The thesis entitled “Studies on thermal and oxidative properties of some natural lipids” deals principally with the thermal and oxidative changes that occur when natural oils of varying degree of unsaturations are used alone in high temperature frying, as well as when fried with antioxidants derived from a traditional spice, turmeric, and from a traditional flower, marigold. In addition to the study of the effect of frying fish on the quality characteristics of mono-unsaturated fatty acid (MUFA) rich oil viz. mustard oil and poly-unsaturated fatty acid (PUFA) rich oil viz. soybean oil used for frying, it also deals with a comparative study in oxidative stability and composition of long chain poly-unsaturated fatty acids as occurring in fish lipid during microwave oven assisted frying and pan frying.

Four widely used edible oils, viz, soybean oil, sunflower oil, rice bran oil and palm olein oil having distinct physico-chemical characteristics were chosen and their thermal and oxidative stability were studied and compared at frying temperature. The oil samples (1L) were heated for 24 h, on 8 h basis daily for 3 consecutive days. 200 g of potato chips each time were fried twice for 5 min just before completion of every 4 h interval. The temperature maintained during the whole experiment, including the frying operation, was within the range of 180°-190°C. The heating of the oil was carried out in a non-stick frying pan to prevent leaching from utensils. Neither salt nor any other spices were added during frying of the potato chips. Oil samples were collected after every 4 h and kept in refrigeration. At the end of the frying process each day, the oil left was removed from the fryer, cooled under nitrogen and kept in refrigerator. Fresh oil was
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never added to the frying vessel for replenishment. The oil quality parameters viz acid value, iodine value, peroxide value, p-anisidine value and conjugated diene were determined for fresh oil as well as for the heated oil samples collected every 4 h of heating. It was observed that oil degradation started from 4 h and there was increase in free fatty acids or acid value. But the oil sample collected after 24 h of heating showed higher acid value of 1.1 ± 0.02 in case of soybean oil when compared with other oils. Palm olein oil showed the least value of 0.30 ± 0.01. A progressive decrease in iodine value was observed in all oils which can be attributed to the destruction of double bonds by oxidation and polymerization. Significant differences were observed in peroxide value at different time intervals presumably due to variation in the content of tocopherols in the oils that have been investigated. The presence of β, γ and δ- tocopherols in soybean oils showed more stability in the peroxide formation reaction. The sunflower oil showed a greater peroxide value than the other oils as it contains only α-tocopherol which is biologically more active but not that active under in-vitro condition. The palm olein oil showed the minimum peroxide value owing to the presence of low poly-unsaturated fatty acids (PUFA) and high mono-unsaturated fatty acid (MUFA) and also higher degree of saturated fatty acids (SFA). The steady rise of p-anisidine value for all the oils indicated the formation of volatile breakdown products such as aldehydes, ketones and anhydrides of unsaturated fatty acid which can affect the flavor of fried food. The highest increase in conjugated diene content after heating was observed in soybean oil having value of 7.6 ± 0.2 %, whereas the palm olein oil showed the least rise in conjugated diene content having value of 2.7 ± 0.1%, after 24 h of heating. From the investigation it was seen that
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Palm olein oil had a greater thermal stability than others but from nutritional point of view, because of its higher degree of saturation, it is less suitable for human health. Therefore, soybean oil, sunflower oil and rice bran oil were more favourable than palm olein, because they consist of higher amount of unsaturation, MUFA and PUFAs and only low amounts of SFAs. However, a strong disadvantage of these types of oils as frying medium is that the PUFAs like linoleic or linolenic acid are susceptible to oxidation. Considering all the aspects, rice bran oil proved a better option in the choice of frying oil.

The effect of antioxidants derived from traditional spice like turmeric and naturally occurring antioxidants such as lutein ester have been studied as outlined below.

The effectiveness of the natural ingredient, turmeric, in preventing the thermal and oxidative degradation of the soybean oil during deep frying of potatoes marinated with turmeric, was investigated. Curcumin, the active principle of turmeric, is known to act as an anti-oxidant, anti-mutagen and anti-carcinogen. Two sets of experiment were carried out. In one set, 1 L of oil was heated for 24 h on 8 h daily basis for 3 consecutive days and 200 g potato chips (without any marination) each time were fried twice daily for 5 min just before completion of every 4 h interval. About 50 ml of the oil sample was collected after every 4 h. In another set of experiment, another batch of 200 g of sliced potatoes marinated with 0.5 g of turmeric powder was fried each time in another 1 L of soybean oil following the same method as above. Oil samples of about 50 ml were collected after every 4 h and kept in refrigerator (-20 °C) for comparative study with the
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oil sample collected after frying potatoes without marinating with turmeric. The oil quality parameters viz acid value, iodine value, peroxide value, content of 4-hydroxy-2-nonenal (HNE) and fatty acid composition were determined for fresh oils as well as for the heated oil samples collected every 4 h of heating. The acid value showed an increase with increase in duration of frying for both the oils, though the increase was almost in same rate for both of them. The iodine value revealed a higher value for soybean oil in comparison to soybean oil with marinated turmeric, after 20 h of heating. There were distinct differences in the peroxide values between the soybean oil and the soybean oil with marinated turmeric, having a lower value in case of the sample containing turmeric. This may be credited to the antioxidant property of curcumin in turmeric. However, the differences between the peroxide values of soybean oil and soybean oil with marinated turmeric gradually decreased with further increase in duration of time, indicating reduction in the effect of curcumin. It was observed that the content of HNE in the soybean oil containing turmeric was 3.99 ± 0.04μM/gm which was much lower than that of the control soybean oil having value of 4.28 ± 0.07μM/gm till 16 h of heating. The antioxidant property of curcumin in turmeric along with the natural antioxidant present in soybean oil i.e. the tocopherols might have helped in reducing the oxidation of the oil initially, but with continuous heating for long duration, this property might have become ineffective. The oil sample collected after 24 h of heating showed reverse trend having a bit higher value than the soybean oil which may be because of increase in oxidative deterioration of the oil after the loss of antioxidant property of curcumin. The loss of unsaturated fatty acids was calculated. It was observed that there was a significant and
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gradual increase in total saturated fatty acids (SFAs) with increase in time of heating. The total SFAs percentage in soybean oil increased from 16.57% to 24.33% while in case of soybean oil containing turmeric, it increased from 16.57% to 22.94% after 24 h of heating. On the other hand, the sum of the unsaturated fatty acids (UFAs) for the soybean oil decreased gradually from 83.43% for fresh unheated oil to 75.67% for the oil sample collected after 24 h of heating, indicating a loss of unsaturation of 7.76%. Whereas, in case of oil sample containing turmeric, the sum of UFAs gradually decreased from 83.43% for unheated oil to only 77.06% for the oil sample collected after 24 h of heating, indicating a loss of 6.37% unsaturation. These results indicated higher thermal and oxidative stability of the soybean oil where food marinated with turmeric has been fried. However, the antioxidant potency of curcumin present in turmeric is seen to get reduced with increase in duration of heating of the oil.

Lutein-ester was isolated from Indian marigold flower by solvent extraction method. Two sets of experiment were carried out by taking 1 L of soybean oil. In one set, 500 mL of soybean oil was heated for 24 h on 8 h basis daily for 3 consecutive days. In the second set, 5 mg of lutein ester was added to the remaining 500 mL of soybean oil and the oil was heated for 24 h in the similar manner. In both the oils, 200 g potato chips each time were fried twice for 5 min just before completion of every 4 h interval. Oil samples were collected in every 4 h and the protective effects of lutein ester were assessed by monitoring the colour, viscosity, acid value, peroxide value, p-anisidine value and HNE content. The initial tintometer reading for the soybean oil indicated total colour (Y + 5R) value of 1.1 ± 0.1. After every 4 h of frying the change in yellow colour
was significant and finally after 24 h of frying, the value was found to be 11.3 ± 0.3. However, the soybean oil with added lutein ester showed a reverse trend. The initial tintometer indicated value of 53.9 ± 2.2. After every 4 h of heating the decrease in yellow value was significant and finally after 20 h of heating the value was found to be 11.2 ± 1.5. The gradual darkening of the colour of soybean oil after heating may be attributed to the polymerization reactions at high temperatures. In soybean oil with added lutein ester, the dark colour at 0 h of heating can be attributed to the orange colour of the lutein ester. As the duration of heating increased, the colour pigments degraded and the colour of the oil became lighter. But oil sample collected at the end of the experiment i.e. after 24 h showed increase in the yellow value from the one at 20 h, due to the usual factors of polymerization reactions at higher temperatures. The soybean oil showed a marked increase in viscosity with time than the oil with added lutein ester. The control oil showed an increase in value from 27.19±0.1 at 0 h to 63.39±4.2 at 24 h. The viscosity of the oil samples with added lutein ester collected after 24 h heating showed a value of 40.09±3.8 centipoise which is much less than the viscosity of soybean oil. The acid value, peroxide value and p-anisidine value showed higher reading in soybean oil samples when compared to the oil samples with added lutein ester. The content of HNE, which can be used as an index to monitor the overall progression of PUFA towards oxidation, showed a marked increase in value from 0.02±0.01 µM/g to 10.09±0.16 µM/g in case of soybean oil. However, the soybean oil with added lutein ester showed a value of 1.11±0.02 µM/g even after 24 h of heating at frying temperature, revealing its resistance to lipid peroxidation. This study confirmed that the natural antioxidant viz lutein ester showed a
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greater oxidative and thermal stability at frying temperature even after 24 h of heating of the oil and can be successfully employed in fortification of soybean oil to ensure lesser oxidation of the oil during cooking.

Study was also carried out on comparative basis on the frying characteristics of MUFA rich oil like mustard oil and usual PUFA rich oil like soybean oil in frying protein containing material like fish, *Labeo rohita*. The mustard oil is typically rich in MUFA like erucic acid (54.9%) and significant amount of oleic acid (11.3%) while the soybean oil has high PUFA content like linoleic acid (54.9%) and some amount of linolenic acid (4.5%) in its fatty acid profile. The quality of both the oils, as affected by fish frying at 180°C for 8 h was investigated. The physical and chemical characteristics of the oils were evaluated by drawing out the oil samples from the fryer at an interval of 1 h for first 2 h and then after every 2 h till 8 h of total heating of the oil. The parameters evaluated were colour, viscosity, acid value, peroxide value, p-anisidine value, amount of HNE and fatty acid composition. The initial tintometer reading for mustard oil showed a higher value, as expected in the case of unrefined oil (permitted for direct edible consumption in India), which further increased with the duration of heating. On the other hand, the initial value for refined soybean oil was very less with a sharp increase after 4 h of heating. The viscosity of both the oils increased with the duration of frying. However, the increase is more in case of soybean oil in comparison to mustard oil. Acid value of both the oils did not show significant differences. Soybean oil showed higher peroxide values and p-anisidine values in comparison to mustard oil, the reason of which may be attributed to higher degree of PUFA in soybean oil. The amount of HNE present in soybean oil was
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3.15 ± 0.01 μM/g which was almost thrice to the amount present in mustard oil having value of 1.04 ± 0.03 μM/g after 8 h of frying, showing a higher deterioration in frying quality of soybean oil. The changes in fatty acid composition was evaluated and it was found that in both the oils there was an apparent increase in saturated fatty acid (SFA) content and the polyenoic acid showed a decrease in value with increase in time of heating. The presence of docosahexaenoic acid (C_{22,6}) in the heated samples of both the oils was from the fried fish sample. The total amount of SFAs and unsaturated fatty acids (MUFA+PUFA) were calculated for all the oil samples of mustard oil and soybean oil. The loss of fatty acids, calculated, gave an indication of degree of oxidative polymerization, scission and other side reactions taking place during deep fat frying. The loss of unsaturation was slightly more in case of mustard oil which can be justified by the presence of higher amounts of unsaturates in mustard oil (94.9%) having relatively more linolenic content (12.9%) than soybean oil (84.5%) which has linolenic content of 4.5%. However, the total loss of PUFA was more in soybean oil than in mustard oil. Therefore, the present study indicated the overall better suitability of mustard oil with higher amount of MUFA (66.2%) during high temperature frying than the soybean oil with higher amount of PUFA (59.4%).

The type of fryer used also influences the quality of oils during high temperature frying as reported in the literature and observed in the present study as well. The use of microwave oven for various cooking including frying operations has become a trend in the new epoch because of its fast hassle-free cooking technique. The objective of the present study was to compare different chemical properties of the oil extracted from the
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fish fried in microwave oven and the one fried in pan. Two types of fish, mostly consumed in Indian household, viz Catla (*Catla catla*) and Hilsa (*Tenualosa ilisha*), were procured from the market. The fish pieces, marinated with turmeric and salt (as normally practiced in Indian cuisine), were subjected to two modes of frying i.e., some pieces were fried in microwave oven and the other samples were fried in pan in traditional way. Mustard oil was used as a frying medium. Comparative changes in oxidative stability values in fish lipid in raw fish, microwave oven fried fish and pan fried fish were determined through analysis of the chemical parameters like peroxide value, p-anisidine value, content of HNE and fatty acid composition. Significant differences were observed in peroxide value for the raw fish oil, microwave oven fried fish oil and pan fried fish oil. Peroxide value increased from 11.9 ± 2.4 meq/kg in raw fish oil to 38.7 ± 5.6 meq/kg in pan fried Catla fish oil. The microwave oven fried Catla fish oil also showed marked increase in the peroxide value i.e 20.3 ± 4.6 meq/kg when compared with the raw one, but the increase was much lower than the pan fried fish oil. The Hilsa fish samples also showed a similar trend. However, the peroxide values of all the samples in Hilsa showed a higher value than Catla samples which may be attributed to high PUFA present in Hilsa fish. The p-anisidine value showed an increase in value from the raw fish sample to the fried fish, the increase being more in the pan fried fish oil than in microwave oven fried fish oil in both the Catla and Hilsa fish. The content of HNE showed a minimum value for the oil extracted from the raw fish sample, 0.34±0.08 µM/g for Catla fish and 0.80±0.02 µM/g for the Hilsa fish. The fried fish showed an increase in value, the increase being greater when pan fried than when the fish is fried in microwave oven. The
content of HNE for microwave oven fried fish oil was 0.48±0.07 μM/g for Catla and 0.98±0.001 μM/g for Hilsa. But the oil extracted from the pan fried fish showed 2.5 ±1.02 μM/g and 2.7 ± 0.5 μM/g content of HNE for Catla and Hilsa fish samples respectively. Study on the changes in fatty acid composition in Catla sample revealed that there was decrease in linoleic (C_{18:2}) acid and linolenic acid (C_{18:3}) content in fried fish when compared with the raw fish sample. But the decrease was more pronounced in case of pan fried fish than in oven fried one, indicating greater oxidation. The presence of erucic acid (C_{22:1}) in oil sample extracted from microwave oven fried and pan fried fish, proved the absorption of mustard oil (which has been used as the frying medium) by the food fried. The eicosapentaenoic acid (C_{20:5}) and docosahexaenoic acid (C_{22:6}) content in the fish oil, also decreased in value from the raw sample, after frying. Though, the fatty acid composition of Hilsa fish, showed a decrease in linoleic (C_{18:2}) acid and linolenic acid (C_{18:3}) content in fried fish than in raw fish, but here there was no significant difference in values in microwave oven fried and pan fried. The reason may be due to the presence of high PUFA initially in Hilsa fish sample and thus the mode of cooking is not causing any variance in the fatty acid composition. The analysis of the oils extracted from the fish samples cooked by different methods showed that considerable oxidation occurs when a fish is fried and toxic substances are produced. But the rate of deterioration is far noticeable in pan fried fish than the one fried in the microwave oven. Therefore, it was concluded that food cooked in microwave oven pose a less health hazard than the one cooked traditionally, as in a microwave oven the food is subjected to lesser time of
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cooking and also minimal exposure to atmospheric oxygen and thus is a better choice as a mode of cooking.

The microwave oven is mostly used for reheating the food items before consuming. Therefore, another experiment was carried out by collecting samples of chicken patties and of vegetable patties from different bakery shops in Kolkata and reheating the samples in microwave oven. Since HNE is an important marker of lipid peroxidation, the amount of it was determined and it was found that the HNE content increases when the food was reheated in a microwave oven. Also, when the food was reheated 2\textsuperscript{nd} time, the HNE content increased to a greater extent becoming almost double in some of the cases.

In order to assay the deleterious effect of the mostly consumed commercially available fried products, randomly chosen samples each of 5 different food products were bought. Kachuri, Nimki, Samosa and Vegetable chops were bought from reputed shops in Kolkata, West Bengal, whereas Aloo (potato) chops were purchased from street vendor in Kolkata. The oil quality parameters viz conjugated diene, conjugated triene, amount of HNE and fatty acid composition of the extracted oil were determined for all the collected samples. The conjugated diene and conjugated triene showed the highest value in case of Kachuri sample collected from a reputed shop. However, the HNE content of Aloo chop, which has been collected from the street vendor, showed a maximum value of 12.262 ± 1.757\textmu M/gm indicating use of highly deteriorated oil for frying purpose. Analysis of fatty acid composition revealed that the total amount of SFA present in the oil sample
extracted from vegetable chop, had the highest value of 53.84%. The PUFA in the said oil sample was only 4.53% and the MUFA was 41.63%. On the other hand, the sample Kachuri had the highest amount of PUFA of 42.19%. The total amount of unsaturates in the sample Kachuri was 64.41% which was higher among all the samples. Thus, it was seen that the oil sample extracted from the food product Kachuri was much more stable and the fatty acids were in better proportions in comparison to other oil samples.

From the foregoing work it can be stated that both thermal and oxidative changes in natural oils during frying are associated with some alterations in physical and chemical properties. Antioxidants, derived from traditional spice like turmeric and from flower marigold, showed different degree of effectiveness when used during potato frying in soybean oil at frying temperature for long duration of time. Though curcumin (the active substance in turmeric) became ineffective when the food marinated with turmeric was fried at elevated temperature for long duration of time, but the oil where lutein ester (derived from Indian marigold) has been added showed a greater thermal and oxidative stability even after 24 h of heating at frying temperature. Frying of protein containing food like fish in MUFA rich oil (mustard oil) and PUFA rich oil (soybean oil) indicated marked difference in deterioration in quality of oils but the deterioration was more in soybean oil due to its high PUFA content. The type of fryer also influences the quality of oils during high temperature frying with much greater extent of deterioration in case of pan fried oil. Reheating of fried foods always leads to the formation of more toxic compound such as HNE which is health hazardous. In case of commercial bakery snack
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products, the deterioration of oil isolated from the products is again much more different in case of quality.

It may be pointed out from the present study that oleic rich or MUFA rich oil should be preferred in frying of various food products and so all efforts should be made to promote these oils in frying.