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Thermal and physico-chemical properties of ghee used for frying

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Abstract
Ghee, clarified butter, is an ancient Indian product is the most widely consumed and popular milk product in the Asian, Middle-east and African households. Owing to the characteristic nutty flavour that matches the requirement of fried products, ghee is considered a better cooking /frying medium compared to other animal fats. The objective of this study, thus, was to evaluate the thermal and chemical properties of ghee at different temperatures varying from room temperature to frying temperatures, which could be utilised in food industry for different process control operations. Thermal conductivity was found to increase with increase in temperature from 0.449 to 8.34 W/mK. Similar trend was observed for specific heat and it was found to increase from 0.491 to 0.835 J/KgK. Thermal stability of ghee after three consecutive frying cycles was done. Due to oxidation and hydrolysis taking place during frying process, a significant increase in peroxide value (from 6.34 to 66.18 meqO_2/kgfat) and free fatty acid content (from 1.12 to 1.46% Oleic acid) was observed in the ghee samples.

Keywords: Ghee, thermal conductivity, specific heat, peroxide value, free fatty acids

Introduction

Ghee, clarified butter, is an ancient Indian product dating back to 1500 BC and is derived from the sanskrit word *Ghrita* (Sserunjogi *et al*., 1998) [1]. It is also called by other names including clarified butter (Kumar and Singhal, 1992) [9], butterfat (Singh and Ram, 1978) [10], Indian butteroil (IDF, 1996) [8], butteroil, anhydrous milkfat (Bajwa and Kaur, 1995) [11] and Indian ghee (Kumar and Singhal, 1992) [9]. It is the most widely consumed and popular milk product in the Asian, Miidle-east and African households. Being the largest producer of milk in the world, ghee is the second largest dairy product produced in Indian market as premium edible fat (Hazra *et al*., 2017) [3]. Prepared mainly by indigenous methods, ghee is solely derived from milk or curd or from desi (cooking) butter or from cream without addition of any preservative or coloring matter (FSSR, 2011) [18]. Owing to the popularity of the product, it is also produced at large scale by commercial dairies in continuous process. The process of ghee production involves direct heat clarification of cream or by first converting cream into butter followed by heat dessication. Principally, ghee is manufactured by four methods *viz*. indigenous milk butter method, direct cream method, creamery butter method and pre-stratification method. At household level, fermentation method is followed, which involves fermenting cream with lactobacilli followed by addition of equal amount of chilled water to obtain fat globules, which are then heat clarified to obtain ghee. Commercially, butter is used and heat dessication is done in a double jacketed stainless steel open steam kettle which is hemispherical in shape.

In the Indian diet, ghee is the major contributor to the nourishment of people of all age groups. It contains sufficient quantity of essential fatty acids (linoleic and arachidonic acid) and fat soluble vitamins (A, D, E, K) (Kumar *et al*., 2010, Chand *et al*., 1986, Rangappa *et al*., 1974) [5, 6, 7] along with the characteristic rich buttery flavour which is the major criterion for its wide acceptability.

Frying is the most common, convenient and traditional technique of food preparation that involves cooking the food in frying oil/fat at higher temperature ranging from 120-170 °C. It is simply a dehydration process in which first evaporation of moisture takes place from the food product forming capillaries, which are filled with the frying medium. The chemical reactions that occur during frying (Maillard browning, caramelisation, denaturation of proteins, gelatinisation of starch) imparts characteristic textural, colour and flavour attributes to the fried product leading to enhanced acceptability. In addition to the sensory attributes, high temperature processing also is beneficial in terms of reduction in bacterial count.

Due to removal of moisture from the product, reduction in water activity takes place (Farkas *et al*., 1996) [14]. These two aspects enhance the shelf life of fried products. Frying medium has the most significant role in frying by acting as the heat transfer medium. Use of various oils and fats and their combination as frying medium has been reported in literature (Serjouie *et al*., 2010) [16]. Owing to the characteristic nutty flavour that matches the requirement of fried products, ghee is considered a better cooking medium compared to other animal fats.

Deep fat frying is done at high temperature of 140-150 °C which involves heat and mass transfer as the basic unit operation, knowledge of the thermal properties of the frying medium is important. The basic thermal properties include thermla conductivity, thermal diffusivity, specific heat and thermal resistivity. The physico-chemical properties of ghee and the thermal stability under conventional heating process has been studied (Patel *et al*., 2014, Rahila *et al*., 2018, Lamsal *et al*., 2020) [12, 13, 15]. However thermal properties of ghee are yet to be reported. The objective of this study, thus, is to evaluate the thermal properties of ghee at different temperatures varying from room temperature to frying temperatures, which can be utilized in food industry for different process control operations. Also the physico-chemical properties of ghee were studied to determine the effect of frying cycles on the peroxide value and free fatty acid content of ghee.

Materials and Methods

This section discusses in detail the experimental techniques and equipments used to fulfill the objective of the study. It includes procurement of ghee, sunflower oil, measurement of thermal properties of ghee and recording the experimental data.

Ghee sample was procured from local market. The common ghee brand (Uttam, AGMARK Desi Ghee, manufactured by Supreme Agrofoods Pvt. Ltd. (unitII), Ludhiana, Punjab, India) used in household for consumption and frying purposes was purchased for analysis. Calculation of thermal properties was done at different temperatures including room temperature, melting temperature of ghee, and frying temperatures i.e. 110, 120, 130, 140 and 150 °C. Temperature of ghee was maintained (Fig. 1) by a water bath was maintained by keeping beaker filled with water on magnetic hot plate (RET Control Visc, IKA, Germany) as shown in fig.

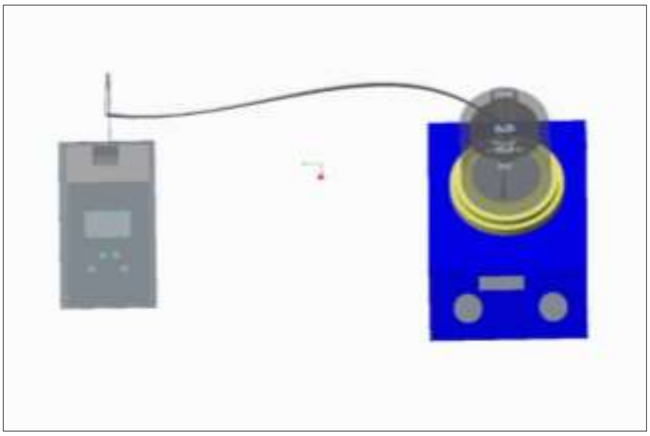

Fig 1: Setup for maintaining oil/ghee temperature during measurement

Determination of thermal properties

The thermal properties including thermal conductivity and specific heat were calculated at different temperatures which are generally used in frying. All the reading were taken in triplicates and average values have been reported. All the four properties were analysed using KD2 PRO thermal properties analyzer (Fig. 2) (Model-KD2 Pro Thermal Properties Analyzer, Decagon Devices, Pullman, Washington, USA), which is known to meet the ASTM D5334 standards. The principle behind its working for measurement of thermal properties is transient line heat source method, which is based on the physical model of an infinite line source with constant value of power per meter. The thermal properties analyzer provides 4 different probes for analysis of different samples *viz*. KS-1, TR-1, SH-1 & RK-1. For high viscosity oils like sunflower oil and ghee, KS-1 is suggested according to the user manual of the analyzer. The KS-1 sensor, which is a 6 cm long 1.3 mm diameter single needle measures thermal conductivity and resistivity. The sensor allows very small amount of heat to be applied to needle to avoid free convection currents in liquid samples. The dual needle SH-1 sensor is used for thermal diffusivity and thermal resistivity. The specifications of both the probes are given in table.

Table 1: The specifications of the probes

S.No.	SH-1 Probe	KS-1 Probe
Size	1.3 mm diameter x 3 cm long, 6 mm spacing	1.3 mm diameter x 6 cm long
Range	0.02 to 2.00 W/m∗K (thermal conductivity) 50 to 5,000 °C ∗cm/W (thermal resistivity) 0.1 to 1.0 mm^2/s (diffusivity) 0.5 to 4.0 mJ/m^3K (volumetric specific heat)	0.02 to 2.00 W/m∗K) (thermal conductivity) 50 to 5000 °C ∗cm/W (thermal resistivity)
Accuracy	(Conductivity) ±10% from 0.2 to 2 W/m∗K ±0.01 (Diffusivity) ±10% at conductivities above 0.1 W/m∗K (Volumetric Specific Heat) ±10% at conductivities above 0.1 W/m∗K	(Conductivity): ±5% from 0.2 to 2 W/m∗K ±0.01 W/m∗K from 0.02 to 0.2 W/m∗K
Cable length	0.8 m	0.8 m

The temperature profiling is based on the following equation

$$T(t,r) = \left(\frac{Q}{4\pi k}\right) Ei \left(\frac{r2}{4at}\right)$$

Where,

Q is the power per unit length, in $W{\cdot}m^{-1}$

k is the thermal conductivity of the sample, in $W{\cdot}m^{-1}{\cdot}K^{-1}$

Ei is the exponential integral, a transcendent mathematical function

r is the radial distance to the line source
a is the thermal diffusivity, in $m^2 \cdot s^{-1}$
t is the amount of time that has passed since heating has started, in s

The values of Ei could be determined by the method given by Abramowitz and Stegun, 1972. The theory of the working principle of thermal properties analyzer was also discussed in details by Bristow *et al.*, 1994 [19].

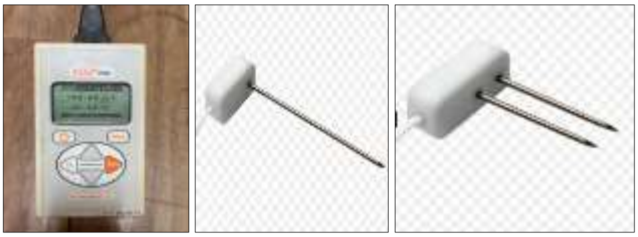

Fig 2: KD2 PRO thermal properties analyzer Peroxide Value

Peroxide Value

Peroxides (R-OOH) are the known to be the primary reaction products produced during the initiation of the oxidation process. Peroxide value of *Ghee* samples were determined by the method as described in IS: 3508 (1966), which is an iodometric method, based on the principle that peroxides can liberate iodine from potassium iodide.

About 5 g of molten Ghee was taken in a 250 ml glass stoppered Erlenmeyer flask to which 30 ml of mixed solvent (2:1 ratio of glacial acetic acid and chloroform) was added to dissolve the fat. Saturated potassium iodide (0.5 ml) was added to this mixture and left undisturbed for a minute. The mixture was heated in a boiling water bath for 30 seconds from the time of vapour formation in the flask. The flask was then cooled under running tap water condense the vapour, followed by addition of 30 ml of distilled water and 0.5 ml of 1% starch indicator resulting in the appearance of a dark blue/brown colour. The mixture was titrated against 0.002 N sodium thiosulphate ($Na_2S_2O_3$) until the disappearance of colour. A simultaneous blank sample was titrated with only the reagents as above. The following equation was then used to estimate the PV of the Ghee sample in meq of O_2 / kg of fat

$$PV = (S-B) \times N \times 1000 \times 8 / W \quad (3.1)$$

Where,
S = Volume in ml of Na2S2O3 required in titration of sample
B = Volume in ml of Na2S2O3 required in titration of blank
N = Exact normality of Na2S2O3 solution
W = Weight in g of sample

3.1.2.2 Free Fatty Acid Value

Free fatty acids are usually considered as an indicator of hydrolytic rancidity but some oxidative changes also may result in FFA. The FFA content of the Ghee samples were determined by the titration method described in IS: 3508 (1966).

About 5 g of molten Ghee sample was taken in 250 ml conical flask along with 50 ml of freshly neutralized 95% ethanol and 1 ml of phenolphthalein indicator. The mixture was heated for about 5 min in a boiling water bath and titrated while hot against standard 0.1 N sodium hydroxide solution with vigorously shaking. The FFA content of the sample, expressed as % oleic acid, was then determined as

$$FFA\ (\%\ oleic\ acid) = 2.82 \times V/W \quad (3.2)$$

Where,
V = Volume in ml of 0.1 N sodium hydroxide used
W = Weight of the Ghee sample in g

Results and Discussion

This section discusses in detail the thermal properties of ghee and sunflower oil samples obtained from experimentation.

Thermal conductivity of ghee

Thermal conductivity of any material is its ability to conduct heat, and is denoted by 'k'. Thermal conductivity of ghee samples as obtained from the probe of KD2 pro thermal properties analyzer inserted into the ghee sample at different temperatures is as shown in figure. As can be seen from the graph there is an increase in the thermal conductivity of ghee with increasing temperature. Also from the graph (Fig. 3), it can be seen that there is sharp increase initially which could be attributed to the melting of fat because at room temperature, ghee is in solid form and starts to melt only after 40-42 °C. The results coincided with Goncalves *et al.*, 2017 [20] who studied the thermal conductivity of dairy products as influenced by temperature and apparent viscosity. Various researchers have worked on the trend of thermal conductivity and found that there is a linear increase in thermal conductivity of dairy products with increasing temperature and increasing water content (Reddy and Datta, 1994; Tavman and Tavman, 1999) [21, 22]. Goncalves *et al.*, 2017 [20] reported an increase in thermal conductivity with increase in temperature values for all the studied dairy products.

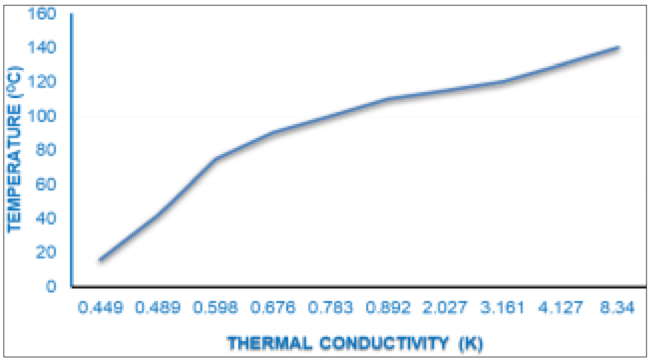

Fig.3: Thermal conductivity vs. temperature curve for ghee

Specific heat values of ghee

Specific heat of any substance is the quantity of heat required to raise the temperature of a body by one degree to that required to raise the temperature of an equal mass of water, denoted in SI units as J/kgK. As can be seen in figure (Fig. 4) the specific heat values are showing an increasing trend with increasing temperature. Hammer and Johnson, 1913 studied the specific heat of milk and milk products in detail and have found a similar trend in high fat products. The authors observed that in case of butter with increase in temperature, the values of specific heat also increased. This increase in specific heat with temperature could be attributed to the increase in average kinetic energy of the molecules with increasing temperature which causes collisions to occur. The collisions cause rotations in the molecules. These rotations gives internal energy to the molecules which in turn increases the specific heat of the product.

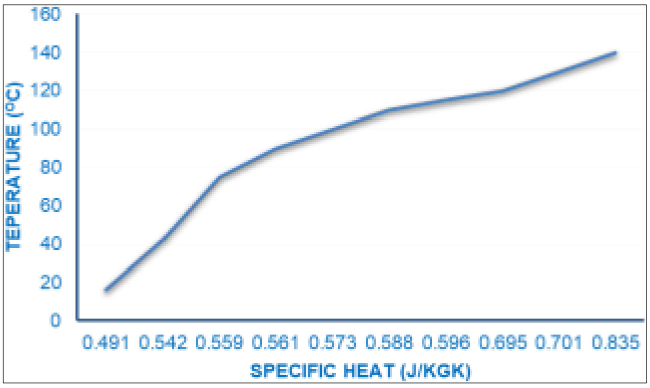

Fig. 4: Specific heat capacity vs. temperature curve for ghee

Table 2: Thermal properties of ghee

Temperature (°C)	Thermal conductivity (W/mK)	Specific heat (J/kgK)
16	0.449	0.491
42	0.489	0.542
75	0.598	0.559
90	0.676	0.561
100	0.783	0.573
110	0.892	0.588
115	2.027	0.596
120	3.161	0.695
130	4.127	0.701
140	8.34	0.835

Evaluation of chemical properties of ghee after frying

Ghee samples were drawn from the lot after first, second and third frying cycles. Each ghee sample was individually analyzed for free fatty acid and peroxide value to assess the effect of frying on the thermal stability of ghee.

4.8.1 Free fatty acid (FFA)

Presence of free fatty acids (FFA) in *Ghee* is considered as an indication of hydrolytic rancidity, though it is also postulated that some free fatty acids may appear in the oils as a result of oxidative breakdown pathways. During frying, the moisture released by the fried product combined with the high temperature trigger the hydrolytic breakdown of fat constituents (Choe and Min, 2009) [23]. Once generated, the amount of FFAs in the frying medium increase with each cycle and its oxidative product lead to development of off flavour. The free fatty acid value of ghee is presented in fig 4.6. As can be observed from the data (Table 3), there was no significant change in the FFA values of ghee. However there is increase in the acidity after three cycles of frying (Fig. 5). It could be attributed to the hydrolysis reactions taking place during frying which result in increased acid value in the subsequent samples of ghee obtained upon consequent frying.

Table 3: Free fatty acid values of ghee after frying cycles

Frying Cycle	Free Fatty acid (%Oleic acid)
0	1.12
1	1.29
2	1.34
3	1.46

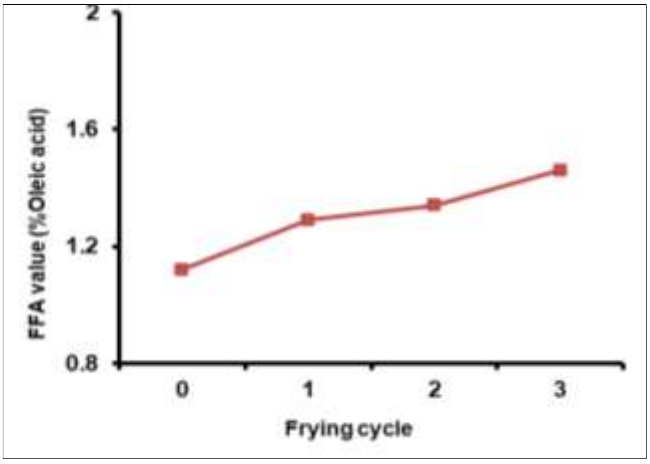

Fig. 5: Free Fatty Acid distribution of ghee samples after three frying cycles

Peroxide value

Peroxides (R-OOH) are known to be the primary reaction products of the fat oxidation and are formed during the initial stages of oxidation (Choe and Min, 2009) [23]. Hence, peroxide value (PV) is widely considered as an indicator of the progress of lipid oxidation. The mean value of peroxide value of *Ghee* samples subjected to conventional frying process across three consequent frying cycles is presented in Fig. 6, the average initial value of peroxide value in ghee was 6.34 meqO_2/kg fat. As frying progressed, there was significant increase in the peroxide values of ghee as observed for three frying cycles (Table 4). Lipid oxidation is one of the major chemical changes that take place during frying, so was seen in the samples of ghee taken after frying. After first, second and third frying cycle, the peroxide values obtained were 31.91, 58.41 and 66.18 meqO_2/kg fat, respectively. From the graph (Fig 4.7), it can be seen that during the initial frying cycles, there is rapid increase in the peroxide value and the increase was much after the third cycle.

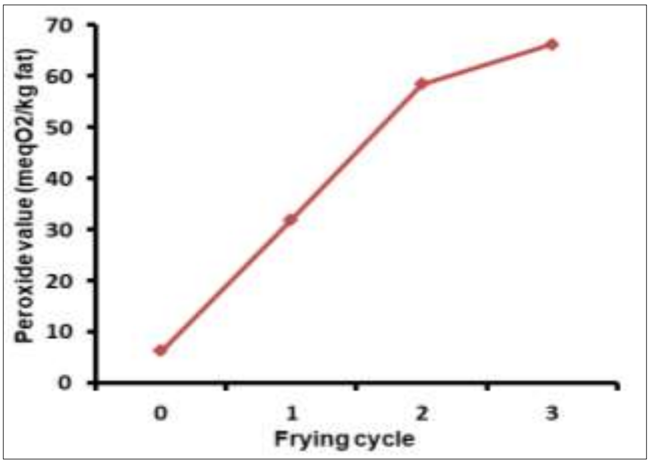

Fig 6: Peroxide value distribution of ghee samples after three frying cycles

Table: 4: Peroxide values of ghee after frying cycles

Frying Cycle	Peroxide Value (meqO_2/kgfat)
0	6.34
1	31.91
2	58.41
3	66.18

Conclusion
Since some amount of fat is absorbed into the product during the frying process, the quality of the frying medium influences the fried product quality and the frying process in terms of its heat transfer. Ghee is considered a supreme frying medium due to the characteristic flavour which it imparts to the fried product. Thermal properties of ghee were observed and thermal conductivity was found to increase with increase in temperature from 0.449 to 8.34 W/mK. Similar trend was observed for specific heat and it was found to increase from 0.491 to 0.835 J/KgK. Thermal stability of ghee after three consecutive frying cycles was done. Due to oxidation and hydrolysis taking place during frying process, a significant increase in peroxide value (from 6.34 to 66.18 meqO_2/kgfat) and free fatty acid content (from 1.12 to 1.46% Oleic acid) was observed in the ghee samples.

References

1. Sserunjogi ML, Abrahamsen RK, Narvhus J. A review paper: current knowledge of ghee and related products. International Dairy Journal. 1998;8(8):677-688.
2. YR D, Kawtikwar PS, Sakarkar DM. Evaluation of physicochemical properties of cow ghee before and after hydrogenation. Evaluation. 2012;4(1):185-189.
3. Hazra T, Sharma V, Saha P, Pratapsinh PM. Physico-chemical properties analysis based approaches to ascertain the purity of ghee-a mini review. Int J Sci Environ Technol. 2017;6:899-907.
4. Bector BS, Abichandani H, Sarma SC. Shelf lifeof ghee manufactured in continuous ghee making system. Indian Journal of Dairy Science. 1996;49(6):398-405.
5. Kumar M, Sharma V, Lal D, Kumar A, Seth R. A comparison of the physico-chemical properties of low-cholesterol ghee with standard ghee from cow and buffalo creams. International journal of dairy technology. 2010;63(2):252-255.
6. Chand R, Sree Kumar S, Srinivasan RA, Batish VK, Chander H. Influence of lactic acid bacteria on oxidative stability of ghee. Milchwissenschaft. 1986;41:335-336.
7. Rangappa KS, Achaya KT. Indian Dairy Products. Mysore City, India: Asia Publishing House; c1974.
8. IDF. Oxidized sterols. Bulletin. InternationalDairy Federation, Brussels, Belgium. 1996;315:52-58.
9. Kumar N, Singhal OP. E§ect of processing condi-tions on the oxidation of cholesterol in ghee. Journal of the Science of Food and Agriculture. 1992;58:267-273
10. Singh S, Ram BP. E§ect of ripening of cream, manufacturing temperature and packaging materials on fla-vour and keeping quality of ghee. Journal of Food Science and πehnology. 1978;15:142-145.
11. Bajwa U, Kaur A E§ect of ghee (butteroil) residue and additives on physical and sensory characteristics of cookies. Chemie, Mikrobiologie, πechnologie der ∏ ebensmittel. 1995;17(5/6):151-155.
12. Patel S, Shende S, Arora S, Singh RRB, Rastogi S, Rawat AKS. Antioxidant potential of herbs and spices during deep frying of ghee. International Journal of Dairy Technology. 2014;67:365-372.
13. Rahila MP, Surendra Nath B, Laxmana Naik N, Pushpadass HA, Manjunatha M, Franklin MEE. Rosemary (*Rosmarinus officinalis* Linn.) extract: A source of natural antioxidants for imparting autoxidative and thermal stability to ghee. Journal of Food Processing and Preservation. 2018;42(2):13443.
14. Farkas BE, Singh RP, Rumsey TR. Modeling heat and mass transfer in immersion frying, model development. Journal of food Engineering. 1996;29(2):211-226.
15. Lamsal B, Bhandari TR, Panta P, Saiter JM, Pokhrel S, Katuwal TB, *et al*. Preparation and physicochemical characterization of ghee and mūrcchita ghṛta. Journal of Ayurveda and integrative medicine. 2020;11(3):256-260.
16. Serjouie A, Tan CP, Mirhosseini H, Bin Che Man Y. Effect of vegetable based oil blends on physicochemical properties of oils during deep-fat frying. American Journal of Food and Technology. 2010;5(5):310-323.
17. Grompone MA. Sunflower oil. Bailey's industrial oil and fat products; c2005.
18. FSSR. File No.1 94/FSSAI/SP/(Labelling). Food Safety and Standards Authority of India (Ministry of Health and Family Welfare). FDA Bhavan, Kotla Road New Delhi-110002; c2011.
19. Bristow KL, White RD, Kluitenberg GJ. Comparison of single and dual probes for measuring soil thermal properties with transient heating. Soil Research. 1994;32(3):447-464.
20. Gonçalves AL, Pires JC, Simões M. A review on the use of microalgal consortia for wastewater treatment. Algal Research. 2017 Jun 1;24:403-415.
21. Fisher GJ, Talwar HS, Xiao JH, Datta SC, Reddy AP, Gaub MP, *et al*. Immunological identification and functional quantitation of retinoic acid and retinoid X receptor proteins in human skin. Journal of Biological Chemistry. 1994 Aug 12;269(32):20629-20635.
22. Tavman IH, Tavman S. Measurement of thermal conductivity of dairy products. Journal of Food Engineering. 1999 Aug 1;41(2):109-114.
23. Choe E, Min DB. Mechanisms of antioxidants in the oxidation of foods. Comprehensive reviews in food science and food safety. 2009 Oct;8(4):345-358.