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.

REFERENCES

1. Zeitschr. Angew. Chem., 563 (1899).
2. Milchw. Forsch., *2*, 24 (1925).
3. Quimby, O. T., R. L. Wille, and E. S. Lutton, JAOCS, *30*, 186 (1953).
4. Sachsse, M., J. Rosenstein, F.u.S., *55*, 26 (1953).
5. Jacobson, G. A., P. J. Tiemstra, W. B. Pohle, JAOCS, *38*, 399 (1961).
6. Luddy, F. E., S. G. Morris, P. Magidman, R. W. Riemenschneider, *Ibid.*, *32*, 522 (1955).

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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.

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-

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TABLE I

Analytical data on Corn Oil and Vegetable Shortening heated at 200C

Fat	Time in hr at 200C	I.V.	NAF [a]	
			%	mol wt
Corn oil	0	123.7	0.5	302
Corn oil	8	118.7	3.5	483
Corn oil	16	115.9	8.0	537
Corn oil	24	111.3	17.5	543
Corn oil	24	112.0	18.0	539
Corn oil	24	110.8	16.8	549
Shortening	0	74.7	0.5	294
Shortening	8	71.0	5.0	454
Shortening	16	68.1	12.0	502
Shortening	24	65.8	15.0	530
Corn oil heated intermittently	24	117.5	4.5	386

[a] Non-adduct forming fatty acid fraction.

dium sulfate. The solvent was then removed by evaporation under reduced pressure.

Urea inclusion. Twenty g of the fatty acids was weighed into a 500 ml flask and dissolved in 200 ml of methanol containing 80 g urea. The flask was heated until a clear solution was obtained and then stored overnight in a refrigerator.

The contents were then filtered through a Buchner funnel and the precipitate was washed with 50 ml portions of cold ethyl ether. The filtrate was evaporated to dryness on a flash evaporator. This fraction was called the non-adduct forming fraction (NAF). To the precipitate, 100 ml water and 10 g sodium chloride were added. The fatty acids were released by heating and then extracted with ethyl ether. The resulting fatty acids were again treated with urea and methanol (5 g urea and 10 ml methanol for each g of fatty acids). The fatty acids were then recovered from the urea inclusion products as described earlier.

Molecular weights were determined by the cryoscopic method using wet benzene (7).

I.V. was determined by the conventional Wij's method, AOCS Official Method Cd 1-25.

Results and Discussion

Distributions of the total fatty acids from the adduct and the non-adduct forming fatty acid fraction (NAF), along with the molecular weights are shown in Table I. Reproducibility of the NAF determination was tested by heating three 100 g samples for 24 hr. The amount of NAF in fresh fat is ca. 0.5%. The yield of NAF was found to increase with the duration of heating. Molecular weights also show a remarkable increase, as would be expected of polymerized material. The molecular weights of fatty acids obtained as urea inclusion products are comparable to those of the original oil and were in the range of 291–296. The percentage of NAF material formed between 16–24 hr increased over 100% with no significant increase in the molecular weight. This presumably is due to other degradation products. The sample of corn oil heated intermittently showed an appreciably lower percentage of polymerized fatty acids and lower molecular weight of the NAF than did the fat heated continuously for 24 hr.

TABLE II

Molecular weights and percentage of non-adduct forming fatty acid fraction obtained from commercial samples of frying oils before and after use in a deep fryer [a]

Sample No.	Fresh Fat		After use in deep fryer	
	% NAF	mol wt	% NAF	mol wt
1	0.52	272.7	0.50	295.8
2	0.45	280.2	0.81	314.7
3 [b]	0.48	294.6	4.82	529.5
4 [b]	0.50	284.0	5.25	550.0
5	0.48	300.3	0.87	348.6
6	0.50	324.3	0.58	386.2
7	0.52	292.4	0.52	358.6
8	0.56	318.2	0.71	358.9
9	0.35	279.3	0.63	287.8
10 [b]	0.35	270.7	4.52	552.6

[a] No record is available as to how long these fats had been used in the deep fryers.

[b] Samples Nos. 3, 4, and 10 were highly viscous.

TABLE III

Percentage and molecular weights of non-adduct forming fatty acid fraction (NAF) obtained in fried foods

Product	Sample No.	NAF	
		%	mol wt
Potato Chip	1	0.60	278.7
	2	0.56	283.4
	3	0.52	280.0
	4	0.48	271.5
Frozen french fried potatoes	1	2.5	366.0
	2	1.5	385.3
	3	1.2	436.5
	4	2.0	427.2

The data on NAF obtained with commercial samples of fat, before and after use in the deep fryer, are shown in Table II. No record was available as to how long these fats had been in use. Three of the samples, after use in the deep fryer, were highly viscous and the molecular weights of the NAF were found to be in excess of 500. In the other fats, after use in the deep fryer, the molecular weights of the NAF were found to range 287.8–386.2.

The results of the analysis of fats extracted from potato chips and frozen french fried potatoes are shown in Table III. The molecular weights of the NAF obtained for the fats from potato chips were found to be similar to those obtained for fresh fats; however, the molecular weights of the NAF for the fats extracted from the frozen french fries were considerably higher.

The rate of fat turnover, the effect of steam distillation due to added moisture, and the presence of food particles and other factors may alter the rate of formation of polymers. In the laboratory the fats were heated at temperatures similar to those used in frying operations; however, the two systems should not be compared without consideration of other factors involved in deep frying. The intermittent heating with added moisture appears to simulate the deep frying operation resulting in lower yields of polymerized material as compared to continuous heating for the same period. Very little information is available on other methods for the estimation of polymerization in heated oils. Frankel et al. (3) reported a liquid partition chromatographic method for dimeric and polymeric products in oxidized oils. The present method is believed to be simple enough for routine analyses of commercial frying fats.

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REFERENCES

1. Bennion, M., and F. Hanning, Food Technol., *10*, 229–232 (1956).
2. Carlin, G. T., R. P. Hopper, and B. N. Rockwood, *Ibid.*, *8*, 161–165 (1954).
3. Frankel, E. N., C. D. Evans, H. E. Moser, D. G. McConnel, and J. C. Cowan, JAOCS, *38*, 130–134 (1961).
4. Johnson, O. C., and F. A. Kummerow, *Ibid.*, *34*, 407–410 (1957).
5. Perkins, E. G., and F. A. Kummerow, *Ibid.*, *36*, 371–375 (1959).
6. Sahasrabudhe, M. R., and I. G. Farn, *Ibid.*, (in press).
7. Smith, W. T., and R. L. Shriner, Examination of New Organic Compounds, John Wiley and Sons, Inc., New York (1956).

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