Storage studies on the stability of cooking oils

Muhammad Munir, Saif Ullah Khan, Ahmad K. Baloch.
Department of Food Science and Technology, Gomal University, Dera Ismail Khan

ABSTRACT

Refined oils of sunflower, soybean, canola and hydrogenated vegetable ghee (Kisan), and locally prepared non-refined Desi ghee were selected to observe the effect of temperature on storage stability. The temperatures of 15°C, 40°C and 60°C, refractive index, free fatty acid, iodine value, saponification value and peroxide value assessed the oil stability. The changes in the quality parameters correlated to the storage temperature. A proportionate increase in free fatty acid value and peroxide value was observed in all the oil samples. Similarly, a considerable decrease in iodine values with simultaneous increase in saponification values was observed in all oil samples during storage at all temperatures. Lowest iodine value of 37.56 was observed in case of Desi ghee samples. Increase in refractive index was also noticed with increase in temperature and highest refractive index of 1.525 was observed in Kisan vegetable ghee. All the samples were found to have $E_2$ values in the range of 13.0 to 71.7 kJ/mole including those of higher amount range for fatty acid values (37.4 to 54.6 kJ/mole) and peroxide values (37.5 to 68.2 kJ/mole), and of lower amount range for iodine values (13.9 to 29.4 kJ/mole) and saponification values (13.0 to 45.9 kJ/mole). The overall activation energy having minimum amount of range found in the Kisan vegetable ghee and Soybean oil whereas of a range with maximum amount associated for the Canola, sunflower and Desi ghee samples. The range of $Q_{10}$ values varied with in the normal limit from 1.2 to 2.0. The hydrogenated Kisan ghee and soybean oil appeared relatively more heat stable products.

Key words: Cooking oils, stability, temperature, rate of deterioration, activation energy

INTRODUCTION

Oils and fats play an important role in the economy of any country. For providing energy, fats and oils occupy a higher position than any other energy supplying food. They in fact represent the most concentrated form providing 9 Calories/g fat. So vital is the contribution of fats and oils to the life processes of human beings which cannot synthesize certain of the unsaturated fatty acids like linoleic acid, and show symptoms of deficiency diseases and die prematurely if their food does not contain these essential fatty acids. However, these being polyunsaturated in nature are modified readily and are badly affected by environmental factors like oxygen and temperature.

Clark and Serbia (1991) reported that the free radicals formed by fatty acids react with oxygen to generate peroxides which enter into a multitude of reactions, producing numerous products such as aldehydes, ketones, acids, esters and polymerized fat. These compounds make the food unpalatable and even harmful. Rajesh and others (1992) studied the thermal stability of tertiary butyl hydroquinone (TBHQ) in ghee and observed the efficacy and stability of the diphenolic antioxidant, during continuous heating at 100, 150, 200°C. The addition of TBHQ at conc. of 5, 10, and 20 mg /100 g resulted in retardation of oxidative deterioration of ghee heated at 100 and 150°C as assessed by the peroxide value. Ahmad and others (1996) used cooking oils to observe the effect of deep fat frying of potato-fillets for four consecutive days @ 3-4 minutes per day. Quality of frying oils was determined by the peroxide value (POV), anisidine value (AV), iodine value (IV), free fatty acid value (FFA) and color (O.D at 420 nm). The highest average POV (22.94 meq/kg), FFA (0.40) and IV (11.410 g/100g) were observed in sunflower oil while AV (109.8) in corn oil. The maximum change in color (discoloration) was observed in corn oil. All quality parameters increased during frying, except the IV, which showed a decreasing trend in each case. Huygebaert (1998) conducted an experiment to follow the effect of heating on the chemical composition of selected oils and fats (crude soybean oil, refined and partially hydrogenated soybean oil, refined lard and refined beef tallow). He found that the change in free fatty acids was rather limited, saponification value was negatively correlated with high temperature. During heating there was a continuous conversion of the nonpolar fraction into the
polar fraction. The stability was inversely related to the number of double bonds.

The present research work was carried out with the objective to find out the effect of temperature (at which the fatty food is normally held in houses during summer) on the stability of various brands of fats and oils, which are commonly used for cooking purposes.

MATERIAL AND METHODS

Sealed pack of refined, bleached and deodorized (RBD) cooking oils was purchased from the local market. The sample includes Kisan vegetable ghee, Super Habib soybean oil, Sufi sunflower oil, Seasons canola oil and Desi ghee. According to the labels affixed on the packs, these samples were manufactured and packed in the year 2000. While Desi ghee (butterfat of cow) was bought from the countryside. The samples were brought to the laboratory of Food Technology and study conducted in the month of May 2000. Each of the sample was taken in long neck conical flask, fitted with condenser and allowed to heat on water bath at incubation temperatures of 40°C and 50°C for a period of 15 days. The samples were also placed at 15°C in the cold storage. After the storage the packs were left in a refrigerator under tightly packed conditions until required for further study purposes. The stability of the samples was studied by estimation of quality parameters including refractive index (RI), free fatty acid value (AV), saponification value (SV), iodine value (IV) and peroxide value (POV). Rate of deterioration, activation energy (Ea) and temperature quotient Q10 (40°C - 50°C) were also determined for each of the said quality parameter. The analysis was conducted in duplicate and the mean value is recorded.

Refractive index and acid value of oil samples were recorded in accordance with the method described by Triebold and Aurand (1963). Saponification and peroxide values were determined by the method of A.O.A.C (1964). Iodine value was estimated as described by Pearson (1970).

Rate of deterioration. Rate of deterioration per day for each parameter was determined by subtracting the fresh values of a given parameter from its final reading at a particular temperature.

Rate of deterioration/ day = (Initial pre-storage reading - final post-storage reading) / incubation time.

Activation energy (Ea). The energy of activation for each determinant was estimated by Arrhenius plot (Baloch and others 1977) after plotting logarithmic rate of deterioration/day against 1/T, where T is absolute temperature (Fig. 6). The activation energy is calculated from the following equation:

\[ \text{Slope} = -E_a / 2.303R \]

where R is a Gas constant = 1.987 cal/mol

From the Figure 6 given as a specimen, the slope can be determined, and hence from the same graph the apparent energy of activation (Ea) and the temperature quotient Q10 can be calculated for all of the quality parameters.

RESULTS AND DISCUSSION

Physico-chemical constants of oil samples were studied at different storage temperatures. Changes in quality parameters were recorded after exposing the oil samples to the specific temperature for a selected period of time. Moreover rate of deterioration, Ea, Q10 values in temperature range of 40°C - 50°C were recorded for each of the above parameters. The results are tabulated and graphically presented at appropriate places.

Refractive Index

The refractive indices of 1.4767, 1.4787, 1.4737, 1.4450, and 1.5210 were recorded in freshly opened samples of Sufi sunflower oil, Super Habib soybean oil, Seasons canola oil, Desi ghee and Kisan hydrogenated vegetable ghee respectively. The data indicate that the hydrogenated ghee had highest RI value as compared to all other oil samples. All the samples showed an increase in the RI on storage and the rate increased proportionately with storage temperatures. Maximum increase was found at 60°C followed by 40°C. A slight increase was also observed on keeping the samples at 15°C (Fig. 1). These results are in agreement with the those reported by Triebold and Aurand (1963) and Pearson (1970).

Free fatty acid value

Free fatty acid value of 0.32, 0.02, 0.71, 3.20, and 0.33 were recorded in freshly opened samples of soybean (Super Habib), canola (Seasons), sunflower (Sufi), Desi ghee and Kisan ghee respectively. Free fatty acid contents were highest in Desi ghee followed by sunflower, Kisan ghee and soybean. Minimum amount of fatty acid values was found in the canola oil samples (Fig. 2). A considerable high amount of the free fatty acid values of Desi ghee samples indicate that the samples were not properly stored and turned deteriorated. In the rural areas normally the butter is
left for the collection over a week period or so before its conversion to Desi ghee. Most probably the butter was deteriorated considerably which eventually marred quality of the Desi ghee. All these samples after incubation showed an increase in free fatty acid values, which corresponded well with the incubation temperatures. Highest increase was found at 60°C followed by 40°C. A negligible increase was also observed at 15°C. Similar findings have also been reported by Stevenson and others (1984) and Huyghebaert (1998).

Peroxide Value

The initial POV of 0.33 was the lowest in case of Kisan ghee as compared to soybean (Super Habib), canola (Seasons), sunflower (Sufi), Desi ghee which had 4.01, 3.22, 6.02 and 8.21 respectively (Fig. 3). On evaluating the results after storage it is noted that there was corresponding relationship between POV and temperature, and highest increase was observed at 60°C but very little changes occurred at 15°C. These findings collaborate with the work of Steven and others (1994) who had also reported similar results.

Saponification Value

Freshly opened samples of soybean (Super Habib), canola (Seasons), sunflower (Sufi), Desi ghee and Kisan ghee gave initial SV of 185.41, 187.88, 188.34, 218.41 and 190.73 respectively (Fig. 4). Although all the samples showed an increase in SV after incubation at higher temperatures but the extent of the increase did not correspond with the rise in the temperature. Huyghebaert (1998) reported similar observations in this parameter of cooking oils.

Iodine Value

Fresh sample of soybean (Super Habib), sunflower (Sufi), canola (Seasons), Kissan ghee and Desi ghee displayed the iodine value of 137.66, 134.56, 108.91, 98.43 and 37.56 respectively (Fig. 5). It appears that soybean, sunflower and canola samples had higher amount of unsaturated fatty acids whereas hydrogenated and Desi ghee samples had considerably lower amount of these acids. On storage, the incubation temperature considerably exerted a negative effect and the values were reduced after 15 days of storage with maximum reduction at 60°C. However, the decreases were not at 15°C as it was at the elevated temperatures. These results are in accordance with Ahmad and others (1996).

Activation Energy and Q10 values

The data regarding activation energy and Q10 are recorded in Table 1. The Ea varied from 13.0 to 71.7 kJ/mol for all of the quality parameters studied. The overall minimum levels of activation energy varying from 13.9 to 35.1 kJ/mol and 13.0 to 45.9 kJ/mol were estimated for iodine and Saponification values respectively. Whereas values of much higher level were found for the other quality parameters. Iodine values appeared to proceed with out being much affected by the temperature variation, but PO, Free fatty acid and RI values appeared to be highly temperature dependent. As regards the activation energies of the oil samples the Kisan vegetable ghee and Soybean oil possessing overall lower activation energies are likely much less affected by the variation of temperature in the studied range. However, the Canola, Sunflower and Desi ghee samples are likely to depend on the temperature rises. The Canola, Sunflower and Desi ghee samples may not show much deterioration at relatively lower temperatures but these are very likely to deteriorate at much rapid rates by increasing the temperatures. The findings indicate that all of the cooking oil samples require fairly high amount of the energy to allow and to continue the deterioration process, and remain stable so long as they are placed at lower temperatures. The fact that all of the samples had comparatively lower activation energies with regard to IV and SV maintains that the samples are likely to be deteriorated initially by those factors which affect the measurement of iodine and saponification values. Similarly, Q10 values varied from 1.2 to 2.0 (Table 1). The results indicate that the rate of quality deterioration becomes 1.2 to 2.0 times faster with 10°C rise in the temperature between 40°C to 50°C. Similar findings have also been put forwards by Baloch and others (1977), and Grivas and others (2002).

CONCLUSIONS

From the above study, all the samples showed significant increase in their FFA and Peroxide values at elevated temperatures. Minute increase was also observed at 15°C. Desi ghee showed rapid increase in its free fatty acid and peroxide values while the refined and hydrogenated fats did not show such a trend in these parameters. There was increase in refractive index of all cooking oils. Whereas a decreasing trend is given out for the iodine values in all oils samples and the trend was prominent at higher temperatures. The SV showed also a slight increasing trend in this study for all the samples. However this increase was not as significant. The hydrogenated vegetable ghee afforded higher stability whereas the Desi ghee samples responded ease to deterioration.
Table 1. Activation energy (KJ/Mol) and $Q_{10}$ values of the oil samples during storage.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Refractive index</th>
<th>Free fatty acid value</th>
<th>Peroxide value</th>
<th>Saponification value</th>
<th>Iodine value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$</td>
<td>$Q_{10}$</td>
<td>$E_a$</td>
<td>$Q_{10}$</td>
<td>$E_a$</td>
</tr>
<tr>
<td>Desi ghee</td>
<td>28.3</td>
<td>1.4</td>
<td>54.6</td>
<td>1.9</td>
<td>58.2</td>
</tr>
<tr>
<td>Soybean oil (S.Habib)</td>
<td>27.5</td>
<td>1.2</td>
<td>49.3</td>
<td>1.7</td>
<td>63.6</td>
</tr>
<tr>
<td>Sunflower oil (Sui)</td>
<td>54.0</td>
<td>2.0</td>
<td>51.1</td>
<td>2.0</td>
<td>68.2</td>
</tr>
<tr>
<td>Canola oil (Seasons)</td>
<td>71.7</td>
<td>1.6</td>
<td>47.3</td>
<td>1.8</td>
<td>85.3</td>
</tr>
<tr>
<td>Kisan vegetable ghee</td>
<td>20.8</td>
<td>1.3</td>
<td>37.4</td>
<td>1.5</td>
<td>37.5</td>
</tr>
</tbody>
</table>

Fig. 1. Effect of temperature on RI of cooking oils

- Desi ghee
- Soyabean oil
- Sunflower oil
- Canola oil
- Hydrog. Ghee

Temperature

RI

1.4 1.44 1.48 1.52 1.56
Fig. 2. Effect of temperature on free fatty acid values of cooking oils

Fig. 3. Effect of temperature on peroxide value of cooking oils
Fig. 4. Effect of temperature on saponification value of cooking oils

![Graph showing the effect of temperature on saponification value of cooking oils.]

- Desi ghee
- Soyabean oil
- Sunflower oil
- Canola oil
- Hydrog. Ghee

Fig. 5. Effect of temperature on iodine value of cooking oils

![Graph showing the effect of temperature on iodine value of cooking oils.]

- Desi ghee
- Soyabean oil
- Sunflower oil
- Canola oil
- Hydrog. Ghee
LITERATURE CITED


