Factors Affecting the Rate of Deterioration in the Frying Quality of Fats[1] II. Type of Heater and Method of Heating

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Abstract

Using a commercially prepared hydrogenated lard and heating methods simulating those currently employed in commercial fryers, it was found that the rate of fat deterioration varied inversely with the temp of the heating element. This has been attributed to differences in the rate and duration of convection circulation, a measure of the amt of fat-air contact, and therefore, thermal oxidation. When element temp were increased from 900–2400F, while thermostatically maintaining the fat temp at 375F, it was found that the rate of convection circulation increased while the duration of convection circulation decreased, and it is postulated that the overall effect of increasing element temp is one of decreasing the total amt of fat contact with the air.

It was also demonstrated that mechanical circulation of fat, as required in an externally heated fat system, significantly increased that rate of fat deterioration when compared to fat heated by conventional direct gas-heat, if both were heated and maintained at 375F for identical periods of time.

Introduction

It had been established that the deterioration of fat can modify the products fried therein (1–4,7,10, 11) and, therefore, a knowledge of how conditions peculiar to the different systems used today in practical frying operations affect the rate of deterioration is of value both as a guide to the design of new frying equipment and to establish the best methods for handling fats in present commercial apparatus. It has been previously shown (7) that fat heated at the frying temp in the absence of air does not undergo significant changes in its functional properties while equivalent treatment in the presence of air has pronounced effects on the performance characteristics of the fat. One phase of our continuing study of these factors was to evaluate the various types of heating elements and heating methods employed in current commercial practice.

The heating methods used in today's frying equipment are of three basic types: the electric, the direct gas-heated fryers and the heat exchange or indirect heated fryer. Our experiments were designed to determine how these heating methods affect the rate of fat deterioration, using simulated frying systems.

Materials and Methods

The fats used in this study were aliquots of commercially prepared batches of partially hydrogenated lard, iodine number 55–60 and an unhydrogenated corn oil. Both were of a type commonly used in commercial frying operations and the hydrogenated lard was stabilized by the presence of antioxidants, (Tenox 2 from Eastman Chemical Products 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%).

We were interested in fat deterioration, primarily as it affects the product fried therein, and, therefore, only viscosity and titratable acidity were determined because previous work (7,10) had demonstrated a high correlation between these properties and the performance characteristics of the fat. Viscosities were determined in a laboratory-made steam jacketed viscometer (7) and the titratable acidities by the Official Methods of the AOCS (5).

Experimental Procedures

Experiment No. 1. Effect of the Type of Heating Element on the Rate of Fat Deterioration.

Samples (800 g) of hydrogenated lard were heated and maintained, in identical 1-liter stainless steel beakers, at a temp of 375 ±5F for 8,24 and 48 hr using three different types of heating elements: a Meker burner flame, open electric coils supported by a refractory material and an electric hot plate. The temp of the flame and of the coils were approx 2400F and 1400F, respectively, at the heating element-beaker contact points, when determined by the melting of various reagent grade salts and metals of known melting points. The temp of the hot plate, approx 900F, was determined with a Pandux surface thermometer.

Each of the simulated fryers was thermostatically controlled with thermoregulators. In addition, the gas fired "fryer" required a pilot light and a solenoid valve. The pilot was a remote type and did not have any heating effect. A layer of asbestos was wrapped around the reaction vessels to minimize heat losses.

The film temp, i.e., the temp of the surface of the metal beaker in direct contact with the fat at the center of the heating area, were determined by chromel-constantan thermocouples brazed into the inside bottoms of the beakers which recorded the temp variations with time throughout several complete cycles. Each thermocouple was calibrated after brazing by completely submerging the beaker in liquid baths of known temp in the range from 300–520F.

The samples were heated for 8 hr/day and the heating periods began as soon as the heaters were turned "on" and ended when heaters were shut "off." Samples were stored at room temp between heating periods. At the end of the desired heating times, samples were analyzed for viscosity and titratable acidity. The results of this experiment show in Table I.

TABLE I

The Effect of Type of Heater on the Rate of Deterioration of Hydrogenated Lard

Heater element	T of heater element F	Range of film T[a] F	Hr heated at 375F	Viscosity at 212F cs	Titratable acidity % as oleic acid
			Unheated	8.25	0.04
Electric hot plate	900	395–435	8	8.45	0.07
			24	9.05	0.14
			48	11.0	0.32
Electric coils	1400	410–480	8	8.25	0.07
			24	8.95	0.17
			48	10.4	0.27
Gas flame	2400	350–480	8	8.25	0.07
			24	8.65	0.17
			48	9.35	......

[a] Temp of the surface of the metal beaker in direct contact with the fat at the center of the heating area.

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[1] Presented at the AOCS Meeting in New Orleans, 1962.

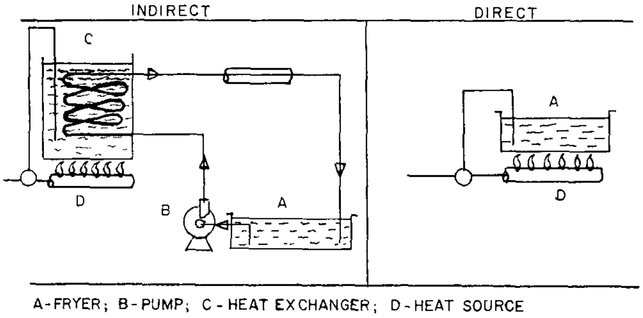

FIG. 1. Model systems of heat exchanger and direct heated fryers.

The relative rates of fat deterioration as measured by viscosity showed large differences in the following order: hot plate > coils > flame. Titratable acidity differences were not significant. It is believed, however, that had the experiment been continued for an additional 24–48 hr, differences would also be apparent in this property and they would be in the same direction shown by the viscosity data. Film temp varied only slightly among the various heating techniques and the results found for the hot plate experiment compared favorably to the film temp measured by a comparable procedure within an electrically heated commercial fryer.

The minimum film temp of the gas-fired beaker was below the fat temp because of the cooling effect of circulation between the bottom of the beaker and the burner when the flame is off. The specific surface area (SSA) or ratio of fat-air interface to the total mass of fat was identical in all beakers (0.106 cm^2/g) and the temp was within the range common to commerical deep fat frying practice.

Experiment No. 2. Comparison of Direct and Indirect Heating Methods on the Rate of Fat Deterioration.

In this experiment, 3.2 kg aliquots of nonhydrogenated corn oil were placed into each of two identical aluminum pans and heated at 375 ± 5F, using systems of heating to simulate direct and indirect heated fryers as shown in Figure 1.

Corn oil rather than a plastic shortening was used for this experiment to avoid the difficulty that would be encountered with solidification of a plastic fat in the pump and piping system during cooling. The specific surface area of fat in contact with the air was identical in both systems. (0.10 cm^2/g).

The frying fat in the externally heated fryer was circulated continuously by means of a stainless steel centrifugal pump so that the fat at the surface moved at a rate of approx 10–15 ft/min. A tube and shell heat exchanger was simulated by submerging a coil of aluminum tubing in an oil bath, heated and thermostatically controlled to maintain a temp of 390–400F. This temp was found to be necessary to maintain a temp of 375 ± 5F in the simulated frying kettle.

The direct heated fryer was heated by three Meker burners spaced equidistant from each other below the fryer, and was thermostatically controlled to maintain a fat temp of 375 ± 5F. The pilot lights for this fryer were located directly below the simulated frying kettle and heated the fat continuously, thereby simulating the "throttled" burner control of commercial fryers.

Both systems were insulated with a layer of asbestos and heated and maintained at 375F for 6 or 6.5 hr/day and allowed to cool overnight at room temp. The time required to heat the samples to 375F was also maintained essentially equivalent by circulating the frying fat through the heat exchanger only *after* the heat exchange fluid had reached a temp of 420F. Circulation of the frying fat through the heat exchanger rapidly lowered the temp of this unit to 390–400F while increasing the frying fat temp to 375F at the desired rate.

Samples were taken for analysis of titratable acidity and viscosity after various intervals of heating and the results show in Table II.

TABLE II
Comparison of Corn Oils Heated at 375F by Different Heating Methods

	Viscosity at 212F cs			Titratable acidity % as oleic acid		
Time:	0 hr	13 hr	25 hr	0 hr	13 hr	25 hr
Type of heating						
Direct	7.20	7.55	7.60	0.06	0.12	0.13
Indirect	7.20	7.70	8.10	0.05	0.12	0.13

It was found that the fat heated by the indirect method deteriorated faster than fat heated by the direct method as measured by viscosity changes. There was no difference in acidity build-up in the two systems. This experiment, like the preceding one, used conditions that were representative of those found in actual commercial operations except for the lack of actual frying and fat replacement (turnover).

Discussion

It has been found, in Experiment No. 1, that the rate of fat deterioration as measured by viscosity varied with heater element type and contrary to what might be expected (8,9) the rate varied indirectly with element temp. A possible explanation is offered by considering another, somewhat unexpected finding of this experiment; i.e., that the film temp varied only slightly between vessels despite the great differences in element temp. Only the stirring action of convection could have overcome these differences in thermal input and a difference in rate or duration of stirring would explain the differences found in the rates of deterioration. This mechanism was supported by the fact that the rate of thermal oxidation of a fat at the frying temp had been shown (6,7) to be a function of the rate at which the reacting species are brought together at their interface.

A repetition of Experiment No. 1, taking particular note of the rate and duration of convection circulation, appeared to confirm convection as the mechanism for the observed phenomena. Although the rate of convection varied directly with element temp, thereby producing essentially equivalent film temp, the duration of the circulation was inversely proportional to the element temp, ranging from ca. 25% of the total heating time in the vessel heated by the gas flame to essentially continuous circulation in the case in which the hot plate was the element. It would appear, therefore, that only the duration of circulation was important; but consideration of Experiment No. 2 shows that rate as well as duration must be considered.

In experiment No. 2, the rate of deterioration measured by viscosity was greatest for the fat heated indirectly and because the duration of circulation was 100% of the heating times in both vessels, only the variation in the rate of circulation could explain these results. The throttled direct heated fryer was on at full heat and, therefore, rapid circulation, for ca. 20% of the total time, whereas in the externally heated fryer, circulation was rapid for 100% of the time.

In light of these results, claims of prolonged fat life in indirect heated fryers because of their low film temp (8,9) require some reinvestigation.

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Synthesis of Triglycerides from Fish Oil Fatty Acids

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Abstract

The generally accepted methods for the synthesis of triglycerides are unsatisfactory when they are applied to highly unsaturated systems such as those present in fish oil. The methods either fail to give sufficiently high yields, or they are prohibitive in cost when applied to large scale production. Of the numerous reactions studied, the most feasible was the zinc-catalyzed esterification of fish oil fatty acids with glycerol. Thin-layer chromatography (TLC) showed that this reaction gave yields of 75–78% triglycerides. Gas-liquid chromatography (GLC) demonstrated the composition of the triglycerides was essentially the same as that of the original fatty acids.

Introduction

During recent years, there has been an increasing demand for highly unsaturated glycerides. This demand has developed because of the growing interest in the effect of highly unsaturated lipids in nutritional and medical research. The fact that naturally occurring sources of triglycerides with a high degree of unsaturation are not available has limited the efforts of some researchers in these fields. Fish oils do contain appreciable amounts of highly unsaturated fatty acids; however, due to the random distribution of the total fatty acids on the glycerol molecules, a conc of highly unsaturated triglycerides is not readily obtainable.

The object of this research therefore was to develop a method whereby highly unsaturated triglycerides could be synthesized in large quantities from fish oil fatty acids.

Classical Methods of Preparation

There have been numerous reports in the literature on the preparation of mono- and diglycerides, but little has been reported on the synthesis of triglycerides. The reviews of Norris (1) and Malkin and Bevan (2) cover the majority of this work thoroughly, and consequently, no effort will be made to discuss in detail the syntheses presented by these authors. In general, the methods they describe are for the syntheses of specific glycerides, which usually are those containing single fatty acids with low or no unsaturation. This is especially true for the synthesis of triglycerides. Some papers have described the conversion of vegetable oil fatty acids to glycerides (3,4), but here again, there is little information regarding the more highly unsaturated compounds.

The acylation of glycerol with unsaturated acid chlorides has been successfully used to obtain good yields of triglycerides (5,6). However, the preparation of kg quantities of the acid chlorides from highly unsaturated fatty acids makes this method prohibitively expensive. For that reason, this reaction was not considered further.

Eckey (7,8), showed that the iodine value (I.V.) of fish oil can be substantially increased by base-catalyzed directed interesterification with simultaneous crystallization. The unprecipitated triglycerides obtained by this method still contain appreciable amounts of low unsaturated entities as well as a certain amount of saturates. Consequently, the I.V. of the product obtained from this process is not as high as would be desired. In addition, the process is lengthy.

Other methods for the synthesis of triglycerides appeared to be more applicable to the highly unsaturated systems found in fish oils. One of the more attractive of these is the base-catalyzed ester-ester interchange between triacetin and methyl esters (9,10). It was found that this method worked well in the preparation of triglycerides, such as tristearin or triolein, but it was not satisfactory for the preparation of mixed triglycerides containing the wide range of chain lengths and degrees of unsaturation found in fish oil methyl esters. Initially, the reaction proceeded quite rapidly at temp of 50–70C, but it then proceeded slowly even when the temp was raised as high as 125C. The amount of methyl acetate condensed and collected in a cold trap indicated yields of better than 90%. Analysis of the reaction products by TLC (11), however, showed that the yields of triglycerides were no greater than 35–40%, with mono- and diglycerides being the major by-products. Use of forcing conditions such as increased temp, change of pressure, varied molar ratios of the reactants, different types and concn of catalysts, and extended reaction times failed to give a more desirable yield.

Since neither directed interesterification or ester-ester interchange proved to be satisfactory for the preparation of highly unsaturated triglycerides, attention was turned toward acid- or base-catalyzed esterification of the highly unsaturated fish oil fatty acids with glycerol. It was found that mineral acid catalysts tended to attack the unsaturated fatty acids even under fairly mild conditions or gave poor yields (<5%). When a strong organic acid such as *p*-toluenesulfonic acid was used, yields up to 30% were obtained. Strong base catalysts proved to be no better than the mineral acids. A number of metal oxides and salts have also been used as catalysts for the esterification of vegetable oil fatty acids with