Effects of Deodorization on the Stability of Vegetable Oils

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MOST vegetable oils used for edible purposes are deodorized by steam stripping in a vacuum chamber. Results are about the same whether the process is conducted in batch or continuous deodorizers. Patent literature especially contains many descriptions of the procedures and equipment designs for commercial deodorization. However, the fundamental knowledge of physical and chemical changes which take place in vegetable oils during this processing stage is rather meager.

Volatile substances which are the principal sources of the flavor and odor of crude oils are removed. The vapor pressures and probably the molecular weights of these materials are comparable to those of palmitic and oleic acids inasmuch as flavor and odor removal usually parallel free fatty acid removal (1). The concentration of these volatile substances, although not measured directly, is in the range of 0.2 to 0.3%since losses in efficient deodorization can be reduced to this amount (2).

Several materials have been identified in deodorizer condensates, and some of these are being recovered. Fatty acids make up a large portion of the distillate. The tocopherols are present in amounts up to several per cent in the seal tank scums from the deodorization of most vegetable oils (3) and are recoverable by molecular distillation or by the preparation of separable derivatives.

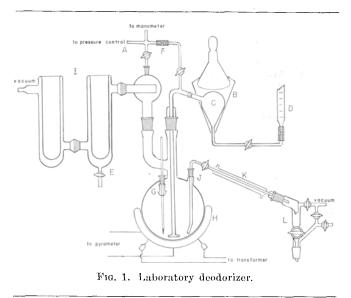
Nonsaponifiable materials are removed up to 60% of the original amount by deodorization under more strenuous conditions than are ordinarily used (4). Aldehydes, ketones, and alcohols are also present, but their identification has been limited by the complexity of the varied mixture of compounds and by the small amount of research on the subject. Methyl nonyl ketone has been identified as one of the volatile constituents of coconut oil, palm kernel oil, and cocoa butter (5, 6, 7).

The removal of those materials from the raw oils produces edible products low in color and relatively free of odors and flavors. Peroxides are decomposed under normal deodorization conditions. In fact, the deodorization of rancid hydrogenated peanut oil has been shown to remove peroxides and impart significant stability. This stability, however, was not as great as before the development of rancidity because of destruction of naturally occurring antioxidants (8). The stability towards oxidative rancidity of deodorized vegetable oils is usually greater than that of the oils prior to deodorization. The reverse is true for animal fats (9). This increase in stability may arise from several factors: pro-oxidants other than peroxides may be deactivated or distilled from the oil; antioxidants may be formed or activated by the heat treatment; peroxides are decomposed and their destruction products are probably distilled from the oil

Corn, soybean, and grain sorghum oils have been deodorized in equipment which permitted controlled deodorizations for specific time intervals. The effects on the stabilities of the oils are discussed in the remainder of this paper.

Equipment

The laboratory deodorization equipment shown in Figure 1 is a modification of that described by Bailey



and Feuge (10). A solenoid valve pressure control device was inserted at (Λ) to facilitate deodorization at any desired pressure. The metal shield (B) greatly increased the heating efficiency of the infrared lamp. Granular charcoal was used in the boiler (C) to replace the carbon-coated asbestos. A burette at (D) provided for the addition of water to the boiler at known rates. A stopcock was inserted at (E) to allow for the inlet of air to break the vacuum and for draining condensate between deodorizations. The connection at (F) permits the release of the vacuum through (E) at the end of a deodorization without either bubbling air through the oil or forcing the oil back into the boiler. The thermometer (G) makes possible deodorization at known oil temperatures. The heating mantel (II) controlled by a variable transformer and connected to a pyrometer offers a clean, simple, and accurate means of heating the oil. It was found that the expensive standard taper stoppers for the dry ice traps at (1) could be eliminated safely. A device for the removal of samples of oil at any time during operation is the feature which makes possible a study of samples deodorized for definite time intervals. By proper manipulation of the various stopcocks it is possible to withdraw oil through the side arm (J) of the flask, cool the hot oil in a water jacketed condenser (K) and remove the oil by means of the fraction cutter (L). When deodorization is conducted under low pressures (0.4 to 7 mm.), there must be a change of a few millimeters in pressure in the deodorization flask during the removal of a sample. However, if the operating pressure is above this level, no change is necessary because a sufficient vacuum can be applied to the fraction cutter to make possible a differential in pressure great enough to force the oil out through (J). Deodorization is not interrupted in either case. At all times the hot oil

should be protected from light by an opaque shield covering the deodorizer flask.

Experimental

Corn oil which had been alkali-refined, bleached, and winterized by commercial processes was deodorized in this equipment at several different pressures. In each case the original charge was two liters of oil in a three-liter flask. The temperature was maintained at 215° C. The amount of steam was varied directly as the absolute pressure, using quantities which corresponded to that used for commercial deodorization. Samples were withdrawn at frequent intervals and determinations of Lovibond colors; free fatty acid (11) were made immediately. The data shown graphically in Figure 2 represent the results of typical deodorizations at 8.0 mm. pressure.

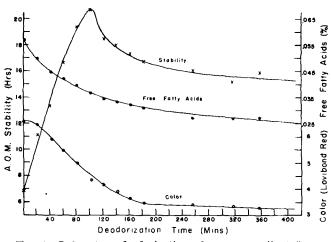


FIG. 2. Laboratory deodorization of raw corn oil at 8 mm. pressure and 215 °C.

The results of laboratory deodorizations were confirmed by similar sampling during commercial deodorization of corn oil (Figure 3). A water-jacketed iron sampling device was attached to the side of a deodorizer below oil level. Samples were withdrawn at intervals of three to four minutes in order to keep the sampler well flushed with oil. When the oil sample was to be saved for analysis, the sampler was flushed with nitrogen and left full of nitrogen so that the hot oil entering the sampler did not come into contact with air. After the oil had cooled, it was analyzed immediately for color and free fatty acids. Samples were kept at -20° C. for stability determinations the following day.

Soybean oil and grain sorghum oil also were deodorized in the laboratory. The results in Table I show that the increases in stability of grain sorghum oil and corn oil were comparable. However, soybean oil, at least in this one case, had a much smaller gain in stability, although its general behavior paralleled that of the other vegetable oils studied.

Discussion

The apparatus which was assembled for this work facilitated the collection of data on the deodorization of vegetable oils for specific lengths of time. Such information could not be obtained by simple deodorization of batches for varying time intervals because of the time required to heat and cool the oil and the attendant variables introduced by this practice.

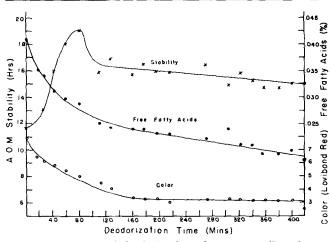


FIG. 3. Commercial deodorization of raw corn oil at 9 mm. pressure and 215°C.

The stabilities of vegetable oils were found to increase rapidly to a maximum as deodorization progressed. After this point was reached, the stabilities fell to a fairly constant value significantly above that of the original raw oil. An explanation of this phenomenon is not readily apparent. It is probably not due to a peculiar effect of the equipment because almost identical results were obtained during both laboratory and commercial deodorizations. Although in these two examples the maximum stabilities were not obtained at the same time, both were found when the temperatures reached 195°C.

Simultaneously with this increase in stability, there is observed a reduction of color and flavor and a decrease in free fatty acids. Heat-bleaching of vegetable oils is a well recognized but poorly defined phenomenon. Usually the increases in bleaching and stability during deodorization have been attributed to steam stripping. However, the data in Table II indicate that heating *in vacuo* causes an increase in stability as well as a decrease in color. In this example raw corn oil was treated in three ways: 1) heated for two hours at 200°C. and 1 mm. pressure, 2) heated equivalently (or comparably) but purged with nitrogen, and 3) deodorized with steam at 200°C. and 1 mm. pressure. The greatest increase

		T Stability of Dec 2 Hours, 215						
Он .	A. O. M. Stability (hr.)		Peroxides (me/kg.)		Lovibond Color (Red)		Free Fatty Acids (%)	
	Raw	Deodorized	Raw	Deodorized	Raw	Deodorized	Raw	Deodorized
Corn Grain Sorghum Soybean	$\begin{array}{r}11.5\\5.8\\6.6\end{array}$	22.0 16.1 8.8	$ \begin{array}{r} 16.7 \\ 27.8 \\ 15.0 \end{array} $	0.5 0.8 0.6	7.6 10.6 10.8	2.3 5.3 2.3	$\begin{array}{c} 0.033 \\ 0.051 \\ 0.045 \end{array}$	0.011 0.025 0.018

TABLE II Heat Treatment of Raw Corn Oil

Treatment of Oil	Flavor	Color Units (R)	Free Fatty Acids (%)	A. O. M. Stability (hr.)
Original	Crude	7.8	0.042	11.6
Heated, 1 mm. pressure, 2 hr. 200°C Heated, 1 mm. pressure,	Crude	2.5	0.092	23.5
2 hr., 200°C., purged with N ₂	Bland	3.0	0.042	21.6
Deodorized, 1 mm. pressure, 2 hr., 200°C	Very bland	3.3	0.021	23.1

in stability and reduction in color took place in the oil which was not stripped with a gas. It was interesting also to note that a bland oil was produced by purging with nitrogen. In this latter case only traces of oily distillate were collected in dry ice traps as compared with none from the heat treatment alone and approximately 0.2% from the steam stripping treatment. No significant change was obtained in the flavor of the heat-treated oil in spite of improvement in stability and color. However, the odor was changed from a crude-oil odor to a pleasant nutty odor. Hence, increased stability and decreased color probably are not associated directly with removal of substances causing raw oil flavors as is often supposed. If the increased stability is due solely to destruction of peroxides and if the destruction products are not pro-oxidant, then a partial answer to the problem is evident. Other explanations may be found in heat deactivation or destruction of other pro-oxidants, and heat activation or formation of antioxidants. However, the reason for the decrease in stability after reaching the early maximum during deodorization is still unexplained.

Summary

Corn oil, soybean oil, and grain sorghum oil have been deodorized in a laboratory unit equipped with a take-off for removal of samples at various times during deodorization. Stabilities of the oils increase rapidly during the initial part of the deodorization and this increase is caused apparently by heat destruction of pro-oxidants such as peroxides rather than by removal of volatile materials through steam distillation. These laboratory results were confirmed by a similar study of commercial deodorization of alkali-refined and winterized corn oil.

Acknowledgment

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