Measuring Flavor Deterioration of Fats, Oils, Dried Emulsions and Foods[1]

JOSEPH A. FIORITI, General Foods Corporation, Technical Center, White Plains, NY 10625

ABSTRACT AND SUMMARY

In fats, oils, and simple systems such as model dried emulsions, conventional measurements such as peroxide values and oxygen absorption measurements usually give a valid measure of sample flavor. In real food systems, this is often not the case. Measures of volatile (CO_2, pentane) and nonvolatile (anisidine reactive compounds) peroxide decomposition products often give a better picture of the organoleptic status of a sample. Unusually large amounts of CO_2 are liberated when fats and oils oxidize in the presence of proteins. The implications of this phenomenon are discussed.

INTRODUCTION

On previous occasions (1,2) we have reported the correlation between various objective measurements and the organoleptic properties of samples subjected to accelerated storage conditions. In the first instance, various commercial fats and oils were oxidized, in bulk, at 38 and 60 C. A comparison between the flavor scores and a number of objective tests revealed that, in most cases, peroxide value, oxygen absorption rate, and pentane level were good indicators of the organoleptic state of the samples. In the subsequent study, a dried emulsion containing safflower oil was used as the model system. In this instance, peroxide value was no longer indicative of the oxidative flavor of the sample. It was apparent that protein and carbohydrates in the system affected the peroxide decomposition rate. Early in the process peroxide breakdown rate exceeds its formation (2). Oxygen uptake and carbonyl formation measurements therefore were more useful in this case. This indicates that the total, potential damage to a dried emulsion can be measured by the rate at which it absorbs oxygen; the actual, organoleptic damage can be better assessed by a method quantifying the decomposition products. During the past months we have examined various food systems to study both the potential (oxidation) and the actual (decomposition) effects of accelerated storage.

EXPERIMENTAL PROCEDURES

Materials

The dry dog food and the bleachable fancy tallow (BFT) were obtained from the Pet Food Division of General Foods, Kankakee, IL. The bacon analog, sold by the same company, was purchased from a local store. The sources of safflower oil and antioxidants have already been cited (2). The soy protein used is sold as "Promine D" by the Central Soya Division, Chicago, IL. The CP grade p-anisidine was purchased from Eastman Kodak Company, Rochester, NY and was used without further purification. Spectral grade iso-octane and CP grade glacial acetic acid were bought from Matheson, Coleman and Bell, Norwood, OH. All other food samples mentioned were prepared in the laboratory using conventional processing techniques.

Methods

The oxygen absorption, carbon dioxide and pentane evolution technique have been cited before (1,2). Therefore, only variations will be mentioned here. Typically, the sample weighed 5.0 g if pure oil or fat and 10.0 g if a food product; it was placed into 100 ml volume serum bottle and stoppered with a rubber septum. The bottles were placed in an oven, usually at 60 C, unless otherwise noted. At regular intervals, 0.2-0.5 ml aliquots of headspace gas were removed with a gas syringe and injected into a gas chromatograph for oxygen, carbon dioxide, and pentane determinations (2). The pentane value in terms of parts per billion was obtained by injecting 0.5 ml of sample headspace gas and comparing the response to those obtained from air dilutions of known pentane concentrations. The anisidine test used was that of Holm, as modified by List et al. (3).

The measurement of stability to oxidation using the oxygen electrode was carried out by using the emulsion system described by Cort (4). The emulsion was prepared by heating 1.6 g MYRJ 52 (ICI, America, Inc., Wilmington, DE), 40.0 g of fat, and 120 ml deionized water to about 70 C on a steam bath and homogenizing the mixture for 2 min using a Tekmar colloid mill (Cincinnati, OH). The oxygen electrode used is a part of a Model 53 Oxygen Monitor (Yellow Spring Instruments, Yellow Springs, OH) attached to a Model 7127A strip chart recorder equipped with a Model 17505A power module both from Hewlett-Packard Company, Moseley Division, Pasadena, CA. In a typical run, 3.0 ml of emulsion was placed in the special cell which was warmed by circulating water at 36 C to prevent fat solidification. The system was allowed to equilbrate by stirring for 3 min. At this time, the stirring was discontinued and the oxygen electrode was carefully placed in the cell so as to exclude all air bubbles. Stirring was resumed and the oxygen meter was set arbitrarily at the 100% saturation line and kept there for at least 2 min to make sure that the baseline was stable. The oxidation run

[1]Presented at the AOCS Meeting, New Orleans, April 1976.

TABLE I

Oxygen Absorption and Flavor Changes in Peanut Products under Accelerated Storage[a]

Sample	Oxygen absorbed (meq/kg)[b]	Flavor
Full fat flakes	15	Stale
Peanut milk[b]	96	Rancid
Full fat flour	36	Nutty, Soapy

[a]8 wk at 49 C.

[b]Based on "as is" weight; all samples = 50% fat.

TABLE II

Accelerated Storage of Fried Noodles[a]

Antioxidant[b]	Evaluation
0.02% TBHQ	Meq O_2/Kg – 40 mM CO_2/Kg – 4.5 Odor – Rancid
0.02% BHA & BHT	Meq O_2/Kg – 66 mM CO_2/Kg – 7.0 Odor – Normal

[a]5 days at 60 C.

[b]In the frying medium. TBHQ = tertiary butylhydroquinone. BHA = butylated hydroxyanisole. BHT = butylated hydroxytoluene.

was initiated by the addition of 10 μl of 0.1 N HCl containing 0.5 mg $FeSO_4$. The reaction was considered complete when all of the oxygen in solution had been consumed, typically 2-30 min.

The BFT (15 kg in a 65 cm diameter aluminum pan) was oxidized at 84 ± 4 C by heating on the steambath, while stirring gently mechanically and irradiating with two General Electric germicidal ultraviolet lamps. The oxidation reaction was also catalyzed by the addition of 2.0 g of ferric stearate. Kg size aliquots were removed at regular intervals (see Table V). Heating and UV irradiation were discontinued after 8 hr; the sample was allowed to stand on the steambath for 18 hr at 40-45 C after which time the former accelerated conditions were restored. The experiment was continued for another 7 hr. The olfactory study of the samples was carried out by a group of five trained members of the Product Evaluation group of this laboratory. The panel members were familiarized with the odor typical of BFT as well as one which was clearly rancid. The samples were stored at -17 C and melted just prior to use when a 35 g portion was placed in an 8 oz jar capped immediately and presented to the panel members in a random fashion at 50-60 C. They were asked to record overall aroma intensity and look specifically for rancid notes. The rating was on a 13 point scale: 0-2, no difference from control; 3-5, slight difference; 6-8, moderate difference; and 9-13, strong difference. The samples were rated on three separate occasions and the values reported are an average of all of the judgments recorded.

RESULTS AND DISCUSSIONS

Among the first of many food samples studied were three samples of peanut products. These, along with their evaluations, are described in Table I. Here the amount of oxygen absorbed is clearly indicative of flavor deterioration. Accordingly, the sample which takes up oxygen most rapidly, the freeze-dried peanut milk, is the one with the worst flavor. This was not the case with the next sample. The accelerated storage of fried noodles (Table II) shows that degree of oxygen absorption and flavor deterioration are not correlated. Although the noodles fried in the butylated hydroxyanisole-butylated hydroxytoluene (BHA-BHT) containing oil had a better aroma, they had absorbed more oxygen. As in most other samples, CO_2 evolution was also measured. We had noted in previous studies that CO_2 evolution increased with the extent of sample oxidation (2). More will be said about this phenomenon later. Here we will merely point out that its presence is indicative of peroxide decomposition and its concentration is related to oxygen absorption.

Tofu, a calcium ion soy protein precipitate, was prepared in the laboratory from a soybean milk in a conventional manner. When the wet curd was dried by three diverse procedures as shown in Table III, the oxidation rate differed. The air dried sample absorbs the most oxygen and has the worst flavor. Carbon dioxide evolution measurement was not as fine an indicator of flavor variability as oxygen absorption in this instance.

TABLE III

Tofu Accelerated Storage[a]

Sample description	% Oxygen	% CO_2	Flavor
Spray-dried	18.9[b]	0.6	Cereal-like
Freeze-dried	19.4	0.3	Bland
Air-dried	17.1	0.6	Rancid

[a]9 days at 60 C; 5.0 g sample in 100 ml stoppered bottle.
[b]Initial oxygen 20.8% O_2; 0.04% CO_2.

TABLE IV

Oxidation of Dry Dog Food[a]

Sample	Headspace analysis			
	% Oxygen	% CO_2	Pentane (ppb)	Odor
A	16.1	2.0	26	Rancid
B[b]	14.8	4.1	24	Green, Pea-like

[a]4 wk at 50 C; fat level = 4%.
[b]FFA rich fat.

Since the next two studies involved the use of dog foods, only olfactory evaluations were obtained. The dry dog food samples analyzed as shown in Table IV contain ca. 4% fat, most of it on the surface of the product. The disparate consumption of O_2 and evolution of CO_2 between the two samples which are, otherwise, identical appear to be due to the fact that one of them, Sample B, has a higher free fatty acid (FFA) level (1 vs. 25% FFA). This suggests that, in some way, FFAs influence the oxidative reaction, probably by accelerating peroxides decomposition. Unpublished results in this laboratory have shown that when substantial amounts of free fatty acids are present in an oil, peroxides do not increase in the conventional manner. This naturally leads one to question the validity of the conclusions drawn from those studies in which peroxide value (PV) alone is the criterion for change. In acid systems PVs are simply not an accurate gauge of oxidation.

Pentane levels were also determined in this study (Table IV); they were not found to be indicative of odor differences. Pentane generation has been shown to be related to peroxide decomposition (5). It has also been found to be a good measure of potato chip flavor deterioration (6). Thus it has become a routine method of analysis in this laboratory when dealing with accelerated storage tests.

The next study (Table V) shows the oxidation of BFT, which is a fat common in pet food products. As the footnote in the table indicates, the last two samples were obtained after the fat had been treated as shown and then allowed to stand overnight at 40-45 C. Here, most of the

TABLE V

Oxidation of BFT[a]

Time (hours)	Peroxide value	Oxidative stability[b]	Pentane value (ppb)	Anisidine value	Olfactory evaluation
0	2.7	31	2.3	2.8	0
4	6.1	15	2.1	4.6	0
8	15.2	3.8	2.8	5.4	3
10[c]	32.4	3.1	3.2	10.9	4
15[c]	46.3	2.0	11.9	15	11

[a]Bleachable fancy tallow at 86 ± 4 C.
[b]By oxygen electrode determination (minutes).
[c]After 18 hr at 40-45 C. See text.

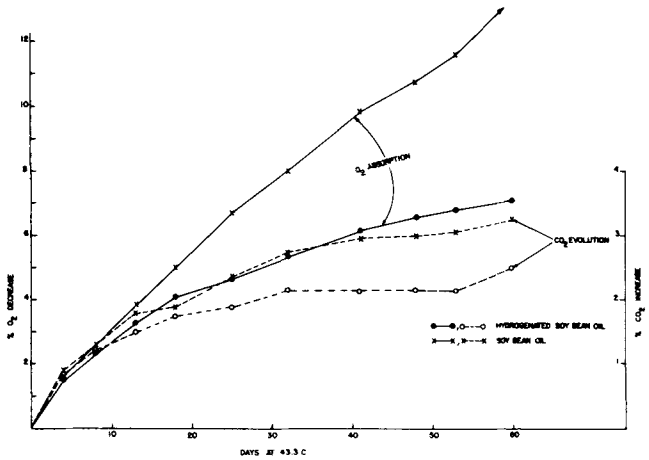

FIG. 1. Accelerated storage of bacon analog samples: O_2 absorption and CO_2 evolution.

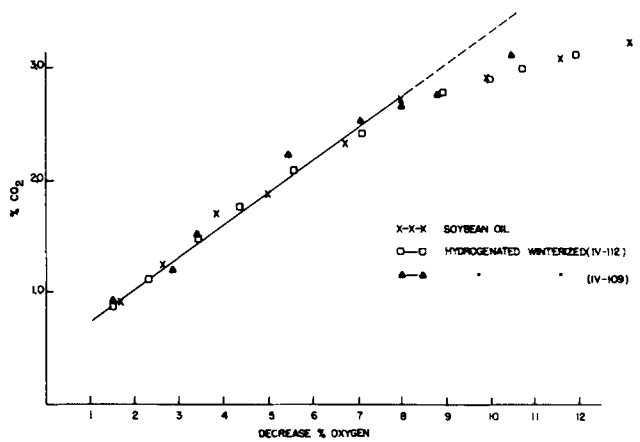

FIG. 2. Oxidation of bacon analog sample: O_2 absorption vs. CO_2 evolution.

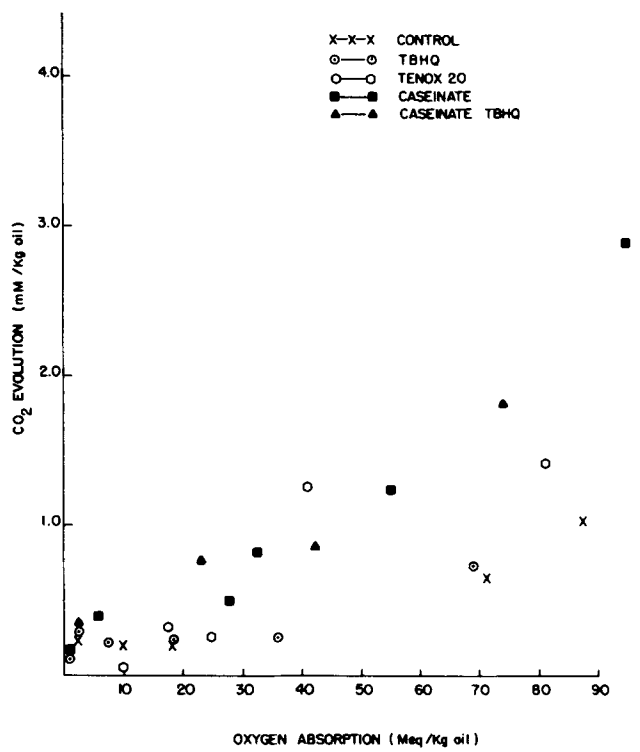

FIG. 3. CO_2 evolution of oxidized dried emulsions. See Ref. (2).

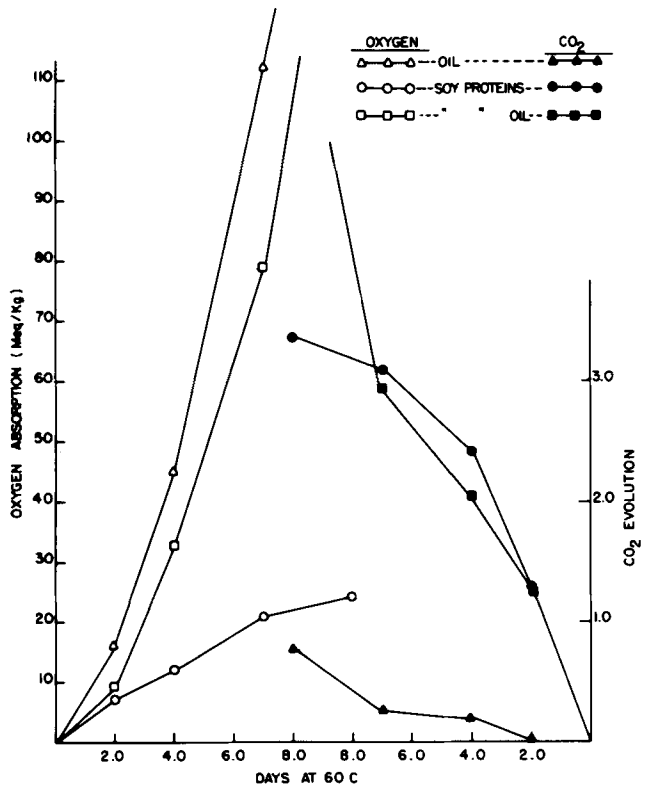

FIG. 4. Accelerated storage of safflower oil, soy proteins, and a 1:1 oil-protein mixture.

methods that are routinely employed in this type of study were used. They all agree fairly well with the olfactory evaluation shown in the last column, where 0 means that the panel saw no difference between the oxidized sample and the control; 3 and 4 signify a perceptible, undefined difference; and 11 means the sample is rancid. Again in this table, the pentane level is that found in the sample's headspace when placed in a stoppered bottle and heated to 60 C. The anisidine value was determined by the method of List et al. (3). It is believed to be a measure of aldehyde level in the sample. The oxidative stability was an abbreviated AOM test run at 35 C using the method of Cort et al. (4), but utilizing a micro oxygen monitor apparatus whereby the stability of less than a gram of fat can be measured rapidly and reproducibly. While all of these methods indicate fat deterioration, the pentane and anisidine values seem to be the best in describing its magnitude.

The oxidation of fat-containing foods and CO_2 evolution was also examined. As postulated by Loury (7) and verified by our experiments (2), peroxides emit CO_2 when they decompose. This is clearly shown in Figure 1 where two meat analogs, which contain two different oils, oxidize at different rates with correspondingly different CO_2 evolution. This evolution is remarkably parallel to the oxidation of the samples. As illustrated in Figure 2, this evolution is proportional to the amount of oxygen absorption, for a good portion of the oxidation path. It suggests a connection between these two phenomena. Looking over some of the data from the study on dry emulsions (2) plotted in Figure 3, we see that when proteins are present in the oxidizing sample, the CO_2 level is usually higher. Is the additional CO_2 coming directly from the proteins or are these causing the oil peroxides to decompose in a manner favoring increase in CO_2 evolution?

To answer these questions, we studied the oxidation of three commercial samples of protein: soy, casein, and gelatin, alone and in combination with an equal weight of safflower oil. Figure 4 shows that soy proteins alone do,

indeed, oxidize. It further shows that they are responsible for most of the CO_2 evolved. Although to a different extent, the same is true of the other two proteins. Since these commercial samples contain 1-3% of ether solubles which, presumably, include lipids, it is still possible that the observed oxidation is due to these rather than to the O_2 attack on the protein side chains. Studies with the solvent-treated protein and pure ovalbumin show a marked decrease (but not the total absence) of lability to oxidation. This suggests that both residual lipids and protein oxidation are involved. We are presently engaged in unraveling these two processes since we believe that they are important both to the stability and flavor of food systems.

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