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Comparative Study on The Effect of Deep Frying on Physiochemical Properties and Qualities of Sunflower *(helianthus annuus l.*) and Soybean (*glycine max*) Oil

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Abstract
The study aimed to compare the changes that occur during the deep frying process with refined sunflower oil and refined soybean oil. Both oils were used as a frying media to fry potato strips for 6 h daily for 5 days. Standard procedures for the measurement of oil degradation such as acid value (AV), peroxide value (PV), iodine value (IV), total polar materials (TPM), and refractive index (RI) were used. As a result, significant changes were observed in both oils in terms of chemical properties. Changes in TPM, IV, and AV show higher stability for soybean oil, while changes in RI and PV show more stability in sunflower oil. As RI is not a reliable test for evaluation of the heating process and PV in our test could not reach maximum value so, soybean oil had superior stability than sunflower oil in our test. Using a study of TPM as the main parameter to check the usability of frying oil, there was no significant difference (P>0.05) in the value of TPM between the two oils according to the final day result hence, as per our study sunflower and soybean oil are similar in action for frying purpose. The maximum value of TPM for commercial frying oils is accepted as 25 and our study shows that 12 hours of frying exceeds the limit value of TPM contents.

Keywords: *Acid value, Peroxide value, iodine value, total polar materials, and refractive index*

INTRODUCTION

Deep fat frying is a process of cooking by immersing food in oil of 150°C-200°C. It is one of the oldest and most common methods of food preparation. Deep frying imparts flavor, golden brown color, and crisp texture an important sensory characteristic of food. Fried products are being consumed by different cultures during different time frames for a long time. Some fried products are typically traditional, while some products like french fries are produced in the family kitchen as well as the industrial level making it the most common as well as the simplest fried food produced and consumed all over the world (Sumnu and Sahin, 2008).

Frying oils thermally and oxidatively decompose around the temperature of 190°C, and volatile and nonvolatile products are formed that can change the functional, and sensory quality of oil (Kathleen Warner, 2002). During deep frying, mass transfer between oil and food causes dispersion of oil, protein, carbohydrate, vitamin, and moisture from fried food while the product uptakes the oil (Krokida *et al.*, 2000). Thus, both frying oil and fried food affect each other and boost the incidence of complex reaction pathways jointly. The main chemical reactions that occur during the deep-fat frying process are oxidation, polymerization, isomerization, and hydrolysis (Sumnu and Sahin, 2008).Reactions at frying temperature eventually help in the production of FFA, aldehydes, hydrocarbons, ketones, cyclic compounds, mono and diglycerides boosting the changes in AV, PV, TPM and many other parameters (Pokorny, 1989).

There has been an increase in the consumption of fried foods despite knowing about the negative results of degraded frying fats and fried foods. It is a well-known fact that different fried foods are produced by street vendors in our country (Goyary *et al.*, 2015). Soybean and sunflower oil is commonly used for frying purposes by both street vendors and households in our locality. These street vendors repeatedly use the same oil several times to avoid monetary losses. This over-exploitation of oil affects both the physical and chemical properties of oil. Almost all volatile compounds get lost and the non-volatile compounds are degraded. The use of this oil for deep frying makes oil unstable even under ambient conditions, which are harmful to the self-life of food as well as the health of consumers (Thakkar, 2014).

There is no proper information on this aspect for both street vendors and consumers. Proper studies on this topic are also not done. Thus, the main goal of this research was to investigate the effect of the repeated process of frying on two different oils refined sunflower oil and soybean oil and to monitor the physicochemical features of these oils after the process of frying degradation has occurred. How long oil should be used is a matter subjected to research and debate and the consequences of ingestion of foods prepared using reused oil need enough attention. This study will largely benefit our consumers to know the level of frying degradation that can occur on the oil. Vendors can get the idea of maximum limit of use of oil without hampering the quality of oil to a great extent.

MATERIALS AND METHODS

Materials

Soybean (*Glycine max*) oil:RBD soybean oil was procured from the market. Marketed by trade name Postman Refined Soybean Oil by PashupatiKhadya Tel Udyog, Sonapur, Sunsari.

Sunflower (*Helianthus annuusL.)*oil:RBD sunflower oil was procured from the market. Marketed by the trade name Celo Refined Sunflower Oil by Bagmati Oil Industries, Katahari 4, Morang.Potato: Fresh potatoes were obtained from the local market of Dharan.

Methods

Experimental Procedure

Potatoes were washed, peeled, and cut into thin slices. 2 liters of sunflower oil were placed in a cooking vessel and heated at 180±5°C for 6 h daily. Each sample of the potato slices (400 g) was randomly selected and deep fried for 7 min each day for 5 days. A similar procedure was done for soybean oil separately. The same oil was used for the next day of the frying process for 5days. At the end of each frying day, frying oil (approximately 300 ml) was filtered into a screw-cap vial and kept in the dark condition at 4°C until analyzed. Blank oil was used as a control. The oil sample was analyzed for its Acid value, peroxide value, iodine value, polar materials, and refractive index

Analytical Procedure

Estimation of Acid value (AV): Acid value was analyzed according to the AOAC official method 940.28 (AOAC, 2005).Estimation of Peroxide value (PV): Peroxide value was analyzed by AOCS-AOAC official method 965.33 (AOAC, 2005). Estimation of Iodine value (IV):Iodine value was analyzed by AOAC official method 920.159 (AOAC, 2005).Estimation of Refractive index: Refractive index was analyzed by using a digital refractometer (by Anton par GmbH, Germany) temperature set at 40 °C

Estimation of polar materials: Polar material was analyzed by using a digital frying oil monitor (by Atago) and dipping the sensor in sample oil at room temperature (29°C).

Statistical analysis

Data for physicochemical analysis were plotted for comparison and were graphically represented using the Microsoft Excel 2007 program by Microsoft Corporation All results of experiments in triplicate were statistically processed by GenStat (12th edition) developed by VSN International Limited for Analysis of Variance (ANOVA). The means of the data will be separated whether they are significant or not by using the Least Significant Difference (LSD) method at a 5% level of significance expressed as the mean ± standard deviation.

RESULTS AND DISCUSSIONS

Acid value

The number of milligrams of KOH required for neutralizing free fatty acids (FFA) present per gram of oil is called the acid value of oil. Fats are found in triglyceride form when freshly extracted, which on prolonged storage begin to break down giving rise to FFA (KC and Rai, 2007). During frying, the rise in the FFA content can be attributed partly to the hydrolysis and partly to component carboxylic groups present in polymeric products of frying. This acidity is formed by hydrolysis of triglycerides, which is promoted by food moisture and oxidation. Several factors should be considered when using this method as the level of FFA in the frying oil not only reflects those formed during the frying process but also includes the level of acidity initially found in the oil before (Sumnu and Sahin, 2008).

In our research acid value was found to be increasing with heating time for both samples, as shown in Fig.1 Sunflower oil exhibited higher AV than soybean oil from the beginning of the test till the end. At the final stage of heating (30h), the AV for soybean and sunflower were 0.3592±0.002 and 0.3925±0.001 mg of KOH /g of oil respectively. During heating, a significant difference ($p \leq 0.05$) was observed between the AV of two samples for 2,3,4 and 5 days of heating.

Results of research done by (Aşkın and Kaya, 2020) and (Sayyad, 2017) with different types of oils are similar to our research. In comparison of AV change in both oils soybean oil exhibited higher stability than sunflower oil because sunflower oil has higher oleic acid content than soybean oil (Codex 2015) making sunflower oil more vunerable to hydrolysis and hence higher FFA formation, this result is supported by (Aşkın and Kaya, 2020) and (K Warner et al., 1994) where it was found that higher oleic acid content in oil shows higher FFA content in the heated oil.

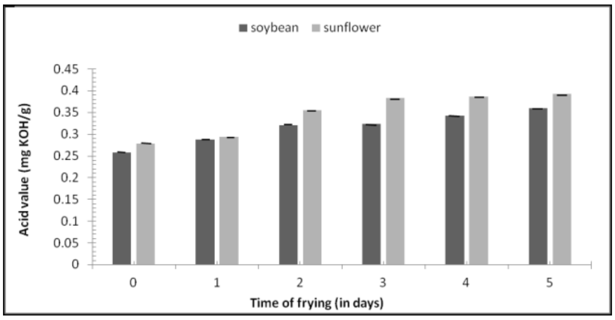

Figure 1: Effect of heating on AV

Peroxide value (PV)

The peroxide value (PV) is a measure of the concentration of peroxides and hydroperoxides formed in the initial stages of lipid oxidation. Peroxide value is a classical method to determine the extent of oil oxidation. It measures the formation of intermediate hydroperoxide in milliequivalent of active oxygen per kg of sample. Hydroperoxide formed in oxidation reacts with iodide ions to form iodine, which is measured by titration with thiosulphate. The peroxide value doesn't distinguish between the various unsaturated fatty acids undergoing oxidation and does not supply information about secondary oxidative products formed by hydroperoxide decomposition, so it can be stated that the peroxide value is an indicator of the primary level of oil oxidation. Peroxides are unstable under frying conditions; there is an increase in peroxide value during the initial stage of frying followed by a decrease with further frying when hydroperoxides tend to decompose to form secondary oxidation products (Sumnu and Sahin, 2008).

In our research initial stages of heating shows higher PV for sunflower, but at the final stage of heating (30h) soybean has higher PV than sunflower. A regular increase in PV was observed for both samples at all intervals as a function of heating time, as shown in Fig.1.2. At the final stage of heating (30 h), PV was 17.104±0.180 and 16.73±0.231 meqv O2/kg of oil for soybean and sunflower oil respectively. A significant difference ($p \leq 0.05$) was observed between the PV of two samples for 1, 2, 3 and 4 days of heating.

Our data confirms the results shown in early studies by (Aşkın and Kaya, 2020)and (Abdulkarim et al., 2007), to the point both studies show an increase in the peroxides until a maximum is reached, followed by a decrease. This decrease can be due to their reactions and degradations of peroxide compounds. But our result shows only an increase in PV thus we can conclude that our sample oil has not reached its maximum or degradation of peroxide compounds in our sample oil is slower to show its effect. As peak value for both oils has not been obtained we cannot rely on result based on PV value.

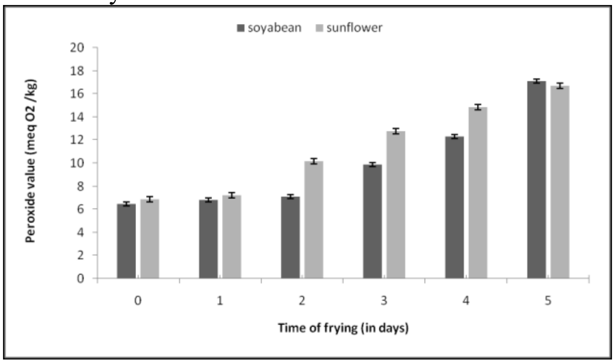

Figure 2: Effect of heating on PV

Iodine value (IV)

The iodine value is the number of grams of iodine absorbed by 100g of fat. Iodine number is a measure of unsaturation of the fatty acids present in fat. Wij's method is universally used to calculate iodine value.(KC and Rai, 2007)As it expresses the amount of unsaturated fatty acids, and the extent of their unsaturation it is a very useful quality parameter during frying. The iodine value tends to decrease when oil is used in the frying. This decrease indicates the increased rate of oxidation while frying due to the consumption of double bonds by polymerization and oxidation. However, the iodine value for fresh oil must be determined to find the rate of change during frying (Sumnu and Sahin, 2008).

In our research decrease in IV was observed for both samples at all intervals as a function of heating time, as shown in Fig. 3. Sunflower oil exhibited lower IV than soybean from beginning to end. At the final stage of heating (30h) IV was 126.697±2.69 and 113.9793±1.25 for soybean and sunflower oil respectively. A significant difference ($p \leq 0.05$) was observed between the IV of two samples for 5 and 6 days of heating.

During heating operation, IVs decreased gradually, this pattern of data confirms the results shown in early studies by (Aşkın and Kaya, 2020)and (Abdulkarim et al., 2007), both studies show a decrease in the IV. Sunflower oil had a higher reduction of IV 28.07 units compared to the initial point, while soybean had a 16.33-unit reduction. This may indicate a change in fatty acids during frying with a high decrease in double bonds due to oxidative loss. Soybean indicate lower oxidative rancidity in comparison to sunflower oil as soybean with lower linolenic acid content compared to sunflower (Codex 2015)have less chance of double bond loss resulting less IV reduction. Reduction in values is slower in rate for the initial 3 days which reduces very sharply after the 3rd day, this may be due to high time–temperature action applied to help polymerization and oxidation action consuming double bonds at faster rate.

Refractive index

The refractive index (RI) of oil is the ratio of the speed of light in a vacuum to the speed of light in the sample oil. The measurement of refractive indices can be used for the identification of fats and testing of their purity as the RI of oil is characteristic to a certain limit. An instrument called an Abbe′ refractometer with temperature control is used for measurement. The refractive index decreases with an increase in temperature, it increases with an increase in the length of the carbon chains and with unsaturation (KC and Rai, 2007).

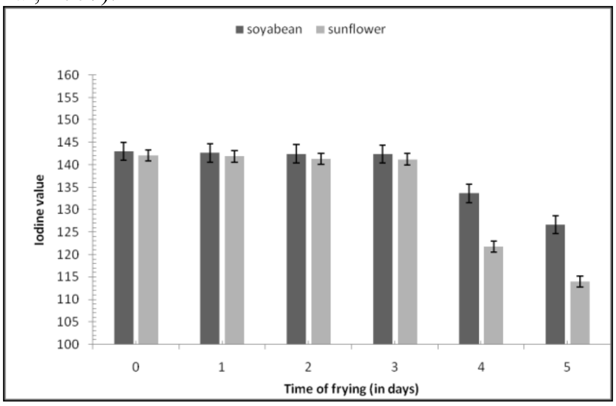

Figure 3: Effect of heating on IV

In our research refractive Index was found to be increasing with the heating time for both samples, as shown in Fig.4. Soybean oil exhibited higher RI than sunflower oil from the beginning of the test till the end. At the final stage of heating (30h), the RI for soybean and sunflower were 1.47238±0.0001 and 1.47161±0.0001 respectively. During heating, a significant difference ($p \leq 0.05$) was observed between the RI of sunflower and soybean oil for each step of heating.

An increase in the RI may be due to the increase in the level of conjugated fatty acids as a result of thermal degradation or due to the mass transfer from a fried substrate. This increase in the number of conjugated acids also conveys an increase in the level of autoxidation. The refractive index increases with an increase in oxidation same as the peroxide value (Godswill *et al.*, 2018). Sunflower oil had a higher increase of RI 0.00469 units, while soybean had a 0.00442 units increase. This indicates the high increase in level of conjugated fatty acids and chain length of fatty acids during frying action, in soybean oil is slightly more in comparison to sunflower oil. RI is not so reliable test for the evaluation of the heating process as the type of frying substrate has a high level of interference in the RI value of oil.

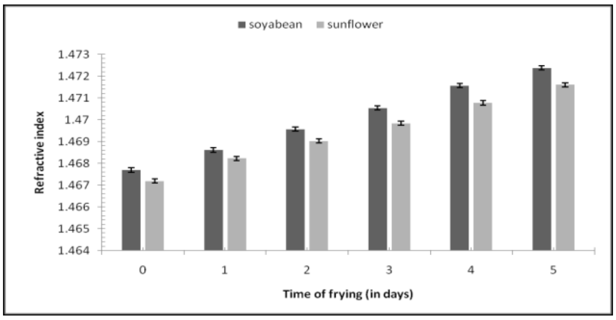

Figure 4: Effect of heating on RI

Total polar compounds

During the heating process, many chemical reactions result in the formation of compounds with high molecular weight or polarity. These compounds are nonvolatile and steadily increase in concentration with heating time. Many researchers consider measuring polar materials to be the most important test for assessing degrading oil. Polar compounds include oxidized and dimerized triglycerides, FFAs, and mono/diglycerides- like materials in frying oil. Polymers are formed through oxidative and thermal reactions. The dark "shellacs" formed on the fryer wall are polymeric. These are excellent chemical markers of oil degradation, although not applicable to monitoring food quality. Oxidative polymers are formed by autoxidation when free radicals terminate each other, they do not always impart an off-flavor to freshly fried food but, because they can decompose during storage of the fried product. Thermal polymers occur due to excessive fryer heat and excessive fryer downtime (Sumnu and Sahin, 2008).

In our research, TPM was found to be increasing with heating time for both samples, as shown in Fig: 5 Soybean oil and sunflower oil showed quite similar results from beginning toend. TPM was 11.5 and 11 for raw soybean and sunflower oil before heating, which increased very sharply on heating; it went out of measuring range for instruments. An instrument used had the highest range of measurement at 40 which crossed in 3rd day of heating, so TPM could not be measured after this point. TPM measured on2nd day of heating for soybean and sunflower were 36.5±0.153 and 36.6 ±0.058 respectively.

During heating, a significant difference ($p \leq 0.05$) was observed between the TPM of sunflower and soybean oil for 1st day of heating but not for 2nd day of heating. This denotes that TPM was significantly different for the initial step of heating but on long exposure to heat, both had similar results. Results show a significant increase in TPM during heating operation, this result was in agreement with conclusions reported by (Aşkın and Kaya, 2020),(Abdulkarim *et al.*, 2007), and (Sayyad, 2017)in their respective studies. The maximum value of TPM, acceptable for commercial frying oils, is accepted as 25(DFTQC, 2022). On the 2nd day of frying, TPM contents exceeded the limit value. These results indicated that the oils used in this study could be used only for 1 day for frying potato slices. If the maximum TPC value for frying oil is accepted to be 25. The increase in TPM was more for sunflower in comparison to soybean oil by subtle difference so, TPM-based stability is slightly higher for soybean than sunflower oil although usability of both oils is similar as there was no significant difference ($p > 0.005$) between two oils for final day result.

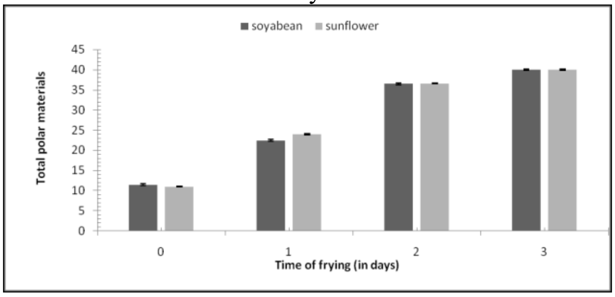

Figure 5: Effect of heating on TPM

CONCLUSIONS

The chemical analysis showed that the quality of both oils severely deteriorated after the frying process. Changes in TPM, IV, and AV show higher stability for soybean while values for RI and PV show more stability in sunflower oil. RI test is not a reliable test in the evaluation of the heating process and PV in our test could not reach maximum value hence, soybean oil was found superior in our test in terms of stability. TPM is the main parameter to check the usability of frying oil and the two oils were not significantly different ($p \leq 0.05$) according to the final day result hence; both boils have similar usability for frying purposes as per our test result. If the maximum value of TPM for commercial frying oils is accepted as 25, in our study, TPM contents for 2nd day of frying exceed the limit value; this result indicates that both oils could be used only for 1 day of frying (6 hr) at the temperature (180±5°C) under continuous frying conditions as used in our test.

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