# A Comparative Study on the Effectiveness of Nitrogen or Carbon Dioxide Flushing in Preventing Oxidation During the Heating of Oil

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**Nitrogen and carbon dioxide gases were evaluated for their ability to protect canola oil from oxidation during heating at frying temperatures. Oil samples were heated in a variety of containers of differing dimensions through which the flow of these gases was regulated. Formation of volatile compounds was analyzed by direct capillary gas chromatography, while chemical analyses included peroxide value and thiobarbituric acid. Flushing with either of these gases at a slow flow rate in 53-mm containers stimulated oxidation rather than arresting it. Carbon dioxide, because of its higher solubility in oil and its density, afforded better protection of canola oil samples during heating. Optimal conditions for minimizing oxidation, such as container dimensions, volume of oil and flow rate of gases, are discussed.**

Thermal treatment of oils and fats is a common practice in the food industry. The nature of the polymerization reaction products formed during thermal treatment has been studied extensively (1-4). Different treatments have been reported as ways of protecting the oil or fat from oxidation. These include flushing them with nitrogen or carbon dioxide or carrying out the reaction in evacuated glass ampules (1-4). Ohfuji et al. (1), for example, heated 1.8 kg of oil with a nitrogen flow of 300-600 cc/min. However, few papers record either the vessel or the procedure used to protect oil or fats during heating. Rarely is the specific flow rate cited other than in such general terms as "strong flow of . . . " or "adequate to protect flow."

This study presents a detailed evaluation of nitrogen and carbon dioxide for their ability to protect canola oil from oxidation during heating in vessels of different sizes.

## EXPERIMENTAL PROCEDURES

*Materials.* Commercially processed canola oil with no antioxidants except citric acid was provided by Canbra Foods, Lethbridge, Alberta, Canada. The quality of the oil was established based on its negligible peroxide and TBA values. Nitrogen and carbon dioxide gases of high purity were used.

*Sample preparation.* Five- and 20-ml volumes of canola oil were heated in test tubes of 14-mm i.d. and 10, 25 and 50 ml in test tubes of 23-mm i.d. Larger volumes of canola oil (90 ml) were heated in a 53-mm i.d. glass beaker. The test tubes were heated by immersing them in containers of hot mineral oil in which the mineral oil was five cm higher than the canola oil level in the tubes. The beakers containing canola oil were heated directly on a hot plate. All oil samples were heated at 195±5 C for 20 min during which time gases were bubbled through the oil using Teflon tubing (1 mm i.d.) at different flow rates. The flow rates were controlled continuously with a ball flow meter at levels of 100, 300 and 600 cc/min.

Experiments also were conducted on the stability of bulk amounts of canola oil. One 0.5-l and two one-l oil samples were heated in specially designed glass containers of 5 and 7.5 cm diameters, respectively. A gas flow rate of 3,000 cc/min was used in the smaller container (5 cm diameter), while 3,000 and 5,000 cc/min flow rates were used in the larger glass container (7.5 cm diameter).

Twenty-five ml of canola oil was also heated in a sealed glass ampule after being flushed with nitrogen for 30 min. Samples of oil heated without gaseous protection in a beaker were included for comparison.

After heating, samples were cooled down immediately by immersion in cooled tap water with respective gases bubbled through. Samples were then packed in vials, flushed for 15 min with nitrogen or carbon dioxide, closed tightly and stored in a freezer at -30 C prior to analyses.

*Gas chromatography (GC).* Volatiles were analyzed by GC using a modification of the Dupuy method developed in our laboratory (5). Fifty μl of sample and five μl of internal standard (tridecane 200 ng/5 μl) were transferred into a glass wool plug in a glass liner. The washed liners and glass wool were heated overnight at 400 C (minimum 12 hr) prior to use. Samples were purged at 175 C for 15 min with a helium flow of 60 cc/min. Volatiles were trapped on a precolumn (packed with bonded Carbowax 20M, Chromatrographic Specialties CSP 20M) cooled with liquid nitrogen. The temperature was then raised to 65 C, held for three min and programmed to 225 C at 6 C/min. Separation of the volatiles was conducted on a fused silica capillary column (60 m × 0.32 mm) coated with bonded Supelcowax 10 of 0.25 μm film thickness. To quantitate the peaks, an internal standard was used with individual compounds identified by comparison with known standards. Thirteen compounds were identified and calculated as the sum and referred to as oxidation products. These compounds included pentane, hexane, hexanal, 2-hexenal, heptanal, 2,4-heptadienal, octanal, 2-octenal, nonanal, decanal, 2-decenal, 2,4-decadienal and 2,4-dodecadienal. The total amount of volatiles on chromatograms also was calculated.

Nitrogen and carbon dioxide were tested for oxygen content. Separation of gases was carried out on a Varian 2740 with molecular sieve 5A packed in a glass column (2 m × 3 mm). Flow rate of helium was 20 cc/min with a thermal conductivity detector with a current of 180 mA and sensitivity 4X. The nitrogen and carbon dioxide gases were found to contain 0.5 and 1.0 ppm oxygen, respectively.

*Chemical analysis.* Peroxide values were determined in all samples according to AOCS procedure Cd8-53 (6). Thiobarbituric values (TBA) were determined following the method of Tarladgis et al. (7).

## RESULTS AND DISCUSSION

The following engineering parameters were calculated for all samples analyzed:

- Ratio of height of oil to diameter of vessel.
- Linear velocity of gases.
- Critical flow for chain bubbles formed (8).
- Reynolds number (dimensionless parameter used for comparing different objects with flow) (8).

All samples were analyzed for the presence of oxidation products (total carbonyls and hydrocarbons formed from lipid oxidation) (9), total volatiles, TBA value and peroxide value (PV).

The results presented in Tables 1 and 2 show that oils heated without nitrogen or carbon dioxide flushing underwent rapid oxidation. The peroxide value was four times higher, total volatiles 2.5 times higher and oxidation products 3.7 times higher than in the corresponding fresh canola oil sample. Flushing the samples with nitrogen or carbon dioxide to protect the oil during heating resulted in variable increases in oxidation parameters using the same volume of oil in identical containers. A nitrogen flow rate of 100 cc/min resulted in 1.8 times the amount of oxidation products, 1.2 times more total volatiles and 2.7 times higher peroxide values compared to oil heated without nitrogen flushing. The corresponding results with carbon dioxide were 1.2 times more oxidation products, fewer total volatiles and peroxide value identical to oil heated without flushing. Flushing with nitrogen resulted in ca. 50% more oxidation products and 30% more total volatiles than did flushing with carbon dioxide. This could be attributed to the fact that oxygen is twice as soluble as nitrogen in oil, while carbon dioxide is seven times as soluble as oxygen in oil (10). A difference in density (nitrogen 1.2506 g/l; carbon dioxide 1.977 g/l) could also play an important role in the elimination of oxygen from the oil and formation of "headspace" over the top of the oil (11).

A 15% increase in oxidation products was evident when higher flow rates of nitrogen or carbon dioxide gases were used. The total volatiles and peroxide value, however, were higher in oils flushed with nitrogen. The flushing of these gases through oil is in the form of chains of bubbles when the flow rate is smaller than the critical flow or as combined bubbles when flow rate is higher than the critical flow (8). The formation of bubbles causes turbulence over the top of the oil (headspace area) in which the used gas mixes with oxygen from the air. The bubbles blow up on the surface of the oil so that an enlarged area is available for oxygen penetration. This probably is responsible for higher oxidation levels associated with nitrogen and carbon dioxide flow. The procedure using the 5.3-cm diameter container is the most likely one with nitrogen protection during heating (1).

For analyzing conjugated compounds, the AOAC recommends a nitrogen flow rate of 50-100 cc/min in a test tube of 2.3 cm diameter (12). These conditions were followed; the results are shown in sample 5 in Table 1 and sample 16 in Table 2. Peroxide values were 4.3 and 3 times higher, total volatiles 2.4 and 1.8 times greater, and oxidation products were 4.7 and 3.5 times higher in the samples flushed with nitrogen and carbon dioxide, respectively, than in fresh oil. Using the recommended procedure, the oil underwent considerable oxidation. A nitrogen flow rate of 300 cc/min caused little oxidation above that of the fresh oil, although with carbon dioxide this was not observed. When a smaller container of 1.4 cm diameter was used, a nitrogen flow rate of 100 cc/min was sufficient to almost prevent oxidation (Sample 7, Table 1). Carbon dioxide, however, was much more effective in protecting the oil from oxidation (Sample No. 18, Table 2, Fig. 1).

The results presented so far were obtained by flushing oils with gases for 15 min prior to heating. If the oil was heated without prior flushing, there was a significant increase in the oxidation parameters measured (Sample No. 9, Table 1). The amount of total volatiles was 1.6 times higher, and peroxide value and the amount

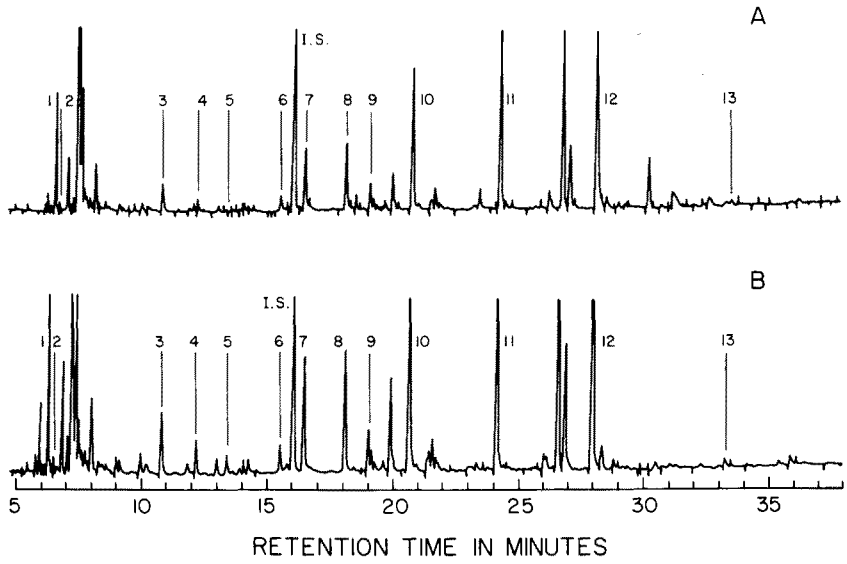


**FIG. 1. Chromatograms of volatiles produced in heated oils flushed with (A), carbon dioxide, or (B), nitrogen. 1, pentane; 2, hexane; 3, hexanal; 4, 2-hexenal; 5, heptanal; 6, 2,4-heptadienal; 7, octanal; 8, 2-octenal; 9, nonanal; 10, decanal; 11, 2-decenal; 12, 2,4-decadienal, and 13, 2,4-dodecadienal.**

**TABLE 1**

**The Effect of Heating With or Without Nitrogen Flushing on Oil Oxidation**

| Number | Sample | Diameter of vessel (cm) | Flow of nitrogen (cc/min) | Height of oil / Diameter | Linear velocity (cm/min) | Critical flow (cc/min) | Reynolds number | Oxidation products (mg/100 ml of oil) | Total volatile (mg/100 ml of oil) | Thiobarbituric value (TBA) | Peroxide value (meq/kg of oil) (PV) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Fresh canola oil | | | | | | | 1.68 | 7.30 | 0.02 | 1.20 |
| 2 | Heated oil without nitrogen | 5.3 | | 0.75 | | | | 6.26 | 18.88 | 1.00 | 4.98 |
| 3 | Heated | 5.3 | 100 | 0.75 | 4.53 | 182.76 | 0.42 | 11.19 | 20.86 | 1.32 | 13.26 |
| 4 | oil | 5.3 | 600 | 0.75 | 27.20 | 182.76 | 2.50 | 13.08 | 29.12 | 1.86 | 19.98 |
| 5 | with | 2.3 | 100 | 2.83 | 24.70 | 182.76 | 0.96 | 7.85 | 17.32 | 1.08 | 5.14 |
| 6 | nitrogen | 2.3 | 300 | 2.83 | 72.20 | 182.76 | 5.76 | 1.86 | 7.72 | 0.42 | 2.06 |
| 7 | | 1.4 | 100 | 5.14 | 64.90 | 182.76 | 1.58 | 1.92 | 8.30 | 0.48 | 2.16 |
| 8 | | 1.4 | 300 | 5.14 | 194.93 | 182.76 | 4.74 | 1.83 | 7.36 | 0.12 | 1.18 |
| 9 | Heated oil without prior flushing | 2.3 | 300 | 2.83 | 72.20 | 182.76 | 5.76 | 4.19 | 9.49 | 0.39 | 2.96 |
| 10 | Heated oil in ampule | 2.3 | | 2.83 | | | | 1.60 | 7.60 | 0.05 | 1.12 |
| 11 | Bulk | 5.0 | 3,000 | 5.08 | 152.79 | 44,410.21 | 13.27 | 1.37 | 6.86 | 0.03 | 1.13 |
| 12 | heated | 7.5 | 5,000 | 3.02 | 113.18 | 44,410.21 | 14.74 | 1.21 | 7.27 | 0.15 | 1.09 |
| 13 | oil | 7.5 | 3,000 | 3.02 | 67.80 | 44,410.21 | 8.85 | 1.77 | 7.18 | 0.08 | 1.48 |

TABLE 2

**Effect of Heating With and Without Carbon Dioxide Flushing**

| Number | Sample | Diameter of vessel (cm) | Flow of carbon dioxide (cc/min) | Height of oil / Diameter | Linear velocity (cm/min) | Critical flow (cc/min) | Reynolds number | Oxidation products (mg/100 ml of oil) | Total volatile (mg/100 ml of oil) | Thiobarbituric value (TBA) | Peroxide value (PV) (meq/kg of oil) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 14 | Heated | 5.3 | 100 | 0.75 | 4.53 | 126.20 | 0.71 | 7.34 | 16.16 | 1.09 | 5.10 |
| 15 | oil | 5.3 | 600 | 0.75 | 27.20 | 126.20 | 4.26 | 8.58 | 18.20 | 1.15 | 6.80 |
| 16 | with | 2.3 | 100 | 2.83 | 24.70 | 126.20 | 1.64 | 5.80 | 12.70 | 0.50 | 3.60 |
| 17 | carbon | 2.3 | 300 | 2.83 | 72.20 | 126.20 | 4.91 | 2.50 | 7.20 | 0.20 | 1.20 |
| 18 | dioxide | 1.4 | 100 | 5.14 | 64.90 | 126.20 | 2.69 | 1.80 | 6.40 | 0.03 | 1.00 |
| 19 | | 1.4 | 300 | 5.14 | 194.93 | 126.20 | 8.07 | 1.20 | 4.60 | 0.02 | 0.90 |
| 20 | Heated oil without prior flushing | 2.3 | 300 | 2.83 | 72.20 | 126.20 | 4.91 | 1.95 | 7.18 | 0.20 | 1.56 |
| 21 | Heated oil with prior flushing | 2.3 | 300 | 2.83 | 72.20 | 126.20 | 4.91 | 1.69 | 6.96 | 0.03 | 1.12 |
| 22 | Bulk | 5.0 | 3,000 | 5.08 | 152.70 | 30,665.65 | 22.59 | 1.26 | 6.74 | 0.02 | 1.13 |
| 23 | heated | 7.5 | 5,000 | 3.02 | 113.18 | 30,665.65 | 25.099 | 1.24 | 6.12 | 0.02 | 1.13 |
| 24 | oils | 7.5 | 3,000 | 3.02 | 67.80 | 30,665.65 | 15.06 | 1.76 | 6.68 | 0.03 | 1.18 |

of oxidation products were 2.5 times greater than the original fresh oil. In the case of carbon dioxide, flushing for 5 min prior to heating essentially eliminated oxidation (Sample 21, Table 2).

For complete protection against oxidation and to prevent volatiles forming during thermal decomposition of hydroperoxides and other components, oil was heated in a glass sealed ampule which had been flushed with nitrogen before sealing. The results obtained using this procedure are presented in Table 1, Sample 10. All parameters measured were identical to those of the original fresh oil.

Bulk samples of oil were also heated and flushed with nitrogen and carbon dioxide gases and the results included in Tables 1 (Samples 11, 12 and 13) and 2 (Samples 22, 23 and 24). Carbon dioxide proved to be much more effective than nitrogen flushing in protecting against oxidation. The lower amount of total volatiles, oxidation products and peroxide values was also attributed to the purging process including gas flow and thermal treatment (9,13).

To prevent oxidation of oils and fats during thermal treatment, the following are recommended:

- Carbon dioxide is more soluble in oil and of a higher density than nitrogen, and thus gives better protection against oxidation.
- The ratio of oil height to the diameter of the container should be a minimum of 3.
- The linear flow of nitrogen and carbon dioxide in containers should be 50 cm/min.
- The container should be filled to a maximum of 70% of its height with oil.
- To eliminate any dissolved oxygen in the oil or fat, a minimum of 15 min for nitrogen and 5 min for carbon dioxide flushing is recommended prior to heating.
- The last four parameters should be met for each particular container and for heating.

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