Physicochemical Characterization and Frying Quality of Canola and Sunflower Oil Samples

[1]SHAZIA TABASUM, [1]SANIA ASGHAR, [1]SADAF NAZ ASHRAF, [2]HAFIZ BADARUDDIN AHMAD*, [2]NAEEM AKHTAR AND [3]KHALID MOHAMMED KHAN

[1]*Department of Chemistry*, *Government College Faisalabad*, *Pakistan.*

[2]*Department of Chemistry Bahauddin Zakariya University Multan*, *Pakistan.*

[3]*H. E. J. Research Institute of Chemistry*, *International Center for Biological and Chemical Sciences*, *University of Karachi*, *Karachi-75270*, *Pakistan.*

(Received on 11th January 2011, accepted in revised form 15th October 2011)

Summary: Frying quality of canola and sunflower oils was evaluated. Stimulated frying experiments were performed on oils with French fries as the fried food. Samples of oils were used to fry potato chips for four days. Physical and chemical characterization was carried out to determine the change during frying. Comparison of frying oil samples was then made with their control counterparts (i.e. oil samples without frying). There was a gradual increase in refractive index, viscosity, acid value and colour with time of frying. Iodine value decreased significantly with time of frying. Peroxide value first increased up to 12 h of frying and then decreased. Colour change and viscosity increase with increase in frying time. Amount of free fatty acid gradually increase during frying. Refined oil showed better performance than the crude oil due to the presence of impurities in the latter.

Key Words: Frying quality, Canola oil, Sunflower oil

Introduction

Sunflower (*Helianthus Annuus*, *Compositae* family) is known for its superior organoleptic characteristics and remarkable antioxidant properties. It contains vitamin A, D, and a sufficient amount of vitamin E [1].Commercially available sunflower varieties contain 39% to 49% oil in the seed. Sunflower accounts for about 14% of the world production of seed oils (6.9 million metric tons in 1985-1986) and about 7% of the oilcake and meal produced from oilseeds. Europe produces over 60% of the world's sunflowers.

Canola oil is extracted from *Brassica napus*, *(Brassicaceae family)*. The Canola Council of Canada states that canola oil is completely safe and is the "healthiest" of all commonly used cooking oils. It has well established heart health benefits and is recognized by many health professional organizations including American Dietetics Association, and American Heart Association [2]. Fatty acid composition in canola oil can be modified to reduce the content of erucic acid and to increase the level of oleic acid [3]. Canola oil contains both omega-6 and omega-3 fatty acids in a ratio of 2:1 and is second only to flax oil in omega-3 fatty acid. According to the Weston A. Price Foundation, Canola oil can have a number of health risks associated with it, as much of the omega-3 fatty acids are converted to transfats during modern refining processes and using it to cut out saturated fats can leave consumers vulnerable to other heart related problems through a lack of saturated fats in the diet [4].

Characteristics of oil change on heating. It is therefore important to note the oil's heat tolerance and to match the oil to its use in cooking [5, 6]. Frying is usually carried out at a temperature of 165±185 °C and is an efficient method of heat transfer that allows quick cooking and adds flavour to fried food [7].

Results and Discussion

Characterization of Oil

Physical parameters are used usually for the identification of oils. Normally more than one character is determined so that the identification can be made with more assurance since the oils vary in their properties. The composition is not constant it depends upon certain factors such as climatic conditions, nature of soil, type of plant and variety of edible oil.

Physical Characterization of Crude Canola and Sunflower Oil

Physical characterization of crude canola and sunflower oil samples have been made during a frying period of 4 days (Table-1). There is a gradual increase in viscosity, specific gravity and refractive index. The viscosity of crude canola oil increases from 83.3 to 113.5, specific gravity from 0.921 to 0.930 and refractive index from 1.475 to 1.48 during four days frying period. The viscosity of crude sunflower oil increases from 73.46 to 93.50, specific gravity from 0.925 to 0.927 and refractive index from 1.474 to 1.479 within four days frying.

*To whom all correspondence should be addressed.

Results show that viscosities of crude oil are always greater than the refined oil. Therefore crude oil may transmit more harmful effects on human health than refined oil.

Physical Characterization of Refined Canola and Sunflower Oil

Changes in Colour

Colour of oils depends upon the nature of colouring material like chlorophyll and carotene present in oil. Canola and sunflower oil samples (refined and crude) have pale yellow colour indicating the presence of colour pigments. Change in colour indicates the deterioration of oil due to oxidation. It is because of accumulation of nonvolatile decomposition products [8]. The colour of oils was darkened during frying. It darkened very fast at start but then the change in colour became slow and finally the colour was persistent.

Changes in Odour

Highly unsaturated oils, on long exposure to air and moisture are oxidized and develop rancid odour due to the formation of aldehyde and ketone. However the canola oil samples (refined and crude) contained no such odour. This may be due to the reason that canola oil has higher number of monounsaturated acids (oleic acid) in it. Some polyunsaturated acids are also present which act as antioxidants. Therefore it may be considered as better edible oil than others.

Changes in Specific Gravity

Specific gravity is considered as a good index of purity of oils. The increase in chain length of fatty acid present in oil tends to increase the specific gravity of oils. The specific gravity of oil samples increases during frying (Table-2). This may be interpreted due to the generation of dipoles on heating of oils which interact with each other and increase the specific gravity of oils.

The specific gravity of crude oil is higher than that of refined oil because of the impurities present in crude oil.

Changes in Refractive Index

During frying of refined canola and sunflower oil samples, the refractive indices increased because of hydrogenation of unsaturated oils on heating (Table-2). The literature value of refractive indices for sunflower oil, is 1.466 (before frying) and 1.478 (after frying) [8] which is inline with the present studies. Refractive index values reported for other oils are 1.466 for Almond kernel oil [10], 1.467 for Cucarbita foetidissima [11], 1.465 for Abutilon panossum [12], and 1.463 for Mango kernels [13] which appear to be almost same to the samples under investigation. The value of refractive index of crude oil is high due to the presence of impurities like dust particles.

Changes in Viscosity

The viscosities of refined canola and sunflower oil samples increase with increase in frying time (Table-2). Viscosity of oil depends upon the density. When density of oil increases its viscosity would increase. Viscosities of other oils are given as 41.98 centipoise for Bauhinia variegate oil [14], 42.8 centipoise for Kolongi Nigella sativa oil [15] and 59 centipoise for Molinga olifera oil [16]. The value of viscosity of crude oil is higher than that of refined oil because of the impurities in crude oil.

Chemical Analysis of Oil

A number of chemical tests have been performed which provide a base for partial determination of chemical composition of oils. All oil tests show some range of values. The chemical test applied to differentiate oils on the basis of chemical composition of various triglyceride values for chemical parameters of different oil samples.

Chemical Characterization of Crude Oils

Chemical properties of crude canola and sunflower oil samples during four days frying period are given in Table-3. There is a gradual increase in acid values of canola oil from 1.12 to 3.36. Saponification and ester values also increase during frying. Change in saponification values occurs from 193.55 to 385.25 during 4 consecutive days of frying. Ester values change from 192.43 to 380.59 during that period. In case of iodine values there is a gradual decrease during frying. It decreases from 115.23 to 102.79 within 4 days. Trend in change in peroxide values is unique. It first increases gradually reaches to maximum and then decreases irregularly. Peroxide values of canola oil samples increased from 3.05 to 5.42 after second day frying then decreased 5.25 and 4.75 after third and fourth day of frying respectively. Free fatty acid percentage in canola oil increases in a sequence from 0.87 to 1.16 before and after four days frying period. For sunflower oil, acid value increases from 0.81 to 0.89 during 4 days frying. Saponification value increases from 194.73 (before frying) to 298.88 (after frying). Ester value was 193.92 before frying and 297.99 after frying. Iodine value was 127 before frying and 111 after frying thus iodine value decreases after frying. Peroxide value was 6.5 before frying and 6.9 after frying. Fatty Acid Composition increases from 2 % (before frying) to 3.9 % (after frying).

Table-1 Physical Characterization of Crude Canola and Sunflower Oil Samples

Samples	Properties	Before frying	After 1 day frying	After 2 days frying	After 3 days frying	After 4 days frying
Canola oil	Viscosity (Centipoise)	83.3	87.2	95.4	106.7	113.5
	Specific Gravity	0.921	0.922	0.927	0.929	0.930
	Refractive Index	1.475	1.476	1.478	1.479	1.48
Sunflower oil	Viscosity (Centipoise)	73.46	77.06	82.32	87.25	93.50
	Specific Gravity	0.915	0.917	0.920	0.923	0.927
	Refractive Index	1.474	1.476	1.477	1.478	1.479

Table-2 Change in specific gravities, refractive indices and viscosities of refined canola and sunflower oil samples during frying

Samples	Change in Specific Gravity		Change in Refractive Index		Change in Viscosity	
	Before Frying	After Frying	Before Frying	After Frying	Before Frying	After Frying
Canola Oil A	0.910	0.916	1.465	1.47	79.2	107.1
Canola Oil B	0.911	0.917	1.465	1.47	78.9	106.9
Canola Oil C	0.911	0.917	1.466	1.471	79.7	108.7
Canola Oil D	0.911	0.917	1.465	1.472	79.9	106.8
Sunflower Oil A	0.914	0.925	1.464	1.47	69.43	75.1
Sunflower Oil B	0.913	0.924	1.463	1.469	68.52	74.25
Sunflower Oil C	0.915	0.926	1.464	1.47	69.68	74.68
Sunflower Oil D	0.913	0.927	1.464	1.47	70.1	74.9

Table-3: Chemical Characterization of Crude Canola and Sunflower Oil Samples during Frying

Samples	Properties	Before Frying	After 1 Day Frying	After 2 Days Frying	After 3 Days Frying	After 4 Days Frying
Canola oil	Acid Value	1.12	1.68	2.24	2.81	3.66
Canola oil	Saponification Value	193.55	232.08	297.07	313.15	384.25
Canola oil	Ester Value	192.43	230.40	294.83	310.34	380.59
Canola oil	Iodine Value	115.23	111.12	107.48	105.42	102.79
Canola oil	Peroxide Value	3.05	4.75	5.42	5.25	4.57
Canola oil	Free Fatty Acid %	0.87	0.93	0.99	1.10	1.16
Sunflower oil	Acid Value	0.81	0.83	0.85	0.87	0.89
Sunflower oil	Saponification Value	194.73	218.23	241.76	273.96	298.88
Sunflower oil	Ester Value	193.92	217.4	240.91	273.09	297.99
Sunflower oil	Iodine Value	127	121	117	114	111
Sunflower oil	Peroxide Value	6.5	7.3	7.6	7.2	6.9
Sunflower oil	Free Fatty Acid %	2.0	2.5	3.0	3.5	3.9

Chemical Characterization of Refined Oils

Changes in Acid Value

It is a measure of free fatty acid contents of oil. Moisture, high temperature and lipolytic enzymes result in an increase of acid value due to hydrolysis of glycerides into free fatty acid. The acid values of oils are sensitive to exposure to air. Changes in acid values for refined canola and sunflower oil samples were determined during frying (Table-4). These values increase during the course of frying. The acid value of refined oil is low as compared to crude oil because acids are removed during bleaching it with alkali.

Changes in Saponification value

Saponification values of refined canola and sunflower oil samples have been determined. The saponification values reported in literature are194.6 for Pinus pumila [17], 188-189 for Bran oil [18] and 188-192.79 for Sunflower oil [19] which are in accordance with our results. Change in saponification values after frying shows gradual increase with the passage of time (Table-4). The values of crude oil are high because some KOH is consumed in reaction with impurities.

Changes in Ester Value

Ester values of refined oil samples are given in (Table-4). They are also comparable with the literature values, i.e. 174 for Kolongi [15], 182.8 for Mathi [20] and 191 for Moringa olifera [16]. Ester values of crude oil are high because of the impurities present in it. Change in ester values on frying shows gradual increase with time.

Changes in Fatty Acid Composition of Oil

Change in free fatty acid values were determined for refined canola and sunflower cooking oils (Table-4). Although the initial free fatty acid values for the samples of the canola and sunflower oils were different yet at the end of the frying period (4 days), these values were found to be almost same in all the samples. Oxidative degradation may be the cause of increase in free fatty acid.

Changes in Peroxide Value

The peroxide value is one of the most important chemical constant as it can be used to determine degree of deterioration of oils. Peroxide values of refined canola and sunflower oil samples are given in (Table-5).

Table-4: Change in Acid Values, saponification values, ester values and free acid percentages in refined canola and sunflower oil samples during frying.

Samples	Change in Acid Value		Change in Saponification Value		Change in Ester Value		Change in Free Fatty Acid %	
	Before Frying	After Frying	Before Frying	After Frying	Before Frying	After Frying	Before Frying	After Frying
Canola Oil A	0.54	0.83	175.83	342.93	175.29	342.1	0.22	0.49
Canola Oil B	0.55	0.84	175.49	342.79	174.94	341.95	0.15	0.42
Canola Oil C	0.56	0.85	176.89	341.42	176.33	340.57	0.17	0.45
Canola Oil D	0.56	0.84	176.71	342.43	176.15	341.59	0.19	0.42
Sunflower Oil A	0.5	0.84	190.7	305.74	190.24	304.9	0.18	0.4
Sunflower Oil B	0.52	0.86	191.7	306.1	191.18	305.24	0.17	0.42
Sunflower Oil C	0.51	0.85	190.78	305.9	190.28	305.05	0.19	0.44
Sunflower Oil D	0.5	0.86	192	312.19	191.5	311.33	0.20	0.45

Table-5: Change in peroxide values of refined canola and sunflower oil samples during frying.

Samples	Before Frying	After 1 Day Frying	After 2 Days Frying	After 3 Days Frying	After 4 Days Frying	Mean	S.D	S.E
Canola Oil A	2.14	3.76	4.67	3.54	2.76	3.374	0.867	0.387
Canola Oil B	2.25	3.76	4.75	3.92	2.25	3.366	1.010	0.451
Canola Oil C	2.15	3.65	4.80	3.83	2.55	3.396	0.948	0.423
Canola Oil D	2.42	3.75	4.68	3.58	2.25	3.336	0.901	0.402
Sunflower Oil A	1.0	1.13	1.15	1.12	1.11	1.102	0.052	0.023
Sunflower Oil B	0.9	1.12	1.14	1.11	1.09	1.072	0.087	0.039
Sunflower Oil C	1.0	1.12	1.13	1.1	1.09	1.088	0.046	0.020
Sunflower Oil D	1.1	1.13	1.15	1.11	1.01	1.11	0.048	0.021

Peroxide value of all the refined canola oil samples first increases reach to its peak level and then decreases gradually. This may be interpreted due to formation of peroxide radicals by increasing temperature. When certain extent is reached re-association of radicals takes place as is obvious with gradual decrease in peroxide value.

Changes in Iodine Value

There is gradual decrease in iodine values of all oil samples during frying (Table-6). Iodine values show the change during four consecutive days of frying. Various reactions take place at high temperatures in which double bond is broken. The change in the iodine value was significant after the first day of frying, indicating shorter inductions periods. Iodine values reported in literature 49.81 for Palm oil [21] and 37.46 for Furfural almaciga [22]. The calculated iodine value of canola oil before and after 4 day frying, in literature is 109.9 to 102.39 which are related to oil samples used for investigation [8]. The iodine value of crude oil is high because some iodine is consumed in reaction with impurities.

Experimental

Canola and sunflower oils (in refined and crude forms) of different companies were purchased from local market and were labeled as canola oils A, B, C and D and sunflower oils A, B, C and D. Fresh China potatoes were purchased from local vegetable market. All chemicals and solvents used were purchased from Merck laboratories (Germany).

Viscosity was determined by Ostwald viscometer, while density was determined by pycnometer. For refractive index, refractomter of Bellingham &Stanley Limited (A 82307 England) was used.

Canola and sunflower oils (one litre for each sample) were used to determine the frying quality. Temperature during frying was kept at 165±5^{o}C. Potato chips were fried for 30 minutes intervals. At start of every day, oil was heated for one hour at 165±5^{o}C before the commencement of frying. Each day, the oil was heated for 6 h in total, with 10 frying cycles performed. The experiments were continued for 4 days. This amounted to a total of 40 frying cycles performed for each batch of oil. For analysis, samples were taken, after keeping the oil overnight at 20^{o}C. First sample was taken before frying as reference. All the samples were analyzed under the same conditions.

Table-6: Change in Iodine Value of Refined Canola and Sunflower Oil Samples during Frying

Samples	Before Frying	After 1Day Frying	After 2 Days Frying	After 3 Days Frying	After 4 Days Frying	Mean	S.D	S.E
Canola Oil A	108.12	106.53	103.79	100.67	97.2	103.26	3.950	1.763
Canola Oil B	108.74	105.43	103.89	101.52	96.78	103.27	4.032	1.801
Canola Oil C	107.9	105.11	103.23	100.4	98.29	102.99	3.389	1.513
Canola Oil D	107.7	105.23	103.4	100.9	98.6	103.17	3.189	1.424
Sunflower Oil A	106.46	100	97	93	90	97.29	5.710	2.549
Sunflower Oil B	102.9	97	93	90	88	94.18	5.311	2.371
Sunflower Oil C	107.57	101	99	95	91	98.71	5.604	2.501
Sunflower Oil D	108.45	102	99	96	92	99.49	5.569	2.486

The physical and chemical characterization of commercial oil samples (before and after frying) was carried out by using standard methods [23-26]. In physical characterization colour, odour, specific gravity, refractive index and viscosity were determined. While in chemical parameters acid value, saponification value, ester value, peroxide value, iodine value and FFA composition were determined. All the methods used for the determination were A.O.C.S. recommended.

Conclusions

Comparison of frying oil samples with their control counterparts shows that there was a gradual increase in refractive index, viscosity, acid value and colour with time of frying. Iodine value decreased significantly with time of frying. Peroxide value first increased up to 12 h of frying and then decreased. Colour change and viscosity increase with increase in frying time. Amount of free fatty acid gradually increase during frying. Refined oil showed better performance than the crude oil due to the presence of impurities in the latter.

References

1. M. Murillo, Z. Benzo, E. Marcano, C. Gomez, A. Garaboto and C. Marin, *Journal of Analytical Atomic Spectrometry*, **14**, 815 (1999).
2. D. M. Lorgerill and P. Salen, *Public Health Nutrition.* **1**, 18 (2006).
3. C. Stewart, *Blackwell Publishing*, Oxoford (2002).
4. M. I. Gurr, *Bulletin of the International Dairy Federation*, **166**, 5 (1983).
5. I. Orna, *The Environmental Magazine*, **4**, 2 (2003).
6. R. F. M. Ali, *Electronic Journal Environmental, Agricultural and Food Chemistry*, **9**, 396 (2010).
7. C. Gertz, *European Journal of Lipid Science and Technology*, **102**, 505 (2001).
8. S. M. Abdulkarim, K. Long, O.M. Lai, S. K. S. Muhammad and H. M. Ghazali, *Food Chemistry*, **105**, 1382 (2007).
9. D. Goburdhun, Jhaumeer-Laullo and R. Musruck, *International Food Science Nutrition*, **52**, 31 (2001).
10. G. Cocks, F. L. Rede, *Journal of the American oil Chemists Society*, **68**, 43 (1996).
11. S. Vascocellos, L. Wen-Hisung, Y. C. Chi, *Journal of the American Oil Chemists' Society*, **10**, 56 (1980).
12. H. Kitter, M. Krishn, K. Subash and Mukul *Journal of the American Oil Chemists Society*, **66**, 63 (1982).
13. S. Asia, *Journal of Agricultural Food Chemistry*, **18**, 265 (1986).
14. F. Perveen, *Journal of Agricultural Food Chemistry*, **19**, 6485 (1986).
15. T. Mamuna, *Journal of Agricultural Food Chemistry*, **19**, 6485, (1989).
16. R. Ghazala, *Extraction and characterization of oil from Molingo Oleifera seeds.* M.Sc. Thesis, Department of Chemistry, University of Agriculture, Faisalabad Pakistan (1991).
17. T. Truchiya and B. Okoubo, *Journal of the American Oil Chemists' Society*, **9**, 385 (1961).
18. S. Daniel, F. A. Norris, A. J. Stirtun, Alexander and K. F. Matil, *International science publishers John Willey and Sons New York*, **22**, 234 (1964).
19. A. M. Hashmi, *Characterization and evaluation of sunflower oil.* M.Sc. Thesis, Department of Food Technology, University of Agriculture, Faisalabad Pakistan (1968).
20. M. Yousaf, *Pakistan Journal of Weed Science Research*, **8**, 35 *(*1990).
21. N. Aini, H. Hanirah and T. S. Tang, *Elaeis*, **7**, 64 (1996).
22. E. C. Fernandez A. M. D. Duldulo, *Journal of the American Oil Chemists' Society*, **48**, 238, (1995).
23. A. O. C. S Method Ca 5a-40. In: Official methods and recommended practices of the American Oil Chemists' Society. Champaign, IL, USA. (1989).
24. T. Ahmad, S. Atta, A. Zeb, S. Gul, *Journal of the Chemical Society of Pakistan*, **33**, 343 (2011).
25. H. Ahsan, A. B. Munshi, S. Shaukat, F. A. Ansari and M. F. *Journal of the Chemical Society of Pakistan*, **33**, 174 (2011).
26. Z. Iqbal, M. Akhtar, T. M. Qureshi, J. Akhter, R. Ahmad, *Journal of the Chemical Society of Pakistan*, **33**, 183 (2011).