of a much smaller magnitude, have been observed in soybean oil.

Use in Conjunction with Trading

By proper utilization of the knowledge of actual refining characteristics of crude oils, as defined by the centrifugal method in contrast to the trading method (cup loss), the more valuable or profitable oils can be identified readily. Examination, by the centrifugal method of a cross section of crude cottonseed oils, revealed that in general the crude oils with lower refining losses are more profitable to refine in terms of yield per dollar invested than the high loss, discounted oils. Also, it becomes evident that crude oils from some mills yield a consistently better return than those from other mills. The same approach can be made when trading is on the basis of total neutral oil as determined by the chromatographic loss method (3). However, in the opinion of the authors, the advantage that might be gained under such conditions is lessened in that differences become less dramatic and the direction is reversed. This applies because chromatographic loss represents an estimate of the amount of oil available for recovery but without reference to the possibility of attaining such levels by specific processing techniques. Examples of the variation of the loss, characteristic of crude cottonseed oils, as determined by cup loss, centrifuge loss and chromatographic loss methods are given in Table III. These data indicate that while the chromatographic loss method gives the minimum loss that might be attained, the refinery loss will vary from this value depending on the characteristics of the crude.

TABLE III

Refining Loss by Different Methods for Crude Cottonseed Oils from Different Sources

Source	Refining Loss %, by Method		
	Cup	Centrifuge	Chromatographic
1	7.4	6.3	3.2
2	7.3	4.5	3.0
3	7.2	6.8	3.1
4	7.1	4.0	3.4
5	6.8	3.6	2.8
6	5.8	2.9	2.6

Analyses for each source are the average of analyses for 3 or more cars of crude oil.

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Quick and Simple Methods for Studying Crystallization Behavior of Fats

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Abstract

A simple method of obtaining reproducible cooling curves has been developed. A microscopical technique is described for determining melting point and transformation time of the unstable α-form, which has a marked influence on the consistency of commercial fats.

A correlation between the transformation time and the shape of the cooling curve has been found. Examples of the application of the cooling curve technique in factory control are given and discussed.

Introduction

THE CRYSTALLIZATION behavior of commercial fats used in margarine manufacture has been studied in order to investigate the causes of variations in the consistency of the margarine. For this purpose we have applied a special cooling curve method, and have also made microscopical examinations of the fats when crystallizing.

Cooling curve methods have long been employed to characterize fats of different kinds (1,2,3) and especially cocoa butter (4). A recent work describes the use of cooling curve analyses in conjunction with Differential Thermal Analyzing techniques (5).

Microscopical studies were made to investigate the behavior of fats when shock-crystallized, and to note the changes of the fat crystals occurring soon after chilling.

Experimental

Cooling Curves. As the cooling curve technique is empirical, the methods described in the literature give curves of different character, depending on the rate of cooling. In the following method the cooling rate is standardized by keeping the fat in a vacuum jacket flask in an ice-water bath. The fat is cooled evenly without stirring. In a horizontal center section of the flask crystallization occurs simultaneously all through the fat. The phase changes during crystallization accompanied by heat effects are detectable from changes in the slope of the curve. Most fats exhibit characteristic behavior, and minor changes in the composition of these fats are reflected by variations in the cooling curve.

Apparatus. The flask used is according to Shukoff (Fig. 1). It is essential to standardize vacuum in the jacket and the dimensions of the Shukoff flask so that the rate of cooling is the same for different flasks. Capacity of the inner tube of the flask is 30 ml and the jacket is evacuated to 10^{-2} mm Hg. Dimensions are given in Figure 1.

The flasks are most easily checked by making a cooling curve for a deodorized liquid oil, i.e., soybean oil. The temperature fall for a liquid oil in the Shukoff flask in an ice-water bath shall be from 40C to 18.5C ± 0.3 in 20 min.

The thermometer range is 0–50C with 0.1C subdivisions; Length is ca. 40 cm; Diameter of bulb 6 mm, length 12 mm. The thermometer is fitted to the flask with a ground joint, with the mercury bulb exactly in the center of the inner flask. The joint could be scratched, making the removal of the thermometer easier.

A Dewar bottle, ca. 1 liter is filled with ice-water at 0C. Times of cooling are measured with a stop watch.

Procedure. Heat the sample to 70C until all crystal

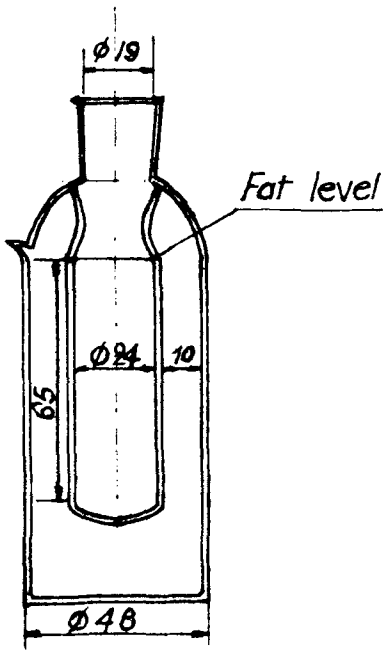

FIG. 1.

nuclei are melted; filter if necessary until the hot oil is clear. Filtration must be done at least 20C above the approximate melting point. Pour oil into Shukoff flask (ca. 25 ml) and insert thermometer when temperature of oil is ca. 50C. Place flask in Dewar bottle with the ice-water bath and start stop watch when temperature of sample passes 40C. Record temperature each minute and draw a time-temperature diagram. Time required for determination of cooling curve is ca. 60 min.

Curves made in this manner have a characteristic shape for each type of fat or fat blend. Figure 2 shows some typical curves. The cooling curve for a liquid oil is superimposed as a solid line.

Curves for tallow, hydrogenated marine oil, and Sheabutter all show an initial point of inflexion, followed by minimum and maximum points. Hydrogenated cottonseed oil (Fig. 4) produces no point of inflexion but distinct minimum and maximum points, the minimum points lying very close to the liquid oil curve. Palm oil curves (Fig. 2) have an inflexion point but no distinct minimum or maximum. This may be due to the slow crystallization of palm oil within this temperature range.

A correlation has been noticed between the slip point of a fat and the inflexion point on its cooling curve or, in cases where there is none, the minimum point for that particular fat. The slip point is generally to be found in a region about 10–12C above these points. An example is given in Figure 3 which shows how the hydrogenated marine oil curves vary according to the degree of hydrogenation.

While curves for different samples of the same natural fats such as coconut oil, palm oil and Sheabutter normally vary only slightly, hydrogenated fats show greater variations. Figure 3 depicts the curves of two hydrogenated marine oils 40–42C, delivered immediately after each other from the same hydrogenation plant. Figure 4 shows two samples of hydrogenated cottonseed oil 36–38C which were also produced almost simultaneously. Slip point, iodine value, and dilatation measurements showed only minor variations for the various types of fats (see Table I), while cooling curves revealed considerable

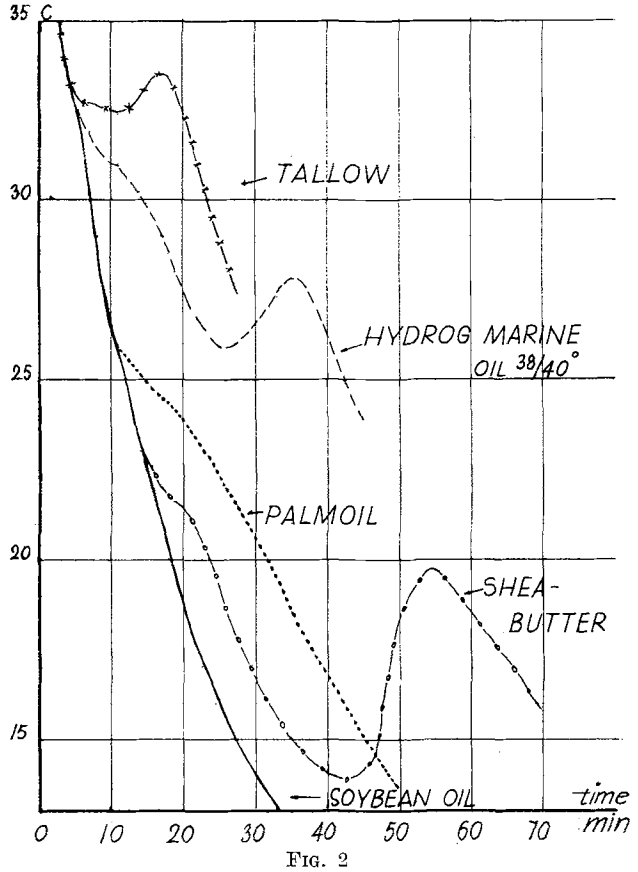

FIG. 2

differences in crystallization behavior.

GLC analysis of the fats indicated different fatty acid compositions as shown in Table II. From this it is evident that the origins of the hydrogenated marine oils were not identical. Sample 2 contains greater amounts of high molecular weight acids (C_{20}–C_{22}) than sample 1, which is instead richer in low molecular weight acids (C_{14}–C_{16}).

Differences in hydrogenated cottonseed oils lay in the *trans* acid content, and in the higher stearic acid content of sample 4. Variations here are not caused by the original oils but must be ascribed to the hydrogenation process.

Such differences in the crystallization behavior of fats as indicated by these curves are of considerable consequence for the consistency of margarine manufactured from them. A margarine based on a fat-phase with 30% of hydrogenated marine oil No. 2, Figure 3, was, despite efficient machine cooling, so soft when moulded that it was almost liquid. This must be due to incomplete crystallization during manufacturing.

The effect of interesterification is clearly reflected on a cooling curve; it has previously been demonstrated by Quimby et al. (3) and Luddy et al. (6). The extent to which such a change in the glyceride structure influences the shape of the cooling curve is shown on Figure 4. The two curves represent a

TABLE I

Fat	Mp°C	I.V.	SFI 20C	SFI 40C
H marine oil 40/42 1)	44.1	56	65	13
H marine oil 40/42 2)	43.7	56	61	12
H. cottonseed oil 36/38 3)	36.2	63	50	1
H. cottonseed oil 36/38 4)	37.5	62	46	1

Mp°C = Slip point
I.V. = Iodine value
SFI. = Solid fat index

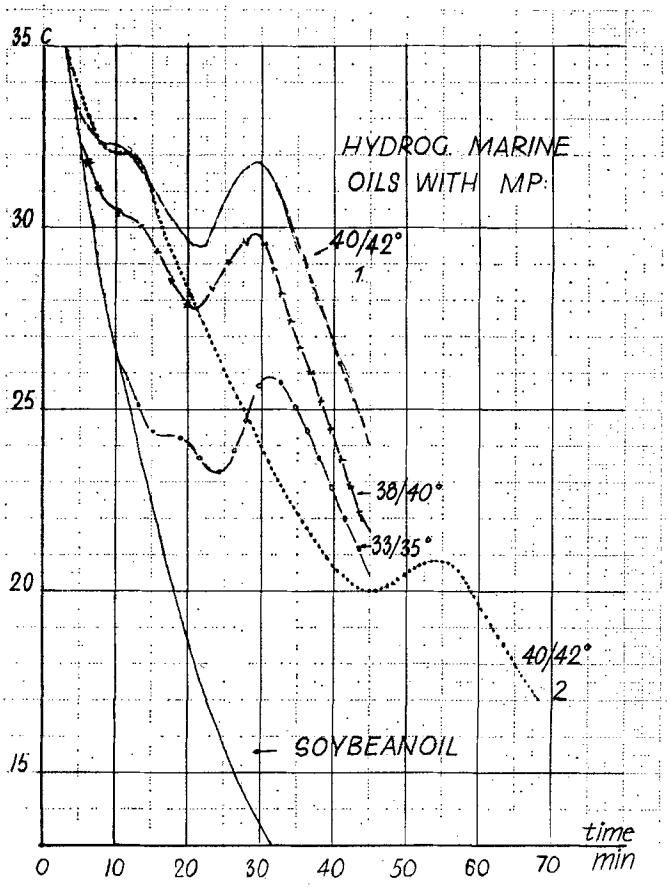

FIG. 3

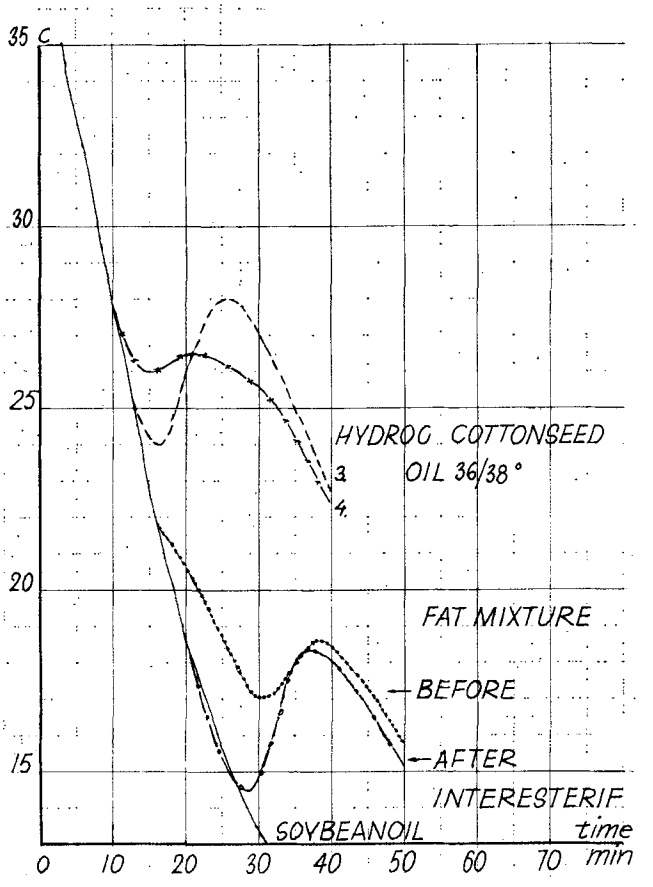

FIG. 4

fat mixture consisting of 30% rapeseed oil, 40% coconut, and 30% hydrogenated marine oil, before and after interesterification, respectively. Before interesterification the curve has the typical inflexion point for hydrogenated marine oil, as well as minimum and maximum of coconut oil character. After interesterification the characteristics of the blend underwent a change. The curve showed no inflexion point but minimum and maximum points in the same manner as coconut oil or some hydrogenated vegetable oil.

This cooling curve method has been used in our laboratory both for special investigations and for checking the composition of crude oils, hydrogenated fats, and fat mixtures for margarine manufacturing. One Swedish factory has for some time been using this method for factory routine control. Instead of a thermometer, a thermocouple is preferably used in connection with a Speedomax recorder. The weighing-in-accuracy of the compounds in the refinery has improved since this method of checking was introduced, and the number of inaccurate fat blends has been appreciably reduced.

Microscopic Studies. The equipment used was a Leitz Ortholux microscope combined with a heating-cooling stage according to Koefler. This stage permits rapid changes in temperature as well as maintenance of the temperature at a constant level. The phase changes in fats at different temperatures can thus be studied, and the accuracy of temperature measurements are 0.5C in the range of 15–60C.

Magnification of 100x has been found advantageous; we use polarized light sometimes with a gypsum plate wedge, which gives the sensitive tint of first order red.

By varying the rate of cooling on the stage it was found that even when the fat is cooled in such a moderate rate as in the cooling curve technique, an unstable crystal is initially formed with an appreciably lower melting point than that normally reported for the fat.

A certain time after the crystals of the low melting form have been produced, crystals of a higher melting form are obtained. In conformity with the commonly used designations for the polymorphic forms of triglycerides we call the least stable, lowest melting crystal the α-form and the next obtained crystal the β'-form.

The melting point of the α-form ($M_p\alpha$) of various commercial fats can be given to the nearest 0.5C. Calculations of the stability have also been made of the α-form, i.e., the length of time ($T\alpha$) before the β'-form becomes apparent.

Method. One drop of the completely melted fat is placed on a very thin (0.13 mm) cover glass 24 × 35 mm, which will serve as a slide. Another

TABLE II

Fat	C_{14}	C_{16}	C_{16}^a	C_{18}	C_{18}^a	C_{18}^a *trans*	C_{20}	C_{20}^a	....	C_{22}	C_{22}^a
H marine oil 40/42 1).....	12	33	13	12	12	..	4	9	3	1	1
H marine oil 40/42 2).....	9	24	11	11	12	..	6	11	3	4	9
H. cottonseed oil 36/38 3).....	2	27	1	7	54	8	..	....	....	....	....
H. cottonseed oil 36/38 4).....	1	22	1	14	59	3	..	....	....	....	....

[a] Unsaturated.

thin glass with smaller dimensions is pressed upon the droplets and the slide is placed on the hot Koefler stage. This is connected with a CO_2 cylinder and, on releasing CO_2, the stage with the sample will be rapidly cooled.

As soon as crystallizing is observed in the microscope the CO_2 release is stopped and the heating coil in the stage is switched on to provide a rapid rise in temperature. The melting temperature of the crystals is estimated and the stage will afterwards be stabilized at this temperature.

A new sample is prepared and cooled outside the microscope on a metal slide tempered to 0C. As soon as crystals appear the sample is placed on the stage which is previously adjusted to the temperature of the approximate melting point of the α-form.

This operation must be carried out in a few seconds lest the β'-form appear and interfere in the observation. Frequently the α-form melts at the first attempt, but by repeating the procedure and adjusting the temperature in 0.5C intervals the melting point can be determined. This is generally sharply defined, but a certain amount of practice is required, especially in cases where β'-form is rapidly formed.

The transformation time ($T\alpha$) of the α-form to β'-form is designated as the interval between the melting of the α-form and the time when β'-form crystals are discernible at constant temperature, i.e., at the melting point of the α-form.

This time interval is measured with a stop watch, but the value will be approximate because the measurements are based on the subjective perception of the light intensity from the first very small β'-form crystals. A series of determinations of the same fat have shown good agrement and the reproducibility is ca. 10–15%.

Photographs in Figure 5 illustrate the various phases when determining the melting point of the α-form and the time for transformation to β'-form in a mixture for a margarine blend. No. 1 shows the α-form immediately after crystallization on the metal plate at 0C and then placed at the Koefler-stage which temperature was 18C. The stage temperature was raised to 22C where the α-form completely melted. After 5 min traces of β'-form crystals were discernible. The following three photographs show the state after 10, 15, and 60 min, respectively.

The transformation time is highly dependent upon temperature and seems to run through a minimum which has not yet been investigated. The determinations of transformation time must therefore be made at a well defined temperature in order to ensure reproducibility. The melting point of the α-form is a suitable temperature for this determination as the formation of new crystals is most easily observed when no α-form crystals are present.

Table III shows α-melting point for some fats, and these values are correlated to the temperature on the cooling curve at which the first deviation from the liquid oil curve (0_{Temp}) occurs.

The length of the transformation time ($T\alpha$) of the fats investigated is from a few seconds to ca. 15 min (see Table III) except Sheabutter, which seems to have a very stable α-form.

The hydrogenated cottonseed oils which do not show any inflexion point on the cooling curve transform very rapidly to β'-form at the temperature for the α-melting point. When the values of the trans-

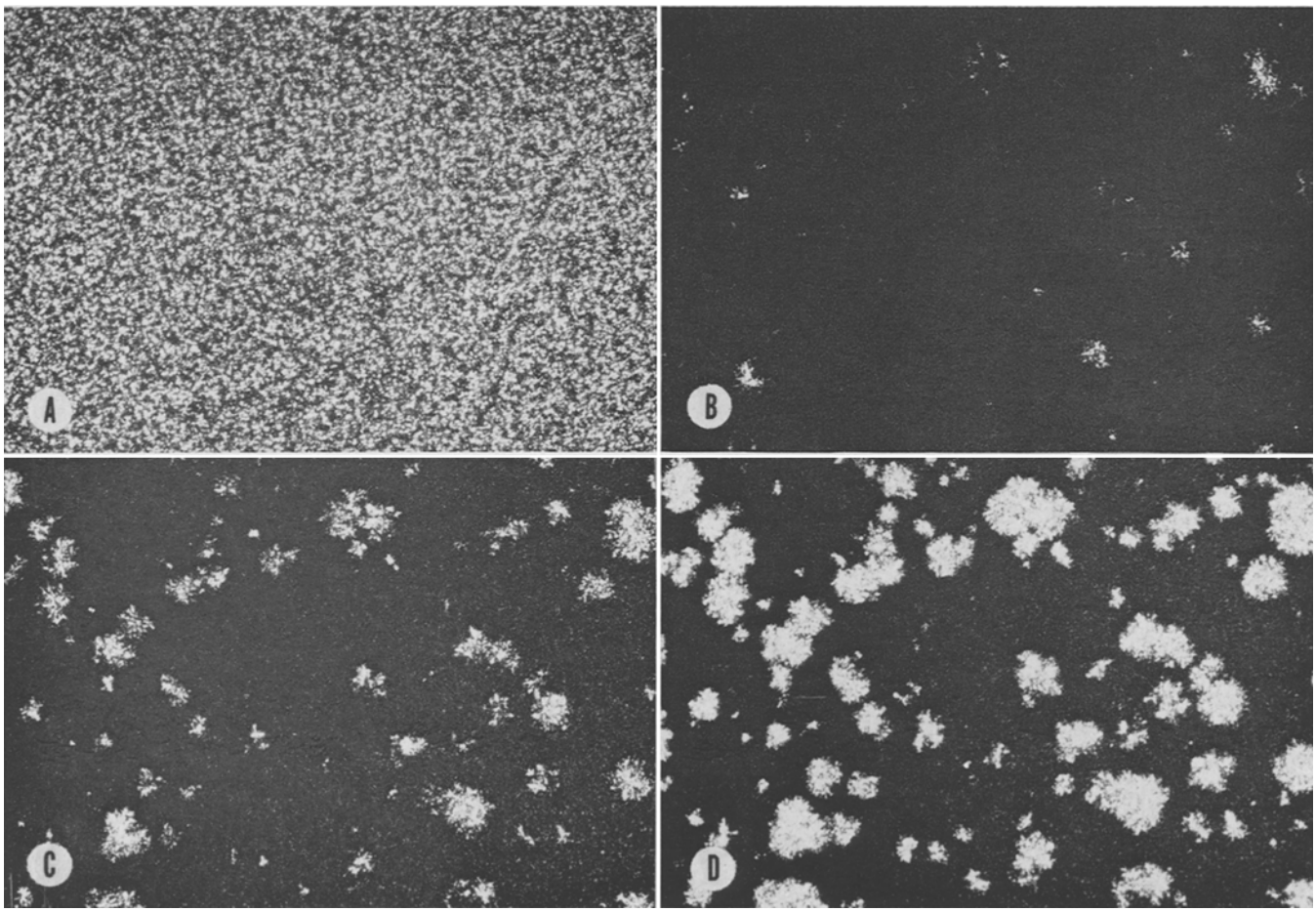

FIG. 5. A) α-form 18C. B) β'-form 22C 10 min after the α-form has melted. C) β'-form 22C 15 min after the α-form has melted. D) β'-form 22C 60 min after the α-form has melted.

TABLE III

Fat	$M_{p\alpha}$ °C	O_{Temp} °C	$T\alpha$ min	$T_{MIN} - T_O$
H marine oil 40/42 1).....	34.5	34	0.5	17
H marine oil 40/42 2).....	36.5	35.5	10	42
H marine oil 38/40	33	32.5	3	22
H. cottonseed oil 36/38 3).....	26.5	25.5	0	3
H. cottonseed oil 36/38 4).....	28	27.3	0	4.5
Palm oil.....	28	26	4	.....
Tallow.....	35	33.5	2	7
Shea butter.....	24	23	100	30

formation time ($T\alpha$) in Table III are set = 0, the time has been less than 30 sec and could not be determined with accuracy.

The transformation time seems to be correlated to the time interval on the cooling curve between the time for the first deviation from the liquid oil curve and the minimum for the fat (T_{MIN}–T_O). Due to their empirical nature, the methods described above give only approximate values for the crysetallization course of fats. They have been devised in order to provide, in a quick and simple manner, an idea of how the crystallization proceeds during cooling processes.

In the manufacture of margarine the crystallization of the fat takes place under vigorous agitation, which certainly promotes the formation of the β'-form. During the cooling process in the factory the transformation time from α- to β'-form seems to be much shorter than the cooling curve and microscopic technique indicate. The methods, however, have proved to be of value in assessing the various factors which may have influence on the consistency of the margarine.

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A Method for the Determination of the Extent of Polymerization in Frying Fats and in Fats Extracted from Fried Foods

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Abstract

A method is described for the isolation of polymerized products in frying fats as a urea non-inclusion fraction (NAF). Analysis of fats used in commercial frying operations and of fats extracted from some fried foods is reported. Amount of NAF obtained by the method appears to be in direct relation to the duration of heating. Oils heated at 200C for 24 hr yield 15–18% of NAF having molecular weights of 500–550. Some of the fats extracted from fried foods yielded up to 2.5% of the polymeric fatty acids.

Introduction

COMMERCIALLY FRIED FOOD products represent a significant portion of foods consumed in North America. During frying the fats are exposed to elevated temperatures and other conditions for a considerable length of time. Thermal degradation of oils at these temperatures has been extensively studied (1–6).

Thermal oxidation of fats proceeds in two stages. The first is accompanied by a decrease in the iodine value (I.V.) of the fat and a rapid increase in the carbonyl value. In the second, the rate of decrease in I.V. is considerably slower while the viscosity increases rapidly. Although I.V. and viscosity determination will indicate the advanced stages of polymerization, these criteria are not of significant value in the earlier stages.

The purpose of this paper is to describe a simple method for the isolation and estimation of the amount of the polymerized material in saponified frying fats and fats extracted from fried foods.

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Experimental

Control Samples. A commercial brand of winterized corn oil, and a hydrogenated vegetable shortening, were used in the study. One hundred g samples of fat were heated in stainless steel beakers to 200C for 8, 16, and 24 hr. The fat was continuously agitated during heating. At the end of the experimental period the fats were transferred to glass stoppered conical flasks and stored under nitrogen in a freezer at −10C. A 100 g sample of corn oil was also heated intermittently at 200C for 4 hr periods each day for 6 days. One ml of distilled water was stirred into the flask each day prior to heating, to partly simulate the moisture added in frying fresh potato chips.

Commercial Samples. For comparison 4 brands each of potato chips and frozen french fried potatoes were obtained from the local market. Ten samples of fats used for deep frying in the restaurants in the Ottawa and Toronto area were also obtained. These oils were primarily used for frying potato chips. All samples were stored under nitrogen in the freezer.

The fried potato products were ground with pestle and mortar and extracted with petroleum ether (40–60C) containing 10% ethyl ether. The extract was washed with water and dried with sodium sulfate, followed by evaporation of the solvent under reduced pressure.

Saponification. Twenty-five g of the fat was saponified by refluxing with 125 ml of 5% alcoholic potassium hydroxide for 2 hr. On cooling, 100 ml water was added and the saponification mixture was acidified with dilute hydrochloric acid (1:1). The fatty acids were extracted with two 100 ml portions of ethyl ether. The combined extracts were washed with water to remove all mineral acid and dried over so-