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The Pharma Innovation

ISSN (E): 2277-7695
ISSN (P): 2349-8242
NAAS Rating: 5.23
TPI 2022; 11(10): 1274-1282

www.thepharmajournal.com
Received: 18-07-2022
Accepted: 26-08-2022

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Monitoring of changes in quality parameters during thermal treatment of ghee

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Abstract
Thermal treatment of fat/oil like frying and heating leads to various degradation reactions during the process depending upon product and process parameters. The concentration of these degradation products over the time exceeds threshold and making the product and oil unsuitable and it will result into health hazard for human. However, these changes are undetectable in time in absence of laboratory setup. Research work was undertaken to determine various chemical, physical and electrical properties of ghee and to develop sensing system for rapid determination of quality of ghee. Capacitive sensing system was designed and developed by simulating capacitive plate area and plate gap for parallel plate type electrode. In this study ghee was used from that 10 samples were prepared by heating upto 40 h at 175°C. Free fatty acids (FFA), peroxide value (PV), total polar compounds (TPC), viscosity and capacitance were analyzed. Capacitance showed correlation coefficient $r \geq 0.95$ with FFA, PV and TPC and $r \geq 0.89$ with viscosity for samples of heated ghee. Capacitive sensing technique showed positive significant correlation with chemical quality indicator and viscosity of ghee and can be useful to check deterioration of oil due to heating and frying.

Keywords: Ghee, total polar compounds, viscosity, capacitance, correlation coefficient

Introduction

In now days fast food become popular among youth as a part of diet. In restaurants and home food cooked by number of different practices among them frying is the popular, favourable and widely used practice of cooking food because it makes food very attractive and tasty. It is also rapid, best and simplest method of cooking because food item can be fried by deeping into the hot oil for a couple of minutes. Deep fat frying is the process of cooking food in oil at a temperature of 150 to 190 °C (Aydınkaptan and Mazı, 2017) [3]. Fried foods have attractive flavour, golden brown outer surface and crispy texture when it was fried with proper conditions. Frying oil can be different types of fatty materials but vegetable oils are used in routine frying practices due to its nutritional importance. Vegetable oil contain fat soluble vitamins and essential fatty acids and serves as an energy source (Choudhary and Grover, 2013; Nayak *et al*., 2016) [7, 22].

Deep frying also involves heat and mass transfers during frying operation (Kita, 2002; Weisshaar, 2014) [18, 35]. During frying process, air and moisture came in contact with high temperature of oil and atmospheric oxygen dissolves particularly during cooling (Zribi *et al*., 2013, 2014) [37, 38] which leads to complex chemical reaction called deteriorative reaction like oxidation, hydrolysis, isomerisation, cyclization and thermal alteration and forms polymers which are hazardous to health (Choe and Min, 2007; Debnath *et al*., 2009; Ghidurus *et al*., 2010; Wang *et al*., 2013; Kalogianni & Karastogiannidou, 2015) [6, 8, 12, 15, 34]. The oil undergoes many chemical reactions which depends on the frying conditions and leads to formation of undesirable compounds and reduces PUFA content of oil (Velasco *et al*., 2009; Zribi *et al*., 2014; Borges *et al*., 2015) [5, 33, 38]. These reactions results into formation of volatile and non-volatile compound. Volatile compounds evaporate with vapour and non-volatile compound remain in the oil which leads to undesirable changes in oil and quality of fried food. Rate of degradation of oils are affected by number of factors like food type, composition moisture, temperature, capacity of fryer etc (Gertz, 2000) [10]. Extensive study of physicochemical changes occurs during deep fat frying was carried out by researchers for different types oils (Siddique *et al*., 2010; Serjouie *et al*., 2010; Rehab and El Anany, 2012; Mishra and Sharma, 2014; Zhang *et al*., 2016) [21, 27, 30, 31, 36]. The effects due to deterioration of frying oil leads to loss of weight, suppression of growth, cellular damage of the liver, thymus, epididymites, etc.

Are happening when the highly oxidized and heated oils are fed to laboratory animals (Lizhi *et al.* 2010) [19]. As human health point of view it is very important to test the oil quality by determining the various chemical and physical indices.

Routine practices in homes, restaurants, food service and cafeteria of determine oil quality includes visual inspection, smoking of oil, fried products taste, colour change, foaming etc. These methods are not suitable to judge frying oil quality because of their subjective nature. This parameter has drawback that it proves oil as degraded quality only when frying oil already degraded (Khaled *et al*., 2015; Gertz, 2000) [10, 16]. Quality of oil used for frying can be determined by some chemical parameter of oil like free fatty acids (FFA), Peroxide value (PV), p-anisidine value, total polar compounds (TPC) etc. Among these chemical quality indicators, total polar compounds considered as important parameter to detect overall quality of oil used for frying and heating (Farhoosh, and Tavassoli-Kafrani, 2010) [9]. Viscosity of oil can be used to predict oil quality but sometimes it not decisive (Khaled *et al*., 2015) [16]. Various methods have been developed like chemosensory system, fourier transforms infrared (FTIR), chromatography etc. but, complication, costs and time of measurement are drawback of these methods.

Food products frying in oil or ghee is most common in India. Generally, vegetable oil is used as frying medium but for preparation of particular traditional sweets like gulabjamun, jalebi etc., ghee is used. Degradation of vitamins, β- carotene, antioxidants, saturated and unsaturated fatty acids in edible oils and desi ghee occur during thermal treatment because it is very sensitive to temperature and it causes the degradation of above said nutritional ingredients. Research work was undertaken to determine various chemical, physical and electrical properties during thermal treatment of ghee. The generated data would be helpful in designing of suitable instrument for non-destructive quality evaluation.

2. Materials and Methods

2.1 Sample preparation

Cow ghee manufactured in experimental dairy of NDRI was taken. Ghee was transferred to 10 glass containers. Each glass container filled with 50 ml of ghee. These glass containers were transferred to hot air oven. Ghee containing 10 glass containers was allowed to heat in hot air oven at 175 ºC temperature. At every 4 h interval, 1 glass containers was removed from oven and allowed to cool at room temperature. This process was continuing for 40 h and 10 samples were drawn. All samples were stored in lab till it was used for analysis.

2.2. Analysis of sample

Prepared sample was analysed for free fatty acids, peroxide value, total polar compound, viscosity and capacitance. Before analysis ghee was heated to 40 °C.

2.3.1 Free fatty acid

The free fatty acids content of ghee was determined by the method as described by Indian Standards Institution (BIS, 1981) [4].

2.3.2 Peroxide value

Peroxide value of ghee was determined by AOAC method 965.33, 2000 [1].

2.3.3 Total Polar Compounds

Total polar compound of oil analyzed by micro method which was developed by Schulte (2004) [29].

2.3.4 Viscosity

The viscosity of ghee was determined using the HAAKE Viscometer iQ (Thermo scientific), controlled by HAAKE Rheowin Software.

2.3.5 Capacitance

Capacitance was measured by custom built capacitive measuring system. Before measurement LC100A meter was calibrated according to instrument operation manual.

2.4 Statistical analysis

Results of capacitance regressed with results of free fatty acid, peroxide value, total polar compound and viscosity by regression analysis with the help of SPSS 16.0 for windows 7.0.

3. Results and Discussion

3.1 Changes in free fatty acid (FFA) content during heating

Fresh ghee sample had 0.34% oleic acid before heating. Once, heating started it was found that free fatty acid content was increased that was 0.73, 1.02, 1.41 and 1.69% oleic acid after heating of ghee upto 8, 16, 24, 32 h respectively (Fig. 1). Maximum value of FFA was found at the end of heating (after 40 h) that was 1.87% oleic acid. Free fatty acid content of ghee was continuously increased with heating time. Free fatty acid initially present was increased significantly with heating time due to breakdown of unsaturated fatty acid. Olaleye (2019) [23] reported that at high temperature FFA content was increased in sesame oil. Rangaswamy and Nasirullah (2014) [26] reported that free fatty acid content increased gradually from 0.25 to 0.63% respectively in rice bran oil during heating at frying temperature. Hydrolysis is responsible more in oil with short and unsaturated fatty acid. FFA was increased due to combined action of thermal breakdown with oxidation and hydrolysis of ghee. There may be major reason for increasing free fatty acid was thermal treatment.

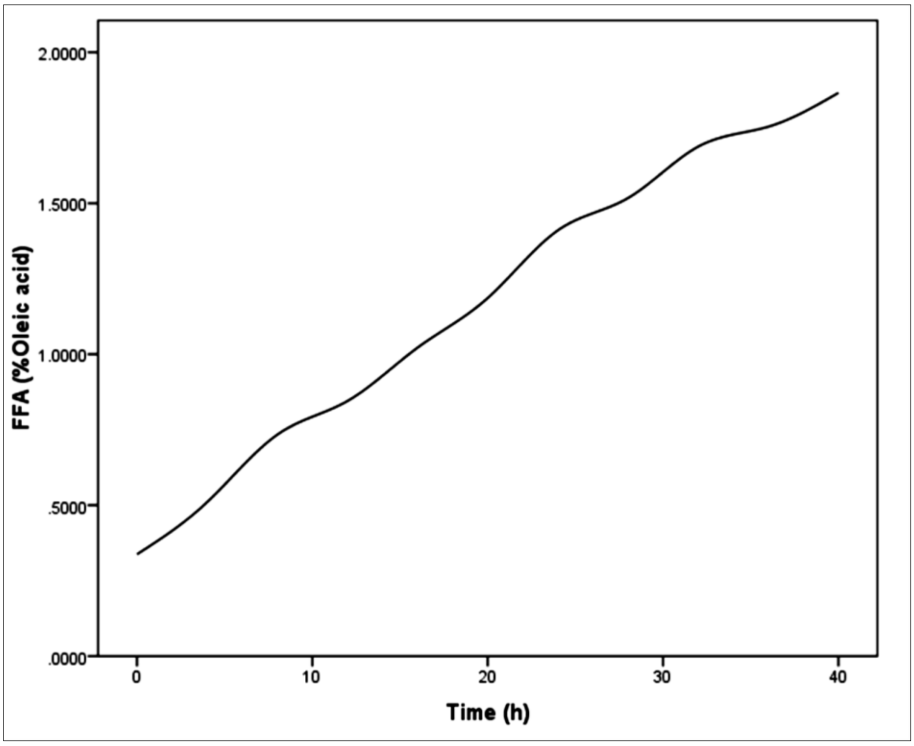

Fig 1: Changes in free fatty acid (FFA) value with respect to heating time in ghee

3.2 Changes in peroxide value (PV) during heating

Ghee sample was analysed and observed from the results of peroxide value that initially it was higher than normal range for fresh ghee hence it was found increasing with heating time. It was increased from 3.400-68.488 mEq O_2/ kg fat when ghee was heated to 40 h (Fig. 2). After 30 h of heating, it was observed that rate of increasing of peroxide value decreases. In the initial stage of hetaing, it is expected to increase peroxide and decreases when it is heated further. Perkins (1967) [25] reported that hydroperoxides breaking down at 180 ºC to form secondary oxidation product. But in our case peroxide value found increasing that may be related to cooling period of oil and storage time of sample at room temperature. Oil was allowed to cool more than 3 h after collecting sample during sample preparation. Augustin and Berry (1983) [2] reported that more hydroperoxides are formed when hot oil is allowed to cool at room temperature in presence of air. Peroxide value of rice bran oil increased gradually from 0.2 to 2.9 mEq O_2/kg of oil during heating at frying temperature (Rangaswamy and Nasirullah, 2014) [26].

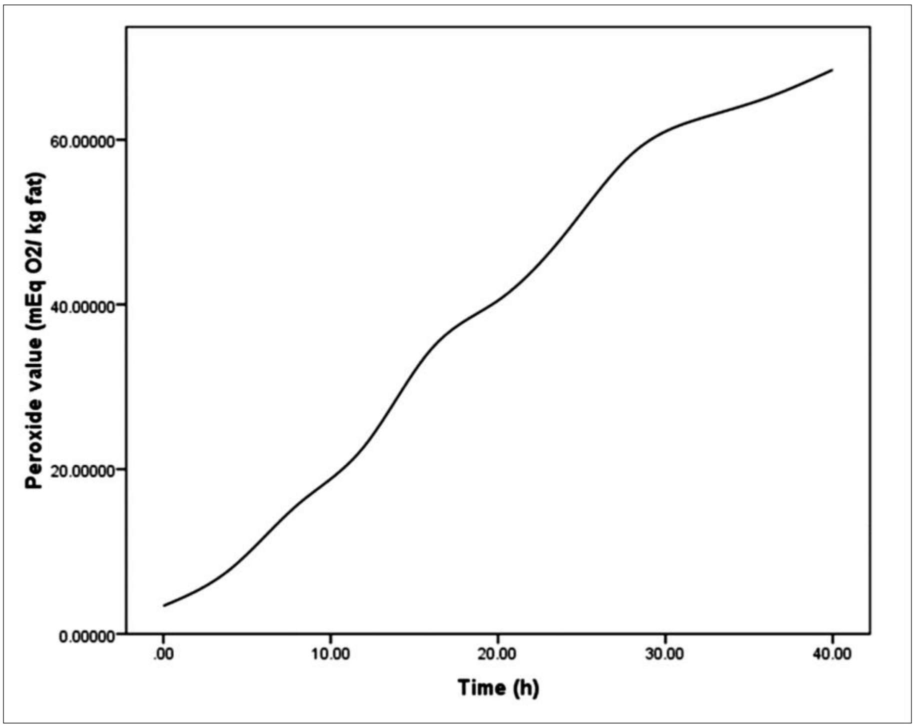

Fig 2: Changes in peroxide value with respect to heating time in ghee

3.3 Changes in total polar compound (TPC) during heating

Total polar compound is used as quality criterion for fats and oil at international level. TPC is non-volatile compound which have higher charge than other compound in oil. In our study initially amount of polar compound was observed 1.54% in ghee and after heating of 8, 16, 24 and 32 h it was increased to 3.12%, 5.29%, 7.66% and 9.00% respectively. At the end of ghee heating after 40 h polar compound was reached to 10.33% (Fig. 3). After heating period of 40 h ghee sample did not exceed limits of polar compound that is 25%. Total polar compound (TPC) increased from 1.0 to1.8% in rice bran oil during heating at 180 ± 2 °C for 8 h (Rangaswamy and Nasirullah, 2014) [26]. Study conducted by Marinova *et al*., (2012) [20] showed that TPC content increased throughout the heating at 180 ± 5 °C in olive oil, corn oil, grape seed oil, sunflower oil and soybean oil. Gil *et al*., (2004) [14] reported that palm oil, soybean oil, shortening and beef tallow having 8% or less amount of total polar compounds when it is fresh and reached to 30% after frying of 80 h except soybean oil. In case of soybean oil it was 15% when 80 h frying was completed.

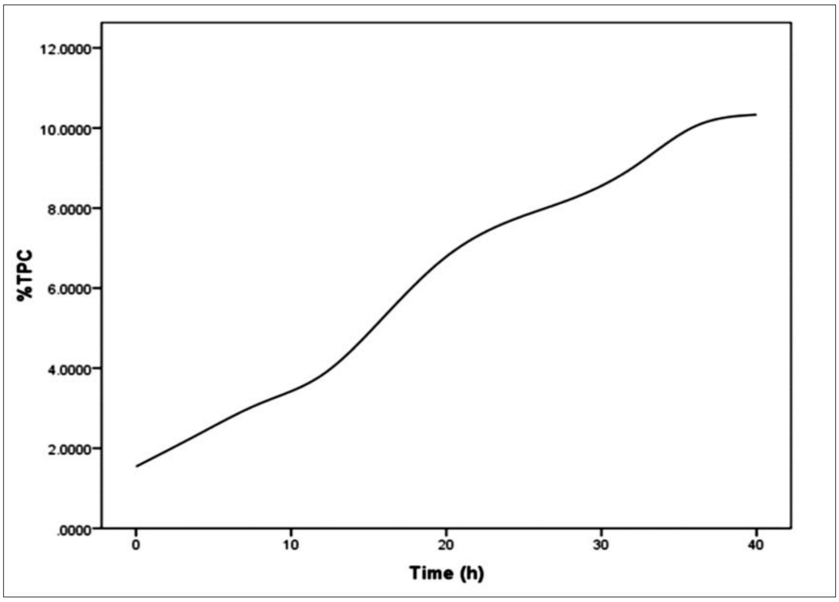

Fig 3: Changes in Total Polar Compound in ghee with respect to heating time

3.4 Changes in viscosity during heating

Heated ghee viscosity values were recorded at 50 s^{-1} shear rate as 0.109, 0.226 and 0.253 Pa.s at 40 ºC for fresh ghee, 20 and 40 h heated ghee sample respectively (Fig. 4). These viscosity values show that viscosity increases with heating time increases. At high temperature in presence of oxygen, auto oxidation reaction catalyzes formation of hydroxyl/carbonyl compounds in oil (Santos *et al*., 2005) [28]. He also reported that oxygen may also form hydrogen bonds which lead to increase in viscosity due to higher inter molecular forces. Polymerized compound also increases due to polymerization reaction. So, it leads to increase in viscosity as long chain compounds are not move easily (Santos *et al*., 2005) [28].

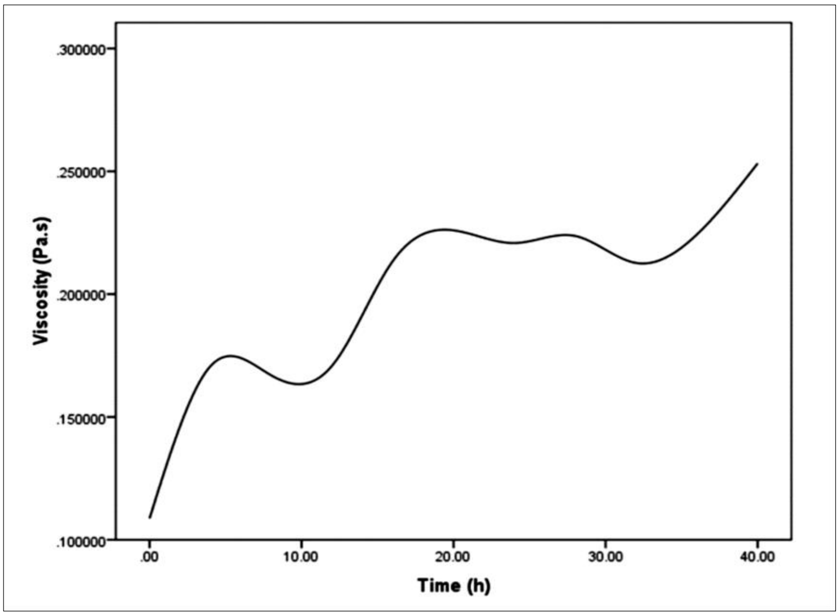

Fig 4: Changes in viscosity in ghee with respect to heating time

3.5 Changes in capacitance during heating
When ghee was heated to 40 h it was observed that capacitance value of ghee was continuously increased with heating time that was presented in fig. 4.48. Ghee sample showed 2.207 pF before heating. Once, heating started it was found that capacitance was increased and that was 3.675 pF, 5.130 pF, 5.905 pF and 6.367 pF after heating of ghee upto 8, 16, 24 and 32 h respectively (Fig. 5). Maximum value of capacitance was found at the end of heating (after 40 h) that was 6.688 pF. Khamil & Mood (2017) [17] and Khaled *et al*., (2015) [16] examined in their research study that capacitance was increased in oil when it was start to deteriorate during thermal treatment, they also correlate it with total polar compound.

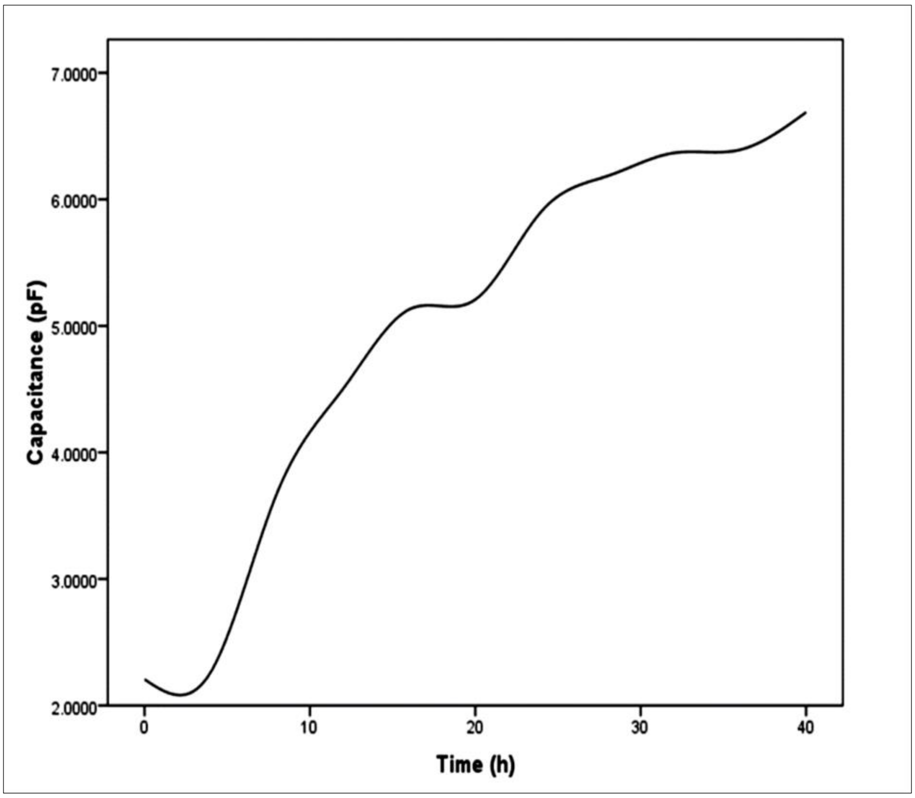

Fig 5: Changes in Capacitance of ghee with respect to heating time

3.6 Relationship of capacitance with FFA, PV, TPC and Viscosity
Relationship of capacitance value with FFA, PV, TPC and Viscosity of heated ghee sample was analyzed statistically from their coefficient of determination (R^2) by regression analysis. Fig. 6 shows the capacitance measurements of the ghee regressed on the FFA values at different heating times. As presented in the graph, it can be observed that the capacitance measurements by designed capacitive sensor have significant positive correlation with FFA values with R^2 of 0.939. Fig. 7 shows the capacitance measurements of the ghee regressed on the PV values at different heating times. As presented in the graph, it can be observed that the capacitance measurements by designed capacitive sensor have significant positive correlation with PV values with R^2 of 0.943. Fig. 8 shows the capacitance measurements of the ghee regressed on the TPC values at different heating times. As presented in the graph, it can be observed that the capacitance measurements by designed capacitive sensor have significant positive correlation with TPC values with R^2 of 0.916. Fig. 9 shows the capacitance measurements of the ghee regressed on the viscosity values at different heating times. As presented in the graph, it can be observed that the capacitance measurements by designed capacitive sensor have significant positive correlation with viscosity values measured by HAAKE Viscometer iQ (Thermo scientific) with R^2 of 0.797. High positive significant correlation of capacitance measurement with FFA, PV, TPC and viscosity values observed for heated ghee sample at different heating time. Similar results for relationship of viscosity and TPC with capacitance were reported by Khaled *et al*., (2015) [16] and Khamil & Mood (2017) [17].

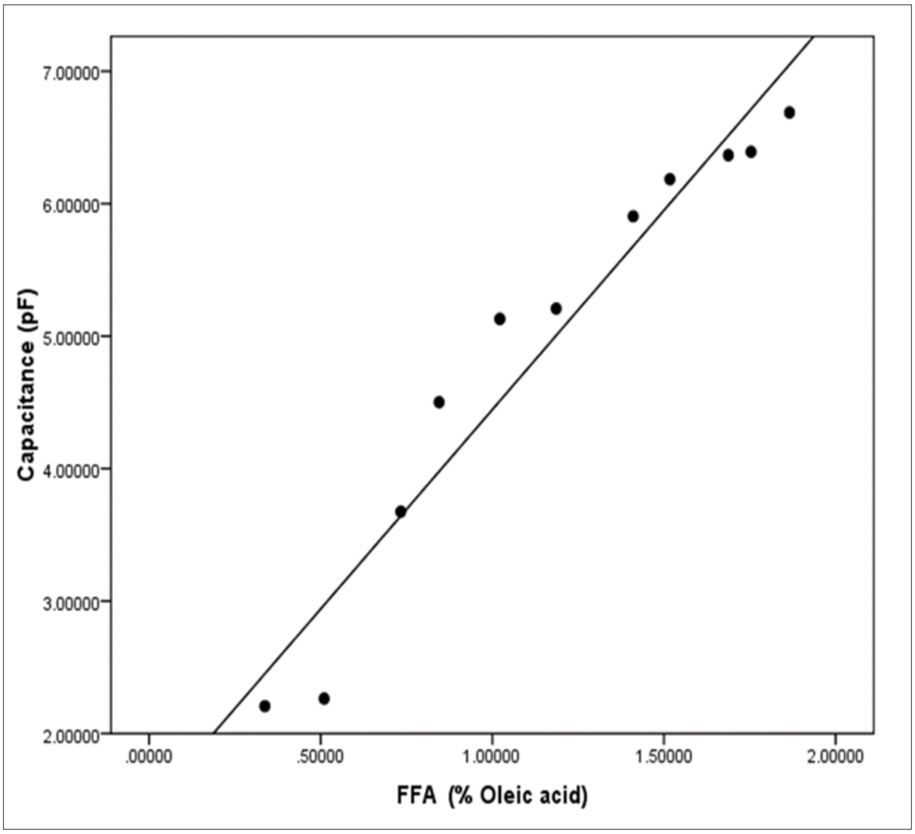

Fig 6: Capacitance measurement of heated ghee regressed on their FFA values

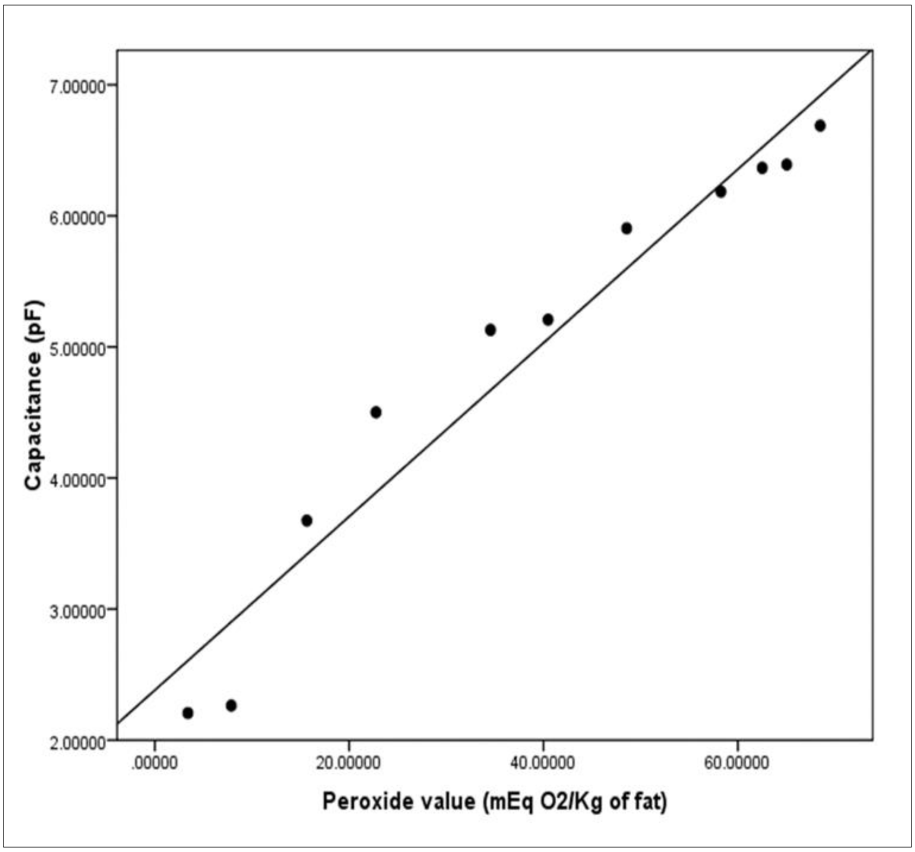

Fig 7: Capacitance measurement of heated ghee regressed on their Peroxide values

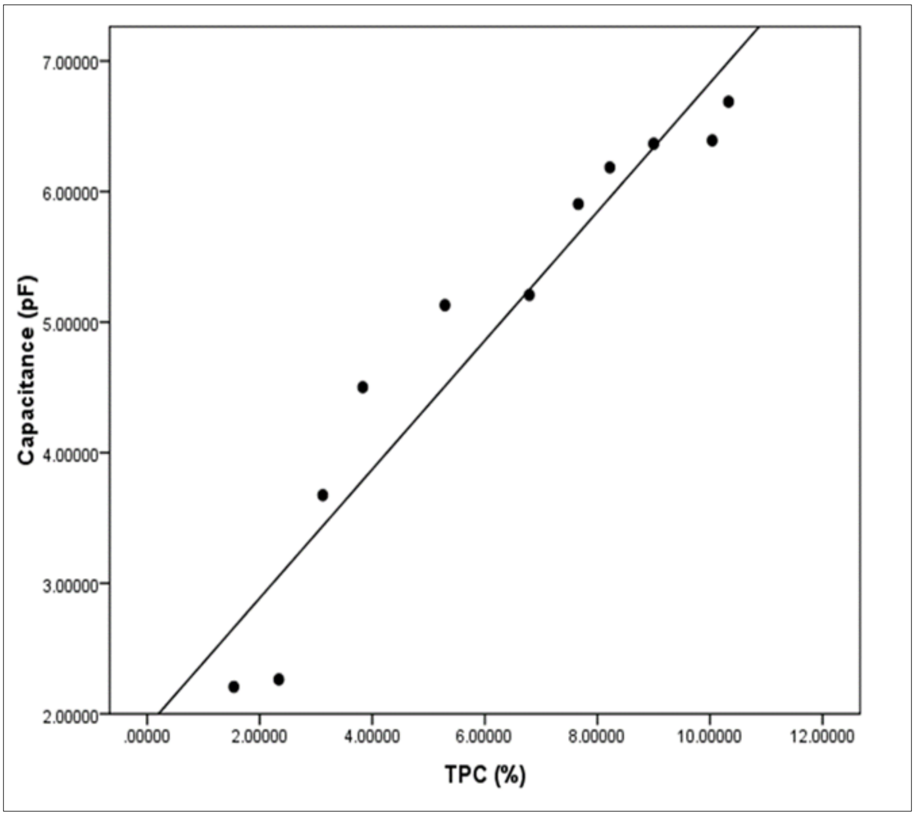

Fig 8: Capacitance measurement of heated ghee regressed on their TPC values

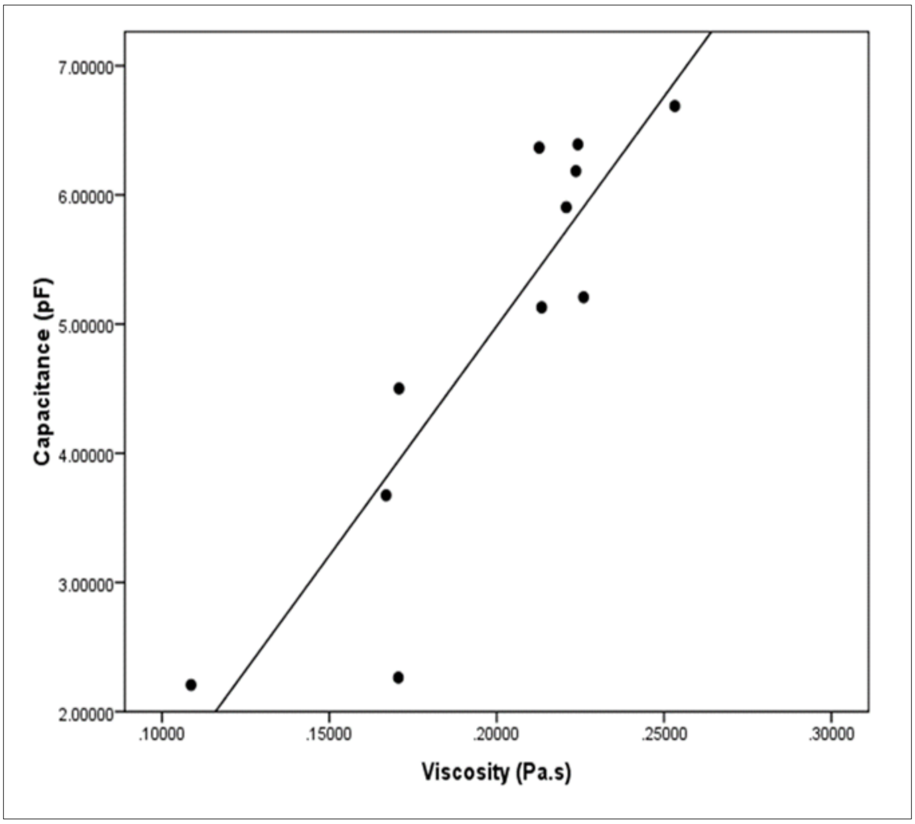

Fig 9: Capacitance measurement of heated ghee regressed on their viscosity values

4. Conclusion

This Research work was undertaken to determine various chemical, physical and electrical properties of ghee and to develop capacitive sensing system for rapid determination of quality of frying ghee and correlate the determined properties with capacitance. Developed capacitive sensing system shown satisfactory results for capacitance measurement for heated ghee sample at different heating time. R^2 values of capacitance with chemical properties of ghee were more than 0.910 and had positive significant correlation between them.

Viscosity values had also positive significant correlation was found with capacitance. As ghee quality degraded with heating time quality indicator of ghee i.e. FFA, PV and TPC values increased and consequently capacitance value also increased. Based on the results obtained it can be predicted that capacitance measurement can also be quality indicator of ghee for degradation assessment during heating. This sensing system can be used for evaluation for quality determination of ghee as well as oil during heating as well as frying. Range of capacitance measurement was found to narrow for prediction of quality of oil at different heating time so, it is recommended that further research on this can improve this sensing system. An improvement is necessary because capacitance measurement was found too sensitive when moisture plays a role.

5. Acknowledgment

This research received funding from ICAR-NDRI, Karnal, under the research project F-25 on Determination of engineering properties of ghee in relation to frying oil quality management. The researchers are grateful to Director, ICAR-NDRI, Karnal, for providing laboratory infrastructure and facilities to conduct the experiments. The first author acknowledges the Institute Fellowship received from ICAR-NDRI, Karnal, Haryana (India), for conducting the study.

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