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Title	The Properties of Thermally Deteriorated Cooking Oils and Their Effects on Fries
Author(s)	TAKAMA, Kōzō ; ZAMA, Kōichi
Citation	北海道大學水産學部研究彙報, 29(1), 48-55
Issue Date	1978-03
Doc URL	http://hdl.handle.net/2115/23629
Type	bulletin (article)
File Information	29(1)_P48-55.pdf

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Bull. Fac. Fish. Hokkaido Univ.
29(1), 48–55. 1978.

The Properties of Thermally Deteriorated Cooking Oils and Their Effects on Fries

Kōzō TAKAMA* and Kōichi ZAMA*

Abstract

The experiments were carried out to determine the relationship between prior use of heated oil and the quality of the foods fried in those oils. The soybean oil had been used for producing "fried kamaboko" from a frozen jelly meat of Alaska pollack. After frying rainbow trout paste meat in the soybean oil, lipid and lipid-free materials were obtained from the fries by extration with acetone and ether. The amount and the composition of the extracted lipid, pepsin and trypsin digestibilities in vitro and the available lysine contents of the lipid-free material were determined, and correlated with the properties of the oils used.

The amount of lipids extracted from the fries was inversely proportional to the viscosity of the cooking oil used. On the other hand, more phospholipids were extracted from fries cooked in thermally deteriorated oils than those cooked in fresh oil. The amount of phospholipd yielded increased proportionally with the viscosity of the cooking oil. There were few differences in the digestibilities of the lipid-free material by pepsin among the samples. Digestibilities by trypsin also showed little differences between the samples, but there was a decrease of 10–15% in lipid-free materials obtained from the fries a compared with that of the material obtained from raw paste. The loss of available lysine was the largest (26%) in the fries cooked in the oil with the most chemically unstable factors in all of the oils used in this study.

The cooking oil used for frying is generally heated at high temperature for many hours, which causes the oil to deteriorate and foam.

Many workers[1–7] have pointed out that the thermally deteriorated oil leads to toxicity and can pose food hygiene problems. They have also pointed out that such oil exerts harmful influences upon the nutritive quality and the digestibility of the fried foods.

Previous studies on the effects on thermally deteriorated oil on fried food qualities are limited to the preparation of the thermally deteriorated oil in the laboratory to keep track of its degree of deterioration.

The present investigation was carried out to determine the properties of thermally deteriorated oil, used in a commercial factory producing "fried kamaboko", and their effects on the amount of available lysine and digestibilities by pepsin and trypsin in vitro of fried meat paste of rainbow trout in fresh oil, and in thermally deteriorated oils.

* *Laboratory of Food Chemistry I, Faculty of Fisheries, Hokkaido University*
(北海道大学水産学部食品化学第一講座)

Materials and Methods

Frying oil Soybean oil which had been heated in a stainless steel duplex-open fryer for frying "kamaboko", a fish paste prepared from a commercially produced frozen jelly meat of Alaska pollack, was donated by a factory for this experiment.

About 600 ml sample of each used oil was taken weekly from the 2nd fryer and kept in a brown screw cap bottle. The head space of the bottle was filled with nitrogen gas and then stored immediately in a freezer until needed for experiment.

POV, OHV, AV, SV, and IV (Wijs) of the sample oil were determined by the standard methods of J.O.C.S.[8] and COV by the method of Kumazawa and Ōyama.[9] Polymers and non-urea adduct forming (NUAF) methyl esters were determined according to the procedures described by Peled et al.[10] The viscosity determination was done at 25°C with a Brookfield viscometer.

Fried fish sample Eight pieces of 5 g samples of rainbow trout paste meat (formed from a disc of 35 mm diameter and 5 mm thickness) were used for each frying oil sample. The samples were fried for 3 min at 180°C, in fresh and thermally deteriorated soybean oils which had been stored in the freezer. After frying, the samples were drained on a filter paper for a few minutes and then cut into fine pieces. A portion of this sample was used for determination of the TBA value (Vyncke[11]). The remainder of the sample was transferred to a wide mouth reagent bottle and the lipid contained in the sample was extracted 3 times with 15 volumes of acetone and ether, respectively. The lipid free samples were dried in a vacuum desiccator and then powdered in a glass-mortar. These powdered samples were analysed for the following: total nitrogen, using Kjeldahl method, digestibilities by pepsin and trypsin, and available lysine.

Digestibility in vitro by pepsin and trypsin The technique devised by Horigome and Kandatsu[12] was used to determine the digestibilities of the powdered lipid-free samples in vitro by pepsin (1:10,000; Difco Lab.). The digestibility in vitro by trypsin (2,000 units/g; Wako Pure Chem. Ind. Ltd.) was determined in a similar procedure except for use of Sørensen buffer, pH 7.7.[13]

Composition of the lipid extracted from the fried fish Thin layer plates coated with silicic acid (Wako gel-BO) were used for separations of the lipid classes. The plates were activated at 110°C for 30 min before use. Solvent systems used were n-Hexane-Diethyl ether-Acetic acid (90:10:1, by vol) for development of non-phospholipid and Chloroform-Methanol-Acetic acid-Water (75:20:1:4, by vol) for development of phospholipid. TLC plates, after developing, were heated on a hot plate sprayed with 50% sulfuric acid solution. The concentrations of located spots were estimated using the OZUMOR-82 densitometer.

The amount of phospholipid was calculated on the basis of content of lipid-phosphorus determined by the method of Fiske and Subbarow.[14]

Fatty acid composition was analyzed by GLC after methylation with methanol containing 10% anhydrous hydrogen chloride. GLC was done with a Hitachi 063, equipped with a stainless steel column (3 mm i.d. and 1 m length), packed with 10% DEGS on Chromosorb WAW (80–100 mesh).

Available lysine The content of available lysine in the lipid-free powdered

samples was determined by the TNBS (2,4,6-trinitro-benzenesulphonic acid) method devised by Eklund[15] with a slight modification as the flask was covered with a beaker,[16,17] instead of sealing the flask. The amount of ε-TNP-lysine was calculated from a standard curve prepared with pure L-lysine-monohydrochloride.

Results and Discussion

Quantitative consumption of sample oils, expressed in amount of oil consumed per 100 kg product, was taken from the past factory records and shown in Table 1. The oil turnover rate, expressed as the percentage of the volume of oil replenished in an hour to the fryer capacity, was 7.4 for sample No. 3 which is the minimum among the samples.

Table 1. *Quantiative consumption and turnover rate of frying oil.*

Sample oil*	Consumption oil Kg/100 Kg product	Oil turnover rate (%/hr)
No. 1	-	-
No. 2	4.5	8.7
No. 3	4.1	7.4
No. 4	4.6	9.0
No. 5	4.7	9.1

* Soybean oil, No. 1 is unheated oil just after replenishment with fresh oil and Nos. 2~5 are heated used oils in a duplex-stainless steel open fryer for producing "fried kamaboko." These oils were collected weekly from the 2nd fryer.

According to Ōta and Yuki[18], cooking oil with a turnover rate of more than 12.5 %/hr is of good quality. For example, oil used for frying "instant rāmen" generally shows low deterioration since its turnover rate is between 10–25 %/hr. They also pointed out that fresh oil turnover rate may differ depending upon the kinds of food to be fried, the cooking oil to be used, and the frying method used. Furthermore, oils used for producing fried bean-curds and fried fish-paste deteriorate appreciably since those oils show low turnover rates, ranging from 1.5 to 7 %/hr. From their descriptions, the sample oils used in this study were not badly deteriorated, because as shown in Table 1, their turnover rates were about 9.0 %/hr except for sample No. 3. The chemical and physical properties of these sample oils are shown in Tables 2 and 3, respectively. Table 2 shows that POV, COV and OHV were highest in sample No. 2 while sample No. 4 gave the highest molecular weight and dark colour among oil samples. On the other hand, sample No. 3 had the highest viscosity, polymers and NUAF content (Table 3). These results indicate that No. 2 oil had the most unstable chemical properties, and Nos. 3 and 4 oils were highly deteriorated in terms of physical properties. These results indicate that suitability of using previously heated oils for cooking is in relations to the turnover rate of the fresh oil.

The disc-formed paste meat prepared from the flesh of rainbow trout was fried in each sample oil. The fries were then used for the determination of TBA value and for the extraction of lipid. The TBA value of the fry, dark color of the

Table 2. *Property of frying oil.*

	AV	SV	IV	POV	COV	OHV
Fresh oil	0.1	193	130.9	0.1	5.0	0.8
No. 1	0.2	193	130.9	0.2	5.1	0.9
No. 2	1.4	198	119.9	10.9	160.0	18.4
No. 3	1.7	198	120.0	9.2	140.3	14.6
No. 4	1.9	200	120.3	8.6	134.5	9.4
No. 5	1.9	200	122.5	6.6	134.8	9.3

Table 3. *Property of frying oil.*

	$E^{1\%\ CCl_4}_{370}$	n^{20}_D	M.W.*	Polymer % in oil	NUFA % in oil	Viscosity cP (25°C)
Fresh oil	0.030	1.4756	889	0.0	0.0	47.3
No. 1	0.033	1.4763	896	5.3	1.0	49.2
No. 2	0.272	1.4789	1,102	22.6	6.1	118.2
No. 3	0.332	1.4798	1,152	43.7	7.1	124.0
No. 4	0.381	1.4798	1,170	42.5	6.8	122.4
No. 5	0.343	1.4798	1,135	40.4	6.3	109.9

* Mean molecular weight determined by means of Hitachi Perkin-Elmer 115 molecular weight apparatus using cholesterol as a standard material.

Table 4. *TBA value of fried rainbow trout paste meat, dark color of lipid extracted from the from the fry and oil absorption rate by the fry.*

	TBA-V E_{538}/10 g paste	$E^{1\%\ CCl_4}_{370}$	Oil absorption* rate (%)
Fresh oil	0.035	0.078	30.8
No. 1	0.043	0.090	30.6
No. 2	0.063	0.390	25.2
No. 3	0.073	0.410	22.1
No. 4	0.072	0.420	24.3
No. 5	0.043	0.370	29.0

* for dry matter

extracted lipid and the amount of oil absorbed by the fry are shown in Table 4. The TBA value was small and showed slight differences between the fried samples. The colored materials in the cooking oil are absorbed by the fries as shown by the visual evaluation of the fried sample, and thus influence the values of foodstuffs and commodities of the fries. The amount of cooking oil absorbed by the fried sample is more when cooked in fresh oil as compared to that when cooked in deteriorated oil; e.g. fresh oil and No. 1 oil, ca. 31% and No. 3 oil, ca. 22% of the dry matter.

The fatty acid composition of the cooking oils and the lipids extracted from the fried sample are shown in Table 5. The heated oils consisted of slightly more saturated and monoenoic acids, and less of higher unsaturated (di-, trienoic) acids than the fresh oil. Since these fatty acid compositions are similar to that of the lipids extracted from the fried sample, the results suggest that a lot of cooking oil

Table 5. *Fatty acid composition of frying oil and lipid extracted from fried rainbow trout paste meat.*

	Frying oil					
	Fresh oil	No. 1	No. 2	No. 3	No. 4	No. 5
16:0	9.4	9.9	11.5	13.2	12.6	13.7
18:0	2.9	3.1	3.9	4.0	4.0	3.7
18:1	22.5	23.0	26.3	26.7	27.1	26.2
18:2	57.8	56.8	53.0	50.4	50.7	50.8
18:3	7.3	7.1	5.3	5.5	5.5	5.6
	Extracted lipid					
16:0	12.4	11.8	15.0	14.7	14.7	14.4
18:0	3.2	3.1	3.6	4.5	4.6	3.9
18:1	25.7	25.1	28.8	29.3	29.2	28.0
18:2	49.8	52.2	45.1	43.6	43.3	45.9
18:3	7.1	6.3	5.2	5.1	5.3	5.5

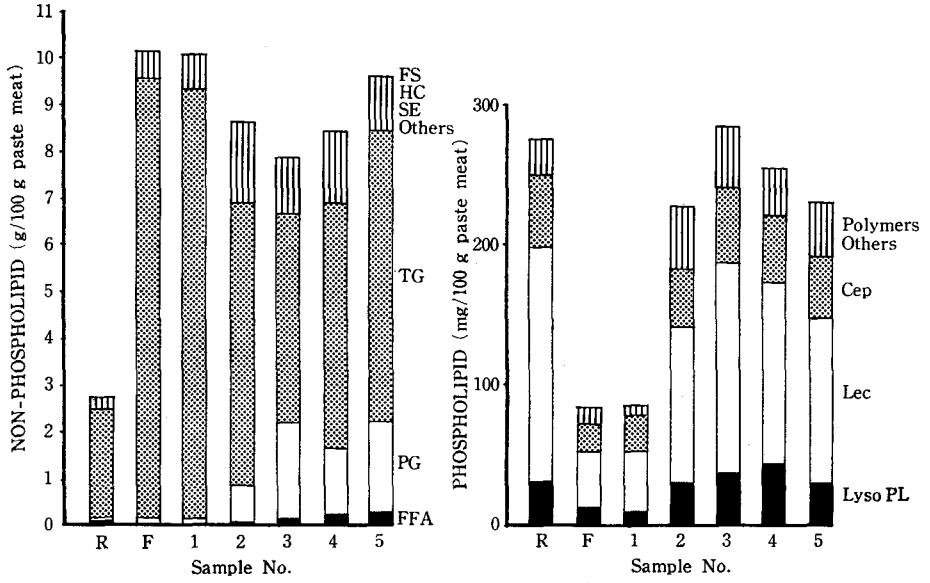

Fig. 1 Composition of lipid extracted from the fry prepared by frying the paste meat of rainbow trout in each sample oil.
R: Extracted lipid from raw paste meat (unfried)
F: Extracted lipid from the paste meat fried in fresh oil

was absorbed by the fried materials.

The composition of lipids extracted from the fried sample was estimated by use of the densitometric procedure after chromatographing on a thin layer plate coated with silicic acid, and represented as g/100 g paste meat in Fig. 1. The fried sample had more extracted lipids after cooking fresh oil as compared to that when thermally deteriorated oils were used. The amount of partial glycerides and free

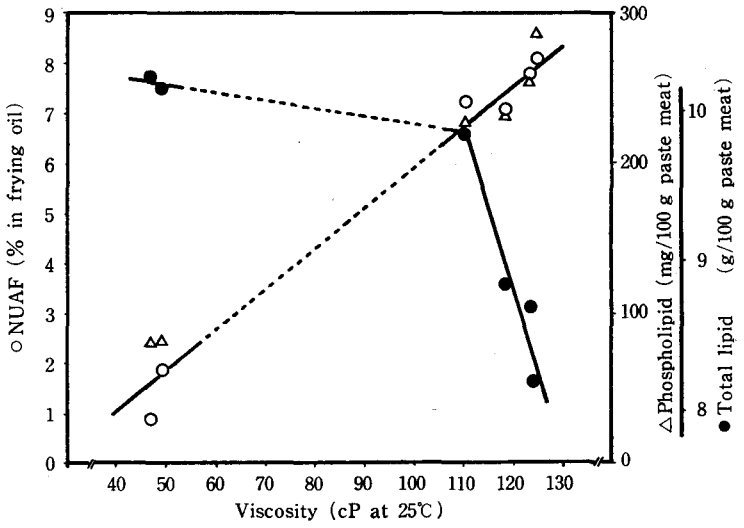

Fig. 2 Relationships of the amount of NUAF methyl ester in frying oil, and phospholipid and total lipid extracted from the fry of rainbow trout paste meat to viscosity of frying oil.

fatty acids increased proportionally as more thermally deteriorated oil was used. Extracted phospholipids, especially lecithin, was more abundant in fried samples cooked in thermally deteriorated oil as compared to that cooked in fresh oil. These results seem to be attributed to the following reasons: (1) fresh oil is more readily absorbed by the fried material than when thermally deteriorated oil was used, (2) reversely absorbing by the fried materials, fresh oil makes phospholipid, contained in the materials, solubilization into the frying oil. Deteriorated oil was, however absorbed on the surface of the frying materials and prevented the elution of phospholipids from the fries during frying. As shown in Fig. 2, the amount of extracted lipids were inversely proportional to the viscosity of the cooking oils. The amount of phospholipids extracted from the fries is apparently proportional to the viscosity of the cooking oils. The amount of lipids extracted from the fried material decreased remarkably in cooking oils which had a viscosity higher than 110. This phenomenon indicates that the amounts of absorbed oil and extracted lipids from the fried material were less when the deteriorated oil was used for frying. This phenomenon is contrary to the knowledge that the amount of cooking oils absorbed by the frying materials is less when cooked in fresh oil and the amount of cooking oils consumed is more when thermally deteriorated oil is used for frying.

Lipid-free materials obtained from the fried samples by extraction with acetone and ether as previously described, were used for determination of the digestibility by pepsin and trypsin and of the content of available lysine (Table 6). The lipid-free material obtained from raw paste meat control, had a digestibility of 91.8 and 79.4% by pepsin and trypsin, respectively. Pepsin digestibility of the fried samples tended to increase when subjected to heat treatment, but there was little difference

Table 6. *Relative digestibility in vitro and available lysine.*

	Digestibility		Available lysine
	Pepsin	Tyrpsin	
Unfried paste meat	100 (91.8%*)	100 (79.4%*)	100 (13.7 g Lysine/16 g N)
Fresh oil	102	86	87
No. 1	101	88	84
No. 2	101	88	74
No. 3	105	87	84
No. 4	106	90	85
No. 5	102	85	85

* TCA soluble-N after digestion × 100/Total-N

in digestibilities among the samples. Trypsin digestibility of the fried samples indicated a decrease of 10–15% as compared with the control. Similarly, there were few differences in the digestibilities by pepsin in these samples.

The control contained 13.7 g of available lysine per 16 g of nitrogen. The content of available lysine showed a decrease of 13% as compared with the control in the fried samples, even when fried in fresh oil. The lowest content of the available lysine is shown in No. 2 sample which was prepared in the oil with the most unstable factors chemically of all the oils used in this study.

It is concluded that the nutritive evaluation of the fries is influenced by the quality of the cooking oil used. Consequently, the properties of the cooking oil absorbed and adsorbed by the frying materials directly influenced the evaluation of the fry.

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