ORIGINALARBEITEN

Z. Ernährungswiss. **21**, 191–201 (1982)

ISSN 0044-264 X

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Decrease in essential fatty acid content of edible fats during the frying process

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(Received February 8, 1982)

The nutritional implications of food processing and distribution in terms of nutrient destruction and loss have become very important in recent years. Oils and fats used for frying serve not only as heat transmitters and flavour carriers, but also as nutrients. The complex chemical and physical changes that occur during the heating or frying operation result in organoleptic failures, a decrease in nutritive value (caused by the decomposition of the essential fatty acids), and the formation of compounds with adverse effects on health.

In fats subjected to deep-frying process, a complex series of reactions produce a great number of decomposition products, both volatile and nonvolatile, about 400 of which have been identified up till now (1–4). After a certain heating time, the breakdown products accumulate to such an extent that the used oil has to be regarded as deteriorated. Chemical spoilage has perceptible effects, too: defects in odour and flavour, darkening colour, formation of foam and smoke, increasing viscosity, etc. (5).

Deterioration of fats is greatly influenced by the degree of unsaturation, the nature of fried food, and the frying conditions (6–10): temperature, duration of use, exposure to oxygen, number of alternating heatings and coolings, frying capacity (kg food/h), mode of heat transfer (electric or gas), metals in contact with fat, removal of sediment, application of antioxidants, anti-foam additives and protective gases. Taking into consideration the above factors, fat degradation may be decelerated.

The biological properties of heated fats are closely related to their chemical properties. Much work has been done to study nutritional and physiological effects of frying fats (6, 11–19). Most reports indicated that only overheated oils and fats may have harmful effects, those used in normal frying procedures do not produce significant changes in animals consuming them.

Deep-fried foods are becoming more and more popular, which results in an increasing frying fat consumption. For this reason, it is of great importance to assess frying oil quality and to determine the appropriate point at which the oil is no longer suitable for use. Relying upon sensory

evaluation, only rough conclusions can be drawn concerning oil quality. Objective, instrumental methods are required for the detection of the changes and the quality assessment. The most suitable methods for this purpose are those measuring all the breakdown products or their typical groups of compounds (20–25).

The greatest number of decomposition products is formed as a result of degradation of polyunsaturated, essential fatty acids being the most susceptible to oxydative breakdown. By determining the decrease in their concentrations, not only fat quality can be evaluated, but the decrease in nutritional value may be detected as well. Several studies on the changes in polyunsaturated fatty acids of heated fats have been published, the results of which have often been contradictory (26–31).

This paper reports the investigation of degradation of some edible fats under different conditions by measuring their changes in essential fatty acids and decomposition products; and comparison of the data obtained.

Materials and methods

Sunflower oil, rapeseed oil and lard containing different amounts of essential fatty acids were chosen for these studies. Twelve experiments with different heating or frying conditions were run, aimed at modelling practice and examining the effects of certain factors. Experimental conditions are presented in table 1. Heating and frying were carried out periodically, i.e., the fats were kept at high temperature for 30 minutes or 5 hours, then allowed to cool to room temperature and later on heated again. After certain periods, samples were taken, so that each experiment yielded a series of samples corresponding to increasing durations of use. Either a stainless steel pan with a diameter of 20 cm, or a 500-cm^3 glass flask was used as vessel. In frying experiments, 150-g portions of pommes frites were fried, each portion for 15 minutes.

Essential fatty acid content was determined by gas chromatography (GLC). The samples were converted into methyl esters according to Szöke et al. (32). When analysing fatty acids of used frying fats by GLC, most oxidized and polymeric compounds formed during heating are not eluted from the column. Consequently, calculation of fatty acid composition using the total area of all peaks having

Table 1. Experimental heating and frying conditions.

Kind of fat	Denotion	Mode of use	Temperature (°C)	Vessel	Periods (hours)
Sunflower oil	N_1	heating	160	flask	0.5
Sunflower oil	N_2	heating	200	flask	0.5
Sunflower oil	N_3	heating	240	flask	0.5
Sunflower oil	N_4	heating	160	pan	0.5
Sunflower oil	N_5	frying	140–180	pan	5
Sunflower oil	N_6	frying	140–180	pan	0.5
Rapeseed oil	R_1	heating	200	flask	0.5
Rapeseed oil	R_2	heating	160	pan	0.5
Rapeseed oil	R_3	frying	140–180	pan	5
Lard	S_1	heating	200	flask	0.5
Lard	S_2	heating	160	pan	0.5
Lard	S_3	frying	140–180	pan	5

appeared on the chromatogram as 100 % would yield an increase in saturated fatty acids (the amount of which remains practically unchanged), while the actual loss of unsaturated fatty acids is underestimated. That mistake can be avoided by employing an internal standard. In our studies, heptadecanoic acid methyl ester was used as internal standard. Before injecting into the gas chromatograph, an aliquot from a solution of known concentration of the internal standard in hexane was added to a similar solution of the sample, so that the standard is close to 20 % of the weight of the total sample. GLC analyses were performed on a Carlo Erba Fractovap model 2400 T, using a 2-m × 4-mm glass column, packed with 10 % EGSSX on 80/100 mesh Gas Chrom Q, at 180 °C.

For detecting the breakdown products formed during the frying operation, we applied measurement of polymeric triglycerides that are one of the most typical groups of decomposition products. Determination of polymer content was carried out by gel permeation chromatography (GPC) as described earlier (10, 33, 34). Analyses were conducted on a 1.5 cm × 110 cm glass column, packed with Sephadex LH-20 in chloroform-methanol 2:1 (v/v). Solvent flow was kept constant (0.3 cm^3/min) with a peristaltic pump and 2.5 cm^3 fractions were collected with a fraction collector (Labor MIM, Hungary Typ. OE 606). 150 mg of the samples dissolved in 1 cm^3 elution solvent was applied to the column for each analysis. Detection was carried out by direct weighing (i.e., fractions were collected in tared test tubes that were weighed after evaporating the elution solvent under an atmosphere of nitrogen), which gave chromatograms similar to those obtained by measuring refractive index. We preferred direct weighing as it is inexpensive and elimi-

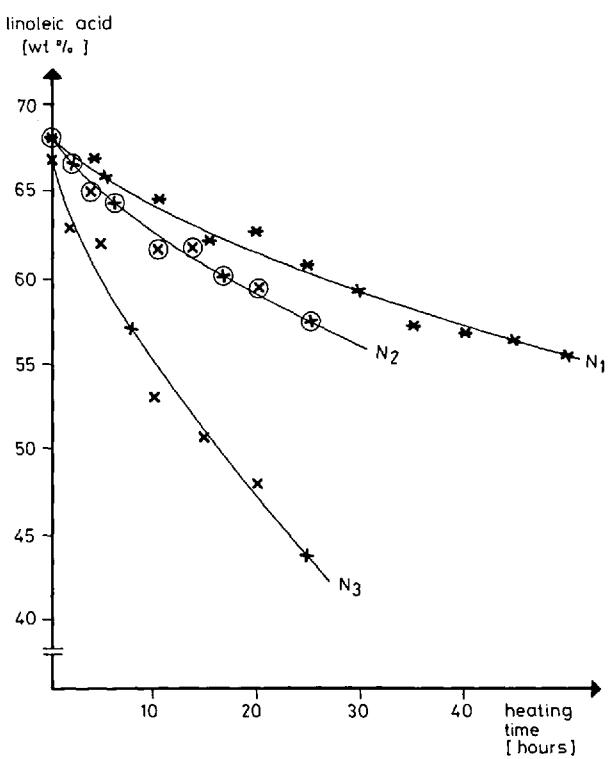

Fig. 1. Decomposition of linoleic acid of sunflower oil during heating.

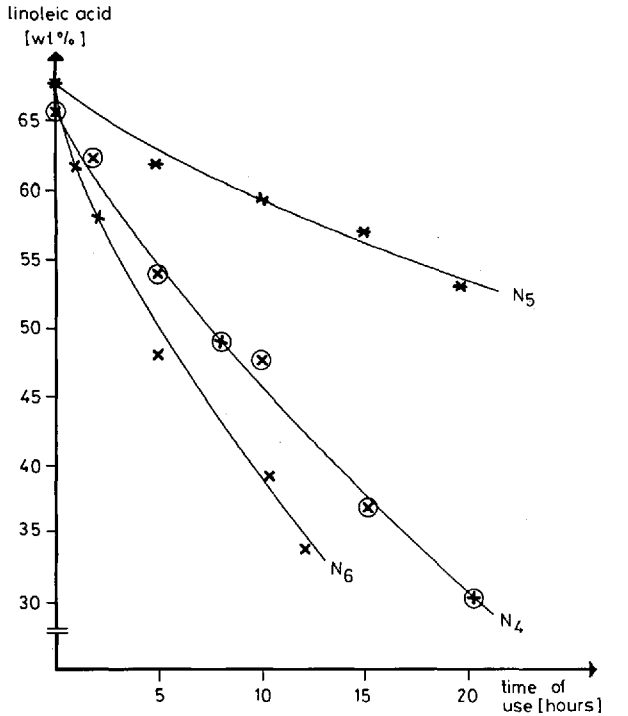

Fig. 2. Decrease in linoleic acid content of sunflower oil during heating or frying.

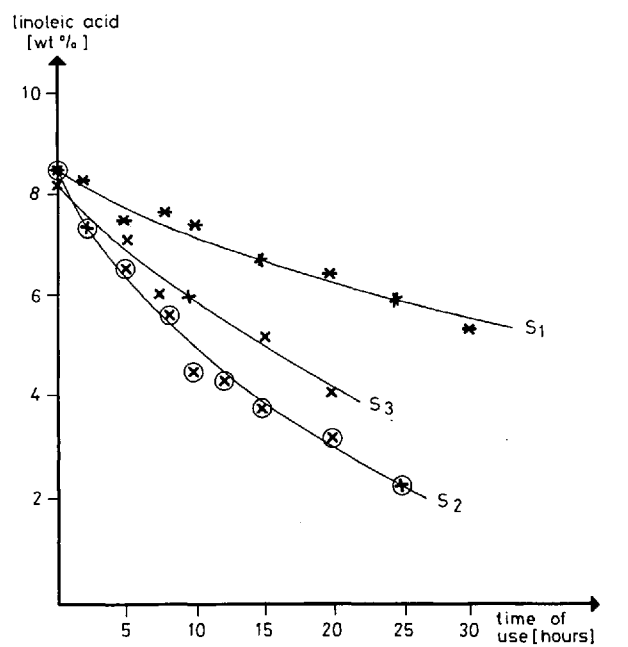

Fig. 3. Decomposition of linoleic acid of lard during heating or frying.

nates calibration. The amount of polymers is calculated as a sum of the quantities of dimeric and higher polymeric triglycerides.

Results and discussion

All the samples obtained in the twelve experiments (110 samples) were analysed by the above outlined methods, i.e., linoleic and linolenic acid concentrations and polymer contents were determined. The data were plotted against time of use, some of the curves are presented in figures 1–7. The conclusions to be drawn are as follows:

1. As regards the effects of frying parameters, our findings are similar to those of other authors (6–9).
   - The amount of decomposition products (i.e., polymer content) increases with advancing time of use, while a loss in essential fatty acids, in accordance with the accumulation of breakdown products, can be observed.
   - Use at higher temperature accelerates fat derioration; this effect intensifies at temperatures over 200 °C (see fig. 1).
   - Alternative heating and cooling are more damaging than continuous heating (see curves N_5 and N_6 in figures 2 and 5), which is due to

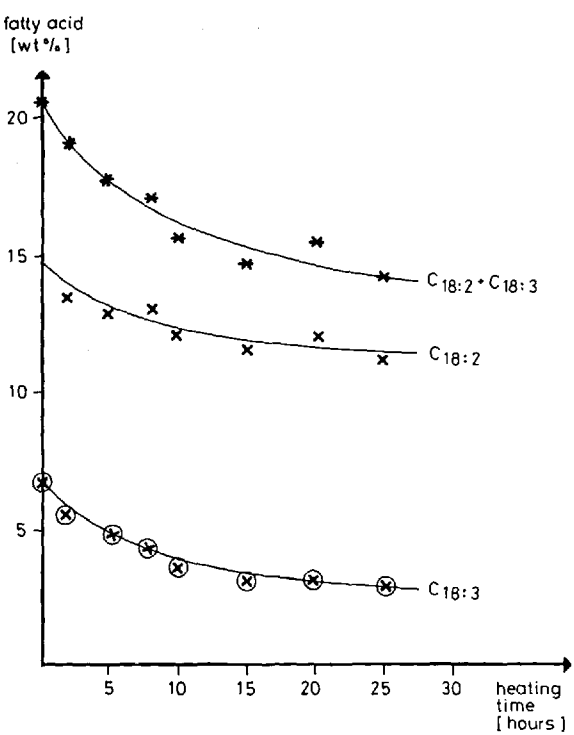

Fig. 4. Decomposition of essential fatty acids of rapeseed oil heated at 160 °C (experiment R_2). After a heating time of 25 hours the decrease in linoleic acid is 24 rel. %, linolenic acid is 56 rel. %, total essential fatty acids is 34 rel. %.

increased peroxide formation and decomposition during the cooling and reheating periods.

- Frying is less destructive than heating alone. Water content of the food is lost during frying, and a steam blanket produced over the vessel protects the fat against atmospheric oxygen.
- The surface in contact with the air, related to the fat volume (surface/volume ratio), influences the rate of degradation to a great extent. The importance of this parameter is illustrated in figures 1 and 2. A huge difference between curves N_1 and N_4 can be observed, which is caused by the fact that the exposure to oxygen (surface/volume ratio) was much greater in pan than in flask. Comparison of curves N_4 and N_6 (figs. 2 and 5) shows that degradation of sunflower oil in experiment N_6 is more significant than in experiment N_4. The reason of this is that during frying the oil absorbed by the food was not replaced by fresh oil, which resulted in an increasing surface/volume ratio. From figures 3, 6 and 7 it is equally clear that the fats in experiments R_2 and S_2 deteriorate more rapidly than those in R_1 and S_1, despite the much higher temperature used during experiments R_1 and S_1. This is also attributed to the difference in vessel. Comparing curves R_1 and R_3 (or S_1 and S_3), it is apparent that the protective effects of frying, lower

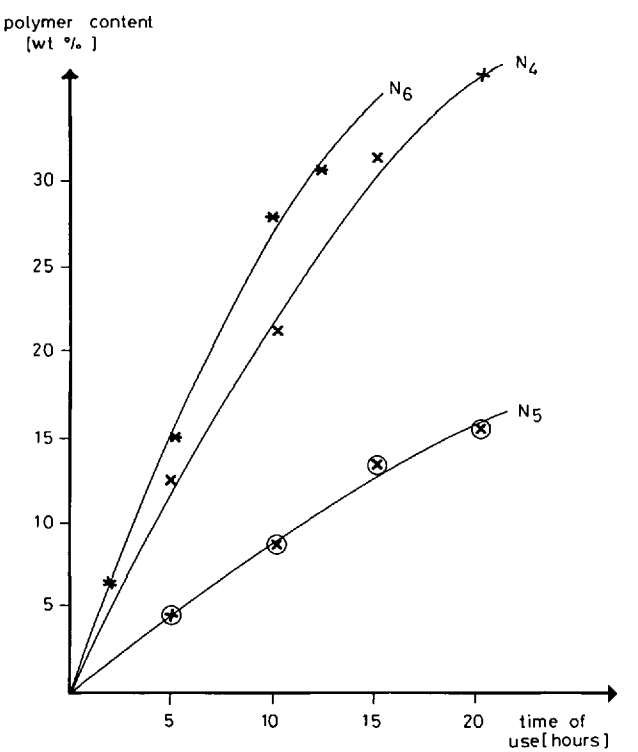

Fig. 5. Formation of polymeric triglycerides in sunflower oil during heating or frying.

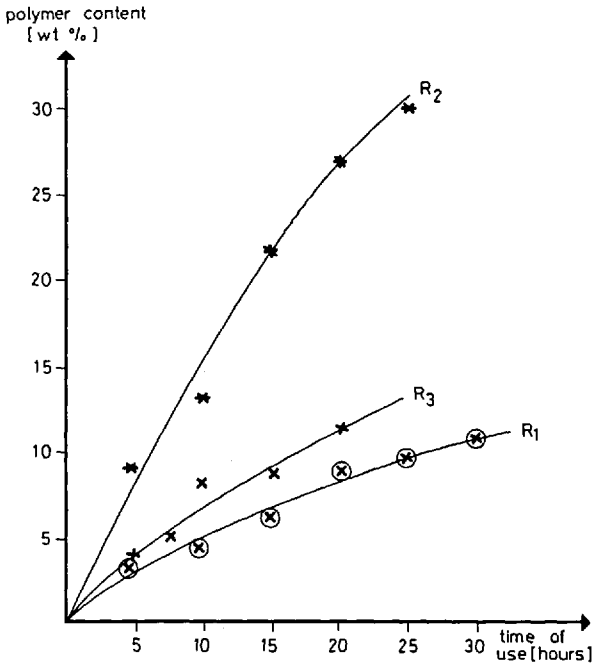

Fig. 6. Formation of polymeric triglycerides in rapeseed oil during heating or frying.

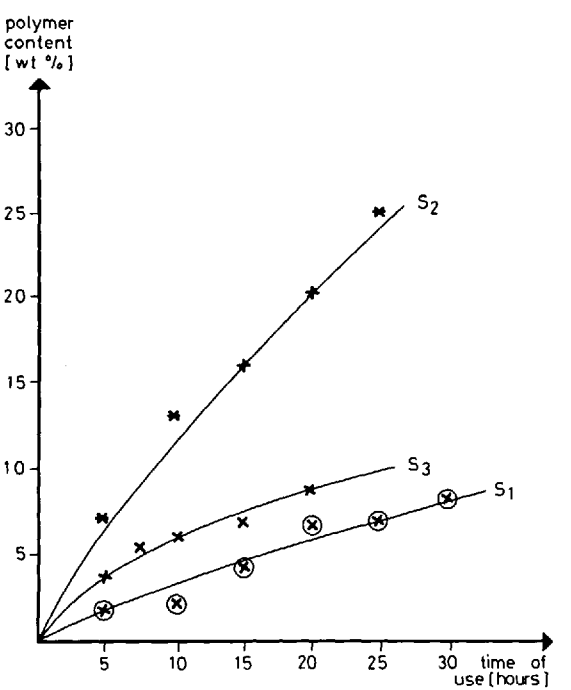

Fig. 7. Formation of polymeric triglycerides in lard during heating or frying.

Table 2. Decrease in essential fatty acid content of sunflower oil during heating or frying.

Denotion of experiment	Decrease in linoleic acid concentration (rel. %) after a time of use of hours					
	5	10	15	20	25	50
N_1	3.2	5.3	9.1	8.0	9.5	19.1
N_2	4.7	7.9	10.8	12.8	15.8	–
N_3	7.5	21.2	24.5	28.4	34.9	–
N_4	19.2	28.6	45.1	55.0	–	–
N_5	7.5	13.2	16.2	21.5	–	–
N_6	29.4	42.9	–	–	–	–

temperature and longer periods of use proved insufficient to compensate the effect of the greater surface/volume ratio.

2. As expected, the nature of fat also affects the degree of degradation.
   - Fats containing more polyunsaturated fatty acids are more susceptible to deterioration. In our studies, lard with a concentration of 8–9 % of linoleic acid showed the best thermostability.
   - Linolenic acid containing three double bonds is lost more rapidly than linoleic acid possessing only two double bonds (see fig. 4).
3. Loss of essential fatty acids means a decrease in nutritive value of fats. Table 2 lists the data characterizing the decrease in nutritive value of sunflower oil expressed as relative percentage:

$$\frac{c_{\text{fresh oil}} - c_{\text{used oil}}}{c_{\text{fresh oil}}} \cdot 100$$

The results obtained by analysing 110 samples suggested that there are relationships between the values measured by GPC and GLC. Plotting the corresponding values against one another, it was apparent that correlation between polymer content and decrease in essential fatty acid concentra-

Table 3. Correlation between polymer content and loss of essential fatty acids.

	Correlation coefficient	Equation of regression line $y = ax + b$*)
Sunflower oil	0.930	$y = 0.96x + 0.72$
Rapeseed oil	0.686	$y = 0.08x + 1.23$**) $y = 0.11x + 1.02$***)
Lard	0.864	$y = 0.23x + 0.76$

*) x = polymer content
y = decrease in essential fatty acid concentration

**) relationship between polymer content and decrease in linoleic acid concentration

***) relationship between polymer content and decrease in linolenic acid concentration

tion ($c_{fresh\ oil} - c_{used\ oil}$) is linear and depends on the nature of fat, i.e., data from different fats should not be combined. Correlation coefficients for each fat are presented in table 3. Student's t-test indicated that all the linear relationships are significant even at a probability level of 99.9 %.

High correlations were obtained in cases of sunflower oil and lard. Correlation coefficient between the data from rapeseed oil is somewhat lower, which is caused by the fact that rapeseed oil contains two kinds of essential fatty acids. A separate calculation for the decrease in linoleic and linolenic acids yields coefficients of about 0.85.

Table 3 also lists equations of regression lines calculated by the method of least squares.

In summary, our study has shown that heating and frying cause a decrease in nutritive value of fats as a result of decomposition of polyunsaturated, essential fatty acids. Since the loss of essential fatty acids is a parallel process to the formation of breakdown products, it is not only suitable for detecting the decrease in nutritive value, but an adequate measure of fat deterioration as well.

The results have also indicated that the rate of degradation is considerably affected by both the degree of unsaturation of the fat and the frying conditions. A subsequent paper will report quantitative studies on these effects.

Study of the relationship between polymer content and decrease in essential fatty acid concentration showed that high, linear correlation depending on the nature of fat can be found. Knowledge of regression lines characterizing the relationship may be useful in quality assessment of frying fats.

Acknowledgement

The author thanks Mrs. V. Huszár and Miss É. Maucha for skilled technical assistance.

Summary

Degradation of sunflower oil, rapeseed oil, and lard during the frying operation was investigated by studying the loss of essential fatty acids compared to the accumulation of decomposition products. Linoleic and/or linolenic acid concentration was measured by GLC, and for detecting decomposition products determination of polymer content by GPC was chosen. Twelve laboratory experiments with different heating or frying conditions were run aimed at modelling practice and studying the effects of certain factors.

The results indicated that loss of essential fatty acids being a parallel process to the accumulation of breakdown products is suitable both for detecting the decrease in nutritive value and for quality assessment of used frying fats. It was also found that the rate of deterioration is considerably affected by the nature of fat and the frying parameters. Study of the relationship between polymer content and the decrease in essential fatty acid concentration (using data from 110 samples) showed that high, linear correlation depending on the nature of fat can be found. Correlation coefficients and equations of regression lines were calculated.

Zusammenfassung

Es wurden die Veränderungen von Sonnenblumenöl, Rüböl und Schweinefett während des Fritierprozesses durch Ermittlung der Abnahme an essentiellen Fett-

säuren im Vergleich zur Akkumulation der Zersetzungsprodukte untersucht. Der Gehalt an Linol- und Linolensäure wurde durch GLC gemessen, und GPC-Bestimmung der polymeren Triglyceride wurde für die Erfassung der Abbauprodukte angewendet. In 12 Fritierversuchen, deren Zweck die „Modellierung" der Praxis und die Untersuchung von einigen Fakten war, wurden die Fette unter verschiedenen Bedingungen ohne oder mit Bratgut belastet und die erhaltenen 110 Proben analysiert.

Die Abnahme an essentiellen Fettsäuren, die im Einklang mit dem Anstieg der Zersetzungsprodukte steht, ist ein Indikator für die Abnahme des Nahrungswertes sowie für die Verdorbenheit von gebrauchten Fritierfetten. Aus den Ergebnissen ging hervor, daß Fettsäurezusammensetzung des Fettes und Fritierbedingungen die mögliche Gebrauchsdauer stark beeinflussen. Es wurde festgestellt, daß zwischen dem Gehalt an polymeren Triglyceriden und der Abnahme an essentiellen Fettsäuren von den Fettsorten abhängige, strenge lineare Korrelationen bestehen. Korrelationskoeffizienten und Gleichungen der Regressionsgeraden wurden berechnet.

Key words: fat deterioration, essential fatty acids, polymeric triglycerides, frying fats, nutritive value

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