## Physical and Chemical Changes in Oil Used for Frying Fish

T.V. SANKAR, K. AMMU, M.R. RAGHUNATH and K. DEVADASAN Central Institute of Fisheries Technology, Cochin 682 029

Coconut oil was repeatedly used for four days for frying mackerel. Changes in the characteristics of fried mackerel and the frying oil were monitored. The oil became darker and more viscous when used for frying consecutively for four days. Total carbonyls and conjugated dienes increased. Iodine value and non-saponifiable matter which were low in the fresh oil increased due to exchange of lipid between fish and frying oil. Saturated fatty acids decreased and mono and polyunsaturated fatty acids increased in the frying oil with progressive frying. There was an increase in saturated fatty acid fraction and decrease in Iodine value of lipids in the fried fish.

Key words: Fried fish, frying oil, physical changes, chemical changes

Fried fish is popular among many fish eaters. During frying mass and heat transfer occur between the frying oil and the food. Water and other nutrients transferred into the frying medium change its composition. The oxygen inclusion at the oil water interface contributes to the changes in the oil (Blumental, 1991) and food material. The temperature and duration of frying and aeration play important roles in the changes.

Oils rich in polyunsaturated fatty acids yield more toxic substances than oils rich in saturated fatty acids (Poling et. al., 1962). Hydrolysis of lipids to monoglycerides, diglycerides and fatty acids; oxidation of fat leading to the formation of conjugated dienes, peroxides, aldehydes and ketones, dimerisation and polymerisation are some of the diverse reactions that take place in oil during frying (Nawar, 1985).

Changes in the oil during frying under simulated conditions have been studied (Alexander, 1977; Kotwal et. al., 1993; Rojo and Perkins, 1987). Effect of frying sardine in different fats (Sanchez-Muniz et. al., 1992) and repeatedly using sunflower oil for frying squid rings on oil fraction (Hellin & Clausell, 1991) also have been studied. In commercial frying, oil is used repeatedly and intermittently with occasional replenishment. Studies on the changes taking place in the oil on its repeated use for frying and also in the fried fish are reported.

## Materials and Methods

Fresh mackerel (Rastrelliger kanagurta) was procured from the local market, eviscerated, washed and frozen at -20°C and stored. Samples drawn every day were thawed in running water, drained well and fried. 0.5 kg fish was fried each time

in an aluminium frying pan in 2 l filtered coconut oil. The temperature of oil at the start of frying was 170°C, which dropped to 130°C on addition of fish, and rose to 150°C in 10 min, by which time the frying was complete. Oil was replenished before frying the next. After frying 14 batches each day, the oil was left overnight in the frying pan, filtered and sampled for analysis. The volume was then made up to 2 l before commencing frying next day and the process was continued for four consecutive days. Meat from all batches of fish fried on each day were pooled, mixed thoroughly, minced in a blender and packed in 12 micron polyester /500 gauge LD/ HDPE co-extruded film and stored at -20°C for analysis.

The oil samples were taken as such after filtration. Lipids from fish/fried fish were extracted with chloroform and methanol (Folch et. al., 1957). Moisture, protein, ash, fat, peroxide value (PV), iodine value (IV) and non-saponifiable matter (NSM) were determined by AOAC (1975) methods. Total sterol in the NSM was estimated by the method described by Rudel and Moriss (1973). Conjugated dienoic acids (CDA) were analysed by the method of AOCS (1957). Total carbonyls were estimated after conversion to hydrazones as described by Ammu et. al. (1986). One gram of oil was diluted to 50 ml with hexane and the optical density was measured at 420nm. Refractive index of the oil was determined in an Abbe refractometer at 25°C. Oil viscosity was measured in an Ostwald viscometer at 25°C.

Fatty acid methyl esters of the lipids were prepared and analysed in a Chrompack CP 9001 gas chromatograph with an Altec RSL500 capillary column (15 m x 0.5mm) and flame ionisation detector. Injector and detector temperatures were 240 and 250°C respectively. The initial column temperature of 120°C was programmed to increase at a rate of 5° per minute to 200°C. Nitrogen was used as carrier gas at a flow rate of 6.1 ml/minute.

## Results and Discussion

Table 1 shows the proximate composition of fresh and fried fish. An average loss of 35% moisture and about 8-fold increase in fat occurred on frying. Sanchez-Muniz et. al. (1992) observed similar increase in fat content on frying and also that the uptake was more in fish fried in oil that was rich in polar fats. They further observed that high temperature at which the fish was fried did not cause much damage to the fish due to its high moisture content.

Table 1. Proximate composition of fresh and fried mackerel

Day of frying	Moisture, %	Protein, %	Fat, %	Ash, %
0 (fresh)	75.2	19.8	2.3	2.8
1	50.0	35.2	13.2	3.1
2	48.4	34.0	14.4	3.2
3	44.9	34.5	16.0	3.7
4	46.0	34.7	15.6	3.9

The changes in chemical and physical characteristics of frying oil used for repeated frying of fish are given in Tables 2 and 3 respectively. Fresh coconut oil has very

low I V (Table 2). It increased due to the migration of unsaturated lipids from the fish during frying and continued increasing as more batches of fish were fried. The high temperature of frying along with mixing of oil with atmospheric oxygen result in lipid oxidation. This is evidenced by increase of PV on successive days though it decreased on the 4<sup>th</sup> day. This could be due to the peroxides, being extremely unstable, breaking down to secondary products of oxidation. This is supported by the accumulation of both conjugated dienoic acids and carbonyls (Table 2). However, Hellin and Clausell (1991) did not observe significant changes in oil repeatedly used 9-10 times for frying squid. The difference, perhaps, is because of the low fat content of squid compared to mackerel. The NSM of fish lipids appear to have migrated into the cooking medium as seen by the increase of total NSM in the cooking medium.

Table 2. Chemical changes in coconut oil as a result of frying

Day of frying	1 V	PV meq/kg fat	NSM g/100g	Sterols mg/100g	Carbonyls mg/100g	CDA g/100g
0 (fresh)	9.7	0.94	0.194	50	8.68	0.03
1	12.7	2.90	0.224	103	38.6	0.051
2	16.4	3.35	0.291	150	78.3	0.084
3	18.5	3.50	0.354	180	114.4	0.130
4	20.2	1.56	0.416	200	121.8	0.147

The oil became darker, increasing to about sixty times the initial value by the end of 4<sup>th</sup> day (Table 3). The relative viscosity of the oil also increased though the refractive index remained more or less same. The increase in viscosity of the oil is due to dimerisation and polymerisation of oils during frying (Nawar, 1985).

Table 3. Changes in the physical parameters of coconut oil as a result of frying

Day of frying	Colour (OD 420)	Refractive index	Relative viscosity
0 (fresh)	0.002	1.452	1.00
1	0.016	1.453	1.17
2	0.055	1.453	1.14
3	0.107	1.454	1.11
4	0.135	1.454	1.16

Absorption of frying oil by fish is reported to be more in the case of lean rather than fatty fish (Sanchez-Muniz et. al., 1992). The exchange of lipids between frying oil and fish during frying is illustrated by the fatty acids of the frying medium and fried fish (Table 4). Coconut oil which was initially rich in saturated fatty acids showed a marked increase in mono and polyunsaturated fatty acids on repeated use to fry the fish. On the other hand the saturated fatty acids in the fried fish was almost double that in the fresh fish. Simultaneously significant reduction in monounsaturated (MUFA) and polyunsaturated fatty acids (PUFA) was noticed. The ratio of PUFA to saturated fatty acids (SFA) decreased by about 85% in the fish as a result of frying with a concomitant reduction in the SFA content and increase in the MUFA content of the

oil used for frying. The I V of lipids of steam cooked mackerel was found to be 125.7 while that of lipids of 1st, 2nd, 3rd and 4th day's fried fish was 33, 30.3, 23.5 and 34.9 respectively. This further supports the observation of the accumulation of SFA in fried fish. There was no considerable difference in the I V of lipids of fish fried on different days, indicating that the absorption of the low I V frying oil by the fish was not dependent on the number of times the oil had been used for frying.

Table 4. Changes in fatty acid composition of fresh and fried mackerel and coconut oil used repeatedly for frying

Sample			Day of frying	ng	
	0 (fresh)	1	2	3	4
Oil					
SFA	89.5	87.8	86.7	85.7	85.8
MUFA	6.5	7.1	7.5	7.9	8.06
PUFA	2.4	3.0	3.3	3.3	2.1
PUFA / SFA	0.03	0.03	0.04	0.04	0.02
Mackerel oil					
SFA	43.0	77.7	81.0	78.8	78.0
MUFA	21.9	8.91	9.01	9.08	9.97
PUFA	29.8	8.4	7.6	8.6	9.0
PUFA / SFA	0.69	0.11	0.09	0.11	0.10

The studies show mass transfer and exchange of lipids between the fried fish and the frying medium. The latter undergoes physical and chemical changes on repeated use.

## References

Alexander, J.C. (1977) in *Proc. Symp. Frying Oils*, p. 711, AOCS, 68th General Meeting, New York, American Oil Chemists Society, Chicago

Ammu, K., Viswanathan Nair, P.G. & Devadasan, K. (1986) Fish. Technol., 23, 134

AOAC (1975) Official Methods of Analysis, 12th edn, (Horwitz, W., Ed) Association of Official Analytical Chemists, Washington DC

AOCS (1957) Official and Tentative Methods of the American Oil Chemists Society 2nd edn (Mehlenbacher, V.C. & Hopper, T.H., Eds) Ka13-56. American Oil Chemists Society, Chicago

Blumental, M.M. (1991) Food Technol., 45(2), 68

Folch, J., Lees, M. & Sloane Stanley, G.H. (1957) J. Biol. Chem., 226, 497

Hellin, C.L. & Clausell, M.P. (1991) Annales de Brimatologia, 43,185

Kotwal, D.S., Vali, S.A. & Shastri, N.V. (1993) J. Food Sci. Technol, 30, 100

Nawar, W.W. (1985) in Food Chemistry, 2nd edn, (Fennema, O.R, Ed.) p. 210, Marcel Dekker Inc., New York

Poling C.E., Warner, W.D., Mone, P.E. & Rice, E.E. (1962) J. Am. Oil Chem. Soc., 32, 315

Rojo, J.A. & Perkins, E.G. (1987) J. Am. Oil Chem. Soc., 64, 414

Rudel, L.L. & Morris, M.D. (1973) J. Lipid Res., 14, 364

Sanchez - Muniz, F.J., Viejo, J.M. & Medina, R. (1992) J. Agric. Food Chem., 40, 2252