4 d

As in 2.4, fresh canola oil was heated in a flask from room temperature to 180 °C under air or carbon dioxide flow and maintained for 4 h, then allowed to stand for 4 d without air/carbon dioxide flow or heating. At 25 and 180 °C (every hour for 4 h), sufficient sample was removed by pipetting through the open neck of the flask to fill a 50 mL brown vial completely. Relative oxygen contents, PVs, and PCs were determined.

2.6 Optimization of carbon dioxide flow

Four liters of fresh canola oil were added into the tub (23 cm × 30 cm) of an electric fryer (KCEF-S; Chubo Center, Chiba, Japan). A wire net covered with nonwoven rayon fabric (AS ONE, Tokyo, Japan) was installed over the fryer tub. The surface to volume ratio was 0.17 cm⁻¹. Carbon dioxide was delivered through stainless-steel tubing (2 mm i.d.) with 0.6 mm holes placed equidistant along the fryer at flow rates of 66 L/h, 40 L/h, and 15 L/h. The tubing was attached to the upper edge of the fryer, and the 0.6 mm holes were 1 cm above the oil surface.

The set up was placed in a draft chamber equipped with a pump exhausting 15,000 L/min of air, heated to 180 °C, and maintained at these conditions for 1 h. Next, the heat source and carbon dioxide flow were shut off and the set up was allowed to stand until the oil temperature dropped below 40 °C. At room temperature, 60, 100, 120, 150, 180, and ca. 40 °C, sufficient sample was removed by pipetting through the cloth to fill a 50 mL brown vial completely. Relative oxygen contents, PVs, and PCs were determined.
2.7 Practical deep-frying under carbon dioxide flow

As in 2.6, frozen shredded potato (Coop, Osaka, Japan) was deep-fried in the electric fryer at 40 L/h carbon dioxide flow; five batches of 250 g of potato were fried for 5 min each at 15 min intervals. One end of the nonwoven fabric cover was opened to allow for the potato to be placed in the oil and subsequently removed during deep-frying. Steam generated during frying was able to easily pass through the nonwoven fabric cover without releasing large amounts of carbon dioxide. Immediately after completion of deep-frying, the heat was shut off, and an aluminum plate was placed tightly on top of the nonwoven fabric cover to prevent the loss of carbon dioxide. Next, the carbon dioxide flow was shut off so that carbon dioxide blanketing was maintained. The next day, the same procedure was repeated. Sufficient sample was removed before heating, during and after deep-frying as well as at room temperature by pipetting through the cloth to fill a 50 mL brown vial completely. Relative oxygen contents and PCs were determined; PC is qualified to be a better index for oil deterioration than acid value and PV.

3 RESULTS and DISCUSSION

3.1 Model experiments

Figure 1A, B, and C show the results obtained in the model experiments using a round bottom flask. Under air flow, the relative oxygen content increased up to 120 {degree}C, then decreased abruptly and reached the minimum value at 180 {degree}C (Fig. 1A). When the oil was allowed to stand, the relative oxygen content showed a small increase, with a sharp increase at 100 {degree}C. PV increased until the oil temperature reached 180 {degree}C, but decreased due to its low thermal stability. When oil was cooled to ca. 100 {degree}C, PV again increased because of autoxidation. PC increased gradually and reached 4.5% at the experimental endpoint.

On the other hand, the heating experiment under carbon dioxide flow (Fig. 1B) and nitrogen flow (Fig. 1C) showed remarkably reduced relative oxygen content, PV, and PC. Moreover, the effects of the former, in which PC did not increase, were greater than those of the latter. Carbon dioxide, which has a greater molecular weight than air, provided a good blanketing effect against the slight influx of air at the neck containing the stir bar. The two gases...
The result of thermal treatment at 180 °C for 4 h followed by standing for 4 d is shown in Fig. 2 (relative oxygen content) and Fig. 3 (PV and PC). Under air, the relative oxygen content and PV increased gradually, while PC increased abruptly during heating and gradually during standing. Under a carbon dioxide atmosphere, the relative oxygen content increased only slightly, with PV of 1 meq/kg and PC of 3%. Thus, it was confirmed that in a system largely protected from the influx of air, such as a flask, carbon dioxide blanketed the oil surface stably for more than 90 h without flowing, resulting in reduced oxidation reaction.

### 3.2 Optimization of fryer carbon dioxide flow

In the electric fryer, carbon dioxide was delivered through tubing and flowed near the oil surface. However, in contrast to the flask set-up, the carbon dioxide flow was not able to completely protect the oil from air contact in the fryer. In response, we installed a nonwoven fabric cover on the fryer insert to reduce the dissipation of carbon dioxide delivered. The relationships between the carbon dioxide flow rate and relative oxygen content/PV/PC are shown in Fig. 4A, B, and C. The carbon dioxide flow and heat source were shut off at the same time. At a flow rate of 66 L/h (Fig. 4A), a small increase in relative oxygen...
content was observed up to 100 °C, reached less than 10% at 180 °C, and remained below 20% while standing. PV increased after the heat was shut off and reached 10 meq/kg at room temperature. PC increased gradually to 4.5.

At a flow rate of 40 L/h (Fig. 4B), relative oxygen content was somewhat higher overall, but PC did not differ from the results at a flow rate of 66 L/h. The results of relative oxygen content at a flow rate of 15 L/h (Fig. 4C) were similar to those under air (Fig. 1A), and PV increased remarkably at below 100 °C during standing. However, the increase in PC resembled that observed at a flow rate of 40 L/h. Thus, a carbon dioxide flow rate of 40 L/h was employed in the electric fryer with nonwoven fabric cover. It is likely that further optimization of the experimental set-up, e.g., tubing, fryer tub dimensions, and nonwoven fabric, could reduce the required carbon dioxide flow rate.

3.3 Practical deep-frying

The result of deep-frying is shown in Fig. 5a. In spite of standing for more than 16 h, the relative oxygen content increased to just 38%. While PC increased 3% during deep-frying and 1% during standing in the control (Fig. 5b), these values were only 2% and 0%, respectively, at 40 L/h carbon dioxide flow. After deep-frying, the oil temperature dropped during standing. The volume of gas in the void volume above the oil in the tub contracts about two-thirds with a temperature drop from 180 °C to 25 °C according to the Charles’ law. At the same time, the capacity of oxygen and carbon dioxide to dissolve in oil is increased. However, the presence of the aluminum plate prevented a drastic increase in the relative oxygen content.

Seven times as much carbon dioxide dissolves in oil at 30 °C compared to oxygen13, 14. Yet vigorous bubbling was not observed during heating to 180 °C on the second day as well as the first day. The surface area of the oil tub employed in this experiment was 690 cm². If another oil tub with the same surface area is used, the required carbon dioxide flow rate should be the same regardless of the oil volume. It is important to note that carbon dioxide also dissolves readily in water. When oil contains water, carbon dioxide generates carbonic acid in the oil, which may nega-
tively affect the taste of foods. However, in the present deep-frying experiment, no organoleptic changes were preliminarily detected in the fried potato.

Using 40 L/h carbon dioxide flow, it is calculated that the oil can be used twice as long as the control before the frying oil reaches the upper limit of PC. while natural antioxidants are active in fresh oil, their effects deteriorate after several hours of heating, a situation where the blanketing effect of carbon dioxide will be emphasized. In industrial deep-frying, the time of heating at frying temperature is prolonged and fresh oil is added intermittently. These factors complicate the above-described calculation.

The maximum concentrations of carbon dioxide immediately above the nonwoven fabric and near where the operator was working were 2.3% and below the detection limit (<0.1%), respectively. Notably, the concentration of carbon dioxide poisoning is >3.4%. Although 2.3% is not a low value, the operator will be protected under the hood that is equipped with a pump, as the smallest pump exhausts 8,000 L/min of air.

Fujisaki heated high-oleic safflower oil at 180 °C under an atmosphere of different oxygen partial pressures and found that the deterioration of the oil was proportional to the partial pressure. Totani reported that a small reduction in atmospheric pressure decreased the thermal oxidation of oil during frying. The reduction of oxygen partial pressure at 1 atm, and reducing total air pressure, produce significantly different effects on the oxidation of oil. Carbon dioxide blanketing is closer to the former. The oil at reduced pressure contains a decreased amount of dissolved oxygen, which makes the initial oxidation reaction slow.

We are continuing to optimize the experimental system, including the method of carbon dioxide flow, type of nonwoven fabric, shape of the aluminum plate, etc. It is expected that further improvements to the carbon dioxide blanketing process will provide superior antioxidative effects to PDMS, even though advance set-up is required. The advantage of the carbon dioxide blanketing is to give

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**Fig. 4C** Relative oxygen content (a) and peroxide value / polar compound content (b) of canola oil heated for 1 h under 15 L/h carbon dioxide flow, then allowed to stand at room temperature. Values are expressed as mean ± SD.

**Fig. 5** Relative oxygen content and polar compound content of canola oil used for deep frying under 40 L/h carbon dioxide flow (a) and under air (b), then allowed to stand at room temperature. Values are expressed as mean ± SD.
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frying oil stable and long antioxidative effects at high and low temperature without the organoleptic changes, while natural antioxidants lose their effects in a few hours of deep-frying and PDMS deteriorates oil in touch, mouth feel and flavor.

CONCLUSION
Carbon dioxide blanketing inhibited the oxidation of oil both at deep-frying temperature and during standing at a practical flow rate and volume. The increase in PC of oil was reduced to half of that of the control.

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