

58. Sargeant, K., A. Sheridan, J. O'Kelly, and R. B. A. Carnaghan, *Nature* 192, 1096-1097 (1961).
 59. Van der Zijden, A. S. M., W. A. A. Blanche Koelensmid, J. Boldingh, C. B. Barrett, W. O. Ord, and J. Philp, *Ibid.* 195, 1060-1062 (1962).
 60. Nesbitt, Brenda F., J. O'Kelly, K. Sargeant, and Ann Sheridan, *Ibid.* 195, 1062-1063 (1962).
 61. De Iongh, H., R. K. Beerthuis, R. O. Vles, C. B. Barrett, and W. O. Ord, *Biochim. Biophys. Acta* 65, 548-551 (1962).
 62. Asao, T., G. Büchi, M. M. Abdel-Karder, S. B. Chang, Emily L. Wick, and G. N. Wogan, *J. Amer. Chem. Soc.* 85, 1706 (1963).
 63. Coomes, T. J., and J. C. Sanders, *Analyst* 88, 209-213 (1963).

64. Broadbent, J. H., J. A. Cornelius and G. Shone, *Ibid.* 88, 214-216 (1963).
 65. "Toxicity Associated with Certain Batches of Groundnuts." Report of the Interdepartmental Working Party on Groundnut Toxicity Research (London) 1963, Appendix B, p. 2-3.
 66. Milner, M., and W. F. Geddes, "Storage of Cereal Grains and Their Products," edit. by Anderson, J. A., and A. W. Alcock, 165, *Amer. Assoc. Cereal Chem.*, St. Paul, Minnesota, 1956.
 67. Austwick, P. K. C., and G. Ayerst, *Chem. Ind.*, 55-61 (1963).

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Factors Affecting the Rate of Deterioration in the Frying Qualities of Fats.¹ I. Exposure to Air

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Abstract

The effect of heating fats in air and the effect of heating fats in an inert atmosphere were compared, and the relationship of air to changes in the frying characteristics of fat studied. The frying characteristics of a fat did not change to an extent that is commercially significant even after 48 hr heating at 375F in the absence of air; fats heated under identical conditions but in the presence of air, changed radically. It was found, also, that fat which had changed appreciably in frying characteristics when heated in air did not continue to change significantly when heated further under nitrogen. Hence, presence of oxygen was shown to be a necessary condition for the deterioration of the frying qualities of fat at frying temp. Rate of change of the frying characteristics was found to be directly proportional to the degree of exposure of fat surface to the oxygen.

Introduction

IN RECENT YEARS the specific chemistry of fat deterioration at the elevated temp of frying has been the subject of considerable study (1-4,7,8) and it is likely that, with the aid of the newer methods of analysis now available to the oil chemist, it will not be long before the mechanisms and products of this deterioration are known, at least qualitatively. Our laboratory has been concerned with frying fat both as a heat transfer medium and as an important ingredient of the fried food, and, therefore, we have concentrated on the functional effects of deterioration on product quality and the methods of minimizing them rather than the specific chemistry.

This paper is concerned with factors that affect the rate of fat deterioration in the frying system, and more specifically thermal oxidation; it excludes other factors resulting from contamination of the fat by the fried product.

Although today it is generally agreed that the deteriorative mechanism for fats heated in air is autoxidative and proceeds through free radical processes, there has been some suggestion (1) that purely thermal reactions are also operative to a degree that would have functional significance. Our purpose in this work, therefore, was twofold: 1) to test the extent to which non-oxygenated thermal changes could affect chemical and physical properties of fat which relate to its frying performance, and 2) to find out

how the rate of oxidation as measured by these same properties was affected by conditions under which the fat was heated.

Materials and Methods

Fat used throughout this study was a portion of a commercially prepared batch of partially hydrogenated lard of iodine #55-60, stabilized by the addition of antioxidants (Tenox 2, Eastman Chem. Prod. Co. Tenox 2 contains 20% butylated hydroxyanisole, 6% propyl gallate, 4% citric acid and 70% propylene glycol and was used at a concn of 0.05%).

In all cases in which reference is made to heating in an atmosphere of nitrogen, the preparation of the samples was as follows: the fat in the reaction vessel was heated and stirred by means of a magnetic stirrer hot plate at 140F while drawing a vacuum until the fat was degassed as evidenced by the absence of bubbles (approximately one hr). While still exhausting, oxygen-free, prepurified nitrogen was passed into the reaction vessel through a tube opening well below the surface of the sample for a period of about 5 min. The vessel was brought to atmospheric pressure by removing it from the vacuum system while continuing to flush with nitrogen. Both intake and exhaust ports were then closed simultaneously to seal the reaction vessel, retaining an atmosphere of nitrogen.

Samples were heated in a radiant-wall oven, thermostatically maintained at $375 \pm 2F$. Temp variations due to location of samples in the oven did not exceed 1F. Reported heating times were taken from the moment samples were placed in the oven to the moment they were removed. A minor but constant error was, therefore, introduced because the time of heating up to the desired temp was not specially treated.

Various fat properties were monitored throughout this work, but only viscosity and titratable acidity were observed constantly. Previous work in this laboratory (9) had demonstrated a high correlation between these two properties and performance characteristics. Actual frying tests were performed in those experiments in which fats were heated in nitrogen because we had no similar experience with fats heated under this condition.

Titratable acidity (Free Fatty Acids), iodine number, and peroxide value were determined by the AOCS Official Methods (5).

Viscosity was determined in a steam jacketed pipet, fabricated in this laboratory, by timing the flow of 20 ml fat at 212F. The pipet was calibrated with NBS viscosity standards (6) covering the range of viscosities experienced in this work.

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TABLE I

Comparison of Fat Heated in Air and in Nitrogen 48 and 96 hr at 375F

	Viscosity at 212F (centistokes)	Titrateable acidity (% as oleic)	Iodine number	Fat absorption (%)
Unheated control.....	8.25 ± 0.10	0.04 ± 0.03	56.4 ± 0.2	18.0 ± 0.2
Heated in air 48 hr ^a	10.45 ± 0.20	0.99 ± 0.05	50.0 ± 0.2	22.0 ± 1.0
Heated in nitrogen 48 hr ^a	8.25 ± 0.10	0.10 ± 0.03	56.3 ± 0.2	18.6 ± 0.2 ^b
Heated in air 96 hr ^a	14.95 ± 0.20	2.09 ± 0.06	44.7 ± 0.2	25.1 ± 1.0
Heated in nitrogen 96 hr ^a	8.25 ± 0.10	0.10 ± 0.03	56.0 ± 0.2	18.6 ± 0.2 ^b

^a 2-lb fat/5-liter flask, specific surface area = 0.34 cm²/g.^b Difference in fat absorption between this sample and the unheated control was found to be significant in the 99% probability range.

Fat absorptions were determined by frying one dozen doughnuts, cut by the extrusion mechanism of a LINCOLN® doughnut machine (DCA Food Industries, Inc.) into a fryer that was weighed before and after frying. The standard fryer was modified so doughnuts were cut externally into another smaller fryer rather than into the self contained unit of the Lincoln®. The fryer was thermostatically controlled, gas heated, and had a fat capacity of 2 lb.

Doughnuts from a high quality, commercial cake doughnut mix were prepared while maintaining the following factors known to effect fat absorption constant: the amount of water used to prepare the dough, the time and type of mixing of the dough, the temp of the dough (±1F), the temp of the frying fat (±5F), the level of the fat in the fryer, the condition and size of the doughnut cutter, the wt of the unfried doughnut, and the doughnut frying time.

Fat absorptions are expressed in per cent and represent the ratio:

$$\text{Loss in wt of fryer} \times 100 / (\text{wt of fried doughnuts} - \text{loss in wt of fryer})$$

Experimental

Experiment No. 1

In order to compare the effects of heating fat in air and in nitrogen, five 2-lb aliquots of hydrogenated lard were placed in 5-liter round-bottom, Pyrex® flasks fitted with ground glass joints and were treated as follows. Three flasks were left open to the air; one kept at room temp acted as the control; while of the other two, one was heated 48 hr and the other 96 hr at 375F. The remaining samples were degassed, sealed under nitrogen; one was heated 48 hr and the other 96 hr at 375F. The results of this experiment are shown in Table I.

Examination of data shows that the sample heated 48 hr in the absence of air showed little or no change in viscosity, titrateable acidity, iodine number or doughnut fat absorption; whereas the sample heated in air for the same time interval was changed radically. The slight increase in fat absorption due to heating in an atmosphere of nitrogen, which was statistically significant, could be due to the formation of a small amount of surface active substances, fatty acids, or other polar compounds which increase fat absorption by lowering the interfacial tension between the fat and the fried product. The formation of these compounds could have been caused by purely thermal splitting at the ester linkages (1) or by oxidative mechanisms at these linkages (2,3) as well as at the double bonds. Incomplete removal of adsorbed oxygen or the presence of oxygenated precursors, such as peroxides, which are known to decompose spontaneously at this elevated temp, could also explain such oxidative mechanisms. Data for fats heated 96

TABLE II

Comparison of Fats Heated in Air and Nitrogen

	Viscosity at 212F (centistokes)	Titrateable acidity (% as oleic)	Fat absorption (%)
A. Efficiency of Degassing Procedure			
Unheated control.....	8.25 ± 0.10	0.04 ± 0.03	18.0 ± 0.2
Heated 96 hr ^a			
a) 48 hr in nitrogen, cooled under nitrogen then an additional 48 hr in nitrogen.....	8.25 ± 0.10	0.10 ± 0.03	18.6 ± 0.2
b) 48 hr in nitrogen, cooled and swirled in air, then an additional 48 hr in nitrogen.....	8.25 ± 0.10	0.10 ± 0.03	18.6 ± 0.2
B. Effect of Heating Oxidized Fat in Nitrogen in Oven at 375F			
Unheated control.....	8.25 ± 0.10	0.04 ± 0.03	18.0 ± 0.2
Heated 48 hr in air ^b	9.15 ± 0.10	0.45 ± 0.05	19.2 ± 0.5
Heated 96 hr in air ^b	9.95 ± 0.10	0.96 ± 0.05	21.9 ± 1.0
Heated 96 hr 48 hr in air followed by 48 hr in nitrogen.....	9.25 ± 0.10	0.57 ± 0.05	19.2 ± 0.5

^a 2-lb fat/5-liter flask, specific surface area = 0.34 cm²/g.^b 2-lb fat/2-liter flask, specific surface area = 0.17 cm²/g.

hr also are presented in Table I. The punishing effects of heating fat in air are again shown and comparison of 48- and 96-hr results helps clarify the chemistry of this deterioration in the absence of air. Fat heated for an additional 48 hr at 375F under nitrogen did not deteriorate further. Thermal mechanisms are, therefore, judged to be unimportant in the deteriorative process since this mechanism of deterioration would have continued throughout the additional 48 hr heating. In order to determine whether residual adsorbed oxygen or some oxygenated precursor was responsible for the slight changes observed when heating in nitrogen, Experiment No. 2 was performed.

Experiment No. 2

To test the efficiency of degassing and the effect of peroxides and other oxygenated deterioration products on the deterioration of fat heated in an inert atmosphere, five 2-lb samples of hydrogenated lard were placed into separate round-bottom flasks with ground glass joints and were treated in the following manner. Two samples in 5-liter flasks were degassed, sealed under nitrogen, and heated in an oven 48 hr at 375F. When removed, one was vented to the atmosphere and placed upon a mechanical shaker. This latter sample was shaken for 3 hr at ca. 140F to entrain air, degassed, sealed again in an atmosphere of nitrogen, and returned to the oven for an additional 48 hr heating. The other sample, which remained at room temp throughout this period sealed under nitrogen, was also returned to the oven and heated an additional 48 hr at 375F.

The remaining three samples in 2-liter flasks were left open to the air and heated 48 hr at 375F, removed, and allowed to cool over night vented to the air. One sample was analyzed at this stage, one was returned to the oven for an additional 48 hr heating period, while the third was degassed and sealed in an atmosphere of nitrogen and then returned to the oven for an additional 48 hr heating. The results are shown in Table II.

The findings in Table IIA show that reintroduction of air followed by degassing between the two periods of heating under nitrogen did not produce any greater change in properties measured—over that produced by heating continuously under nitrogen for 96 hr. Further, it was also shown that the peroxides originally present to a measurable degree in the unheated

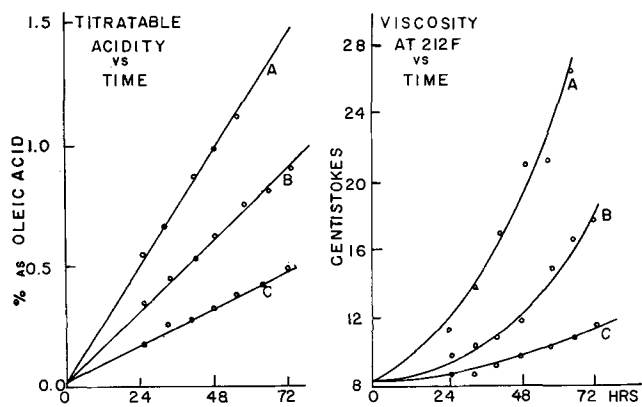


FIG. 1. Comparison of fats heated at different specific surface areas in air at 375F.

- A. Sample heated at specific surface area of $0.644 \text{ cm}^2/\text{gr}$.
 B. Sample heated at specific surface area of $0.322 \text{ cm}^2/\text{gr}$.
 C. Sample heated at specific surface area of $0.161 \text{ cm}^2/\text{gr}$.

fat (0.25 meq/kg) were destroyed by heating in nitrogen and that none were formed in the short aeration period. It is likely, therefore, that the degassing procedure was adequate to remove any functional amount of adsorbed oxygen and that some oxygenated precursor, probably hydroperoxides, were present in only limited supply and were responsible for the small changes observed.

The results in Table IIB show that removal of air from fat, even after a history of appreciable thermal oxidation, almost completely inhibits further changes in properties measured on continued heating. Again, some small degree of deterioration was found when fats were heated under nitrogen, but this change, attributable to hydroperoxides formed during overnight cooling in air, was not significant in terms of properties measured.

Having established the importance of oxygen to functional changes that take place in fat when heated at the frying temp, it was considered important to know which of the conditions inherent in the frying system influenced the rate of such changes. Conditions influencing the amount of oxygen available to the fat should be important, and one factor is defined by the ratio of the surface area of the fat exposed to the atmosphere to the wt of fat (specific surface area). Since the reaction of two essentially immiscible substances, in this case fat and oxygen of the air, must take place primarily at the interface of the two substances, the rate of reaction should be dependent upon the rate at which the reacting species can be brought to this interface; and the greater the area of this interface for a given wt of fat, the greater will be the amount of reacting substance reaching it in any given instant. To test the extent to which this is true in the case of thermal oxidation of fat, Experiment No. 3 was performed.

Experiment No. 3

To determine the rates of deterioration of fats heated in air with different specific surface areas, aliquots of the hydrogenated lard of 200, 100 and 50 g were placed in identical 250 ml stainless steel beakers. The surface area exposed to the atmosphere was the same in each case but the specific surface areas were $0.161, 0.322$, and $0.644 \text{ cm}^2/\text{g}$ respectively.

Six samples of the three different amounts of lard were heated for different lengths of time varying from 16–72 hr. Heating was carried out in an oven

to minimize convection currents. The results of the analysis of these samples are shown in Figure 1.

The rate of change of both viscosity and titratable acidity is shown to be directly proportional to the specific surface area. The importance of oxygen to the deterioration mechanism is clearly defined.

Discussion

In connection with our efforts to learn which factors affect the rate of deterioration of frying fat and the means of controlling them, the preceding experiments were designed to answer essentially two questions: does frying fat change functionally at the frying temp in the absence of air? and how does the ratio of fat-air interface to fat wt affect the rate of deterioration?

The answer to the first question, as determined by Experiments No. 1 and No. 2, appears to be that no functional change will occur in frying fat in the absence of air at frying temp (375F). On the other hand, some change can occur in the absence of oxygen if reactive oxygenated compounds (such as the hydroperoxides) exist in the fat, since compounds of this nature break down at this temp. However, other oxidation products and the triglycerides themselves are apparently stable at this temp in the absence of air, or react forming compounds that have no significant effect on the functional properties of the fat. This latter case is judged to be improbable, however, because most of the chemical changes possible in the absence of oxygen would influence the viscosity, the specific heat, and the surface activity of the fat—all of which play some role in the determination of doughnut fat absorption which did not change. These results are similar to those of Crossley et al. (1) in that the punishing effects of heating triglycerides in air, as opposed to nitrogen at 375F , are demonstrated. Crossley et al. (1), however, using pure 2-oleodipalmitin was able to develop considerably more acidity when heating under nitrogen than we found when heating the hydrogenated lard under nitrogen. Whether this difference in behavior is due to differences in the way the fats were heated or to differences in fatty acid composition of the triglycerides is not known.

Specific surface area has been shown to have an important effect on the rate of thermal oxidation, demonstrating that at least in this oven heating system, diffusion is the factor which determines the rate of reaction. In practical frying operations in which convection and mechanical stirring introduce a faster transport mechanism for the reacting substance, however, it is likely that the effect of diffusion would not be as pronounced.

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REFERENCES

1. Crossley, A., T. D. Heyes, and B. J. F. Hudson, *JAOCs* 39, 9–14 (1962).
2. Endres, J. G., V. R. Bhalerao, and F. A. Kummerow, *Ibid.* 39, 118–121 (1962).
3. Endres, J. G., V. R. Bhalerao, and F. A. Kummerow, *Ibid.* 39, 159–162 (1962).
4. Johnson, O. C., and F. A. Kummerow, *Ibid.* 34, 407 (1957).
5. Mehlenbacher, V. C., T. H. Hopper and E. M. Sallee, "Official and Tentative Methods," 2nd ed., revised to 1960, AOCS, Chicago, Ill., 1959.
6. National Bureau of Standards, Viscosity Standards "L", "M", and "N", Washington, D. C.
7. Perkins, E. G., and F. A. Kummerow, *JAOCs* 36, 371–375 (1959).
8. Ramanathan, W., T. Sakuragi, and F. A. Kummerow, *Ibid.* 36, 244–248 (1959).
9. Stern, S., and H. Roth, *Cereal Science Today* 4, 176–179 (1959).

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