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Abstract

Physicochemical properties like density, viscosity, boiling point, saponification value (SV), iodine value (IV), peroxide value (PV) of Corn and Mustard oils were studied to evaluate the compositional quality of oils and also investigate the effect on same oil used for repeated frying as it ultimately changes the physicochemical, nutritional and sensory properties of the oil. FT-IR spectroscopy was used to evaluate the oxidation after heating and frying processes. Spectra showed that there exists notable difference in the band at room temperature, boiling point and using same oil for three times frying with a piece of potato as the oil composition affects the exact positions of the band and shifts when the proportion of the fatty acid changed. At boiling point and same oil for multiple times frying oils show 2852.7-2926.0 cm\(^{-1}\) frequency while Mustard oil show an additional peak at 3633.8 cm\(^{-1}\) which exhibits the secondary oxidized product formation.

Key words: Edible oils, FT-IR, Physicochemical characteristics, Frying-Heating.

1. Introduction

Lipids and triacylglycerol are naturally occurred in oils and fats. Their chemical composition contains saturated and unsaturated fatty acids and glycerides. Edible oils are used for many purposes like Corn oil which is obtained from seeds of Zea mays an important component is usually used as food and also as vehicle in certain pharmaceutical formulation such as suspension and emulsion. (Alvarez and Rodríguez 2000) as well as Mustard oil from Brassica nigra which is healthy because it has 30 per cent protein, calcium, phytins, phenolics and natural anti-oxidants. Mustard oil contains high amount of mono-unsaturated fatty acids and a good ratio of polyunsaturated fatty acids, which is good for heart. Mustard oil contains the least amount of saturated fatty acids, making it safe for heart patients.

Different physical and chemical parameters of edible oil were used to monitor the compositional quality of oils (Ceriani et al., 2008; Mousavi et al., 2012). These physicochemical properties include iodine value (IV), saponification value (SV),
viscosity, density and peroxide value (PV). Edible oils are one of the main constituents of diet used for cooking processes. Several researchers studied the impact of temperature on the stability, viscosity, peroxide value, iodine value to assess the quality and functionality of the oil (Farhoosh et al., 2008; Li et al., 2010; Jinfeng Pan, 2011).

Deep frying is one of the most common methods for the preparation of food. Repeated frying causes several oxidative and thermal reactions which result in changes in the physicochemical, nutritional and sensory properties of the oil (Che Man and Jasvir, 2000). In the process of deep frying the composition of oils becomes changed due to hydrolysis, oxidation and polymerization processes and the result is the changed flavor and its stability of the compound (Gloria and Aguilera, 1998). During deep frying different reactions depend on some factors such as replenishment of fresh oil, frying condition, original quality of frying oil and decrease in their oxidative stability (Choe and Min, 2007). Structural degradation occurs in the oil when atmospheric oxygen react instantly with lipid and other organic compounds of the oil which are harmful for human health and lost the quality of food (Bhattacharya et al., 2008). Therefore, it is essential to monitor the quality of oil to avoid the use of abused oil due to health consequences of consuming foods fried in degraded oil, to maintain the quality of fried foods and to minimize the production cost associated with early disposal of frying medium (Vijayan et al., 1996).

Different analytical methodologies used for quantitative evaluation of heated oils are Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC), Ultra Visible Spectrometry (UV) and Fourier Transform Infrared (FT-IR) spectroscopic techniques. Advantages of FT-IR technique over the other conventional physical and chemical methods are as it is more ease of sample handling, quick and not required enough quantity of hazardous solvents (Che Man and Jasvir, 2010). It includes dramatic improvement in the signal to noise ratio, reduce the scan time, throughout high energy, all wavelengths are recorded simultaneously with wavelength accurating and nondestructive aspects.

The aim of the present study is quantitative analysis of the properties of the Mustard and Corn oil and the effect of temperature on the properties of oils after heating.
and frying with carbohydrate using potato pieces and also using same oil for three times frying to check the changes in oil quality. The changes in the physicochemical properties of oils are also analyzed by FT-IR analysis to evaluate the oxidation after heating and frying.

2. Materials and Methods

2.1 Material and Chemicals

Hydrochloric acid (HCl), Sodium hydroxide (NaOH), Potassium hydroxide (KOH), Iodobromine (IBr), Sodium thiosulphate (Na$_2$S$_2$O$_3$), Potassium iodide (KI), Acetic acid (CH$_3$COOH) all were A.R Grade and purchased from Merck Darmstadt Germany.

Corn and Mustard oils were extracted from their dried, dehulled and powdered seeds purchased from the local market in Karachi Pakistan.

2.2 Density Measurement

The densities of oil samples at room temperature 35°C (before frying) and after frying with a piece of potato and using same oil for repeatedly three times frying were measured by a R.D bottle with capacity of 10 mL.

2.3 Boiling Point Measurement

The boiling point of oils samples were measured by thermometer ± 1°C. The boiling point depends upon the degree of unsaturation of fatty acids.

2.4 Viscosity Measurement

The viscosity of oils samples before and after frying were measured by Ostwald Viscometer technicomominal constant 0.05 Cs/c, ASTMAD 445 England. The flow time of oil samples were recorded with stop watch (Japan, CBM, and Corp QSQ) least count± 0.01 s.
2.5 Saponification value Measurement

The saponification value is determined by taking 1.0 g of oil sample in conical flask add 15 mL 1N KOH and 10 mL of distilled water and heated under a reserved condenser for 30-40 min to ensure that the sample was fully dissolved. After this sample was cooled, phenolphthalein was added and titrated with 0.5 M of HCl until a pink endpoint was reached. A blank was determined with same time conditions.

2.6 Iodine value (IV) Measurement

A known weight of the oil sample is treated with an excess of iodobromine (IBr) in glacial acetic acid. Unreacted iodobromine is reacted with potassium iodide which converts it to iodine. The iodine concentration is then determined by titration with standard sodium thiosulphate.

\[ IV = (b-v) \times N \times 126.9 \times \frac{100}{w} \times \frac{1000}{1000} \quad (1) \]

Where \( b \) is the mL of sodium thiosulphate used for blank, \( v \) is the mL of thiosulphate for sample, \( N \) is the normality of thiosulphate solution, \( w \) is the wt of oil sample and 126.9 is the molecular weight of iodine. (Singh et al. 1981)

2.7 Peroxide value (PV) Measurement

Peroxide value is a measure of peroxides contained in the oil. PV is determined by measuring iodine released from potassium iodide.

A known measured weight of oil samples are dissolved in an acetic acid then chloroform mixture and saturated KI mixture is added with sample and the amount of iodine liberated from KI by oxidative action of peroxides present in the oil is determined by titration with standard sodium thiosulphate using starch solution as an indicator. Titration was also performed for blanks.

\[ PV \ (\text{meq/Kg oil}) = (S-B) \times W \times N \quad (2) \]
Where $B$ is the volume of sodium thiosulphate used for blank, $W$ is the weight of sample, $S$ is the volume of sodium thiosulphate consumed by the sample oil and $N$ is the normality of standard sodium thiosulphate (AOAC, 1984).

2.8 Frying Process

Potatoes were peeled and cut into pieces (approx 5cm$^3$) and were fried in the frying oil at constant temperature during three frying times. Frying experiments were conducted in duplicate on each frying medium.

2.9 Evaluation by FT-IR

FT-IR spectra of oils sample before and after frying were recorded with the help of Fourier Transform Spectroscopy Model I-R Prestige 21 Shimadzu. It is used to study the saturation and unsaturation composition of heated and unheated oils at room temperature for monitoring the oxidation process in oils.

3. Results and Discussion

The quality of Corn and Mustard oils were analyzed by evaluating physicochemical properties such as density, viscosity, boiling point, peroxide, iodine and saponification values. The results are presented in Table 1. Oils with lower values of viscosity, density are highly appreciable to consumers. In order to design an advanced technological process these properties are very important parameters. The effect of temperature on these properties and the influence of three times frying with carbohydrate (potato piece) up to their respective boiling point using same oil were also studied and results were tabulated in Table 2.

3.1 Viscosity and Density

Oils are mixtures of triglycerides (TGs) and viscosity depends on the nature of the TGs presents in the oil. The viscosity changed due to the different arrangement of the fatty
acids on the glycerol backbone of the triglyceride molecule. Therefore, viscosity is related to the chemical properties of the oils such as chain length and saturation/unsaturation. Table 1 shows that at room temperature 35°C the viscosity is high in Mustard oil as compared to the Corn oil and the Mustard oil has high boiling point relative to Corn oil. It explains that the viscosity and density decreases with an increase in unsaturation and increases with high saturation and polymerization (Kim et al., 2010). Viscosity also depends on sheer stress and temperature. Sheer stress does not have much effect on the storage of the oils which are used for edible purposes but the temperature does affect it. Results tabulated in Table 2 revealed that there is an increase in viscosities was observed for Corn oil while a decrease was observed for Mustard oil at boiling point and at different times frying with a piece of potato. An increase in temperature kinetic energy increases which enhances the movements of the molecules and reduces intermolecular forces so the layers of the liquid easily pass over one another and thus contribute to the reduction of viscosity. This phenomenon is also verified by other researchers since oil viscosity depends on molecular structure and decreases with the unsaturation of fatty acids (Kim et al., 2010). The densities of both oils were decreased with the rise in temperature as well as for using same oil for three times frying with a piece of potato. The densities of oils were related to the standard range of 0.898 – 0.907 g/ mL approved by Standard Organization of Nigeria (SON, 2000). The results tabulated in Table 1 shows that at room temperature 35°C the values of densities are 0.9694 g/mL and 0.9223 g/mL for the Mustard and Corn oil respectively. It may be due to the π bonds that make the bonding more rigid and rotation between C-C bonds becomes more strenuous.

During frying thermo-oxidative or lipid oxidation and hydrolytic reactions take place that results in deterioration of the frying oil (Romero 2000, 2003; Paul and Mittal, 1997). The primary oxidation products that develop in triacylglycerol are hydroperoxides, which may later break down to produce lower molecular weight compounds, such as free fatty acids, alcohols, aldehydes, and ketones, eventually leading to rancid product (Barthel and Grosch, 1974). Lipid oxidation is a main deteriorative process which has an important implication in stipulations of the quality and value of fats and oils, particularly in relation to the off-flavors that develop as an outcome of autoxidation (Xiuzhu et al., 2007).
Normally, frying oils undergo extensive degradation and complex chemical transformations when heated. The presence of air and water accelerated the deterioration of frying oil (Clark and Serbia, 1991) and resulted in an increase in the number of polar molecules as confirmed by viscosity and density data of oils (White, 1991).

3.2 Peroxide value
Peroxide value (PV) is used as a measure of the extent to which rancidity reactions have occurred during storage it could be used as an indication of the quality and stability of fats and oils (Ekwu and Nwagu, 2004). The peroxide value was also found to increase with the storage time, temperature and contact with air of the oil samples. The PVs values tabulated in Tables 1 and 2 for both the oils are ranged from 0.388-2.994 meq/kg. The results show that the peroxide values for Corn oil increased from 0.162 (35°C) to 0.538 meq/kg (boiling point 140°C) and 2.994 meq/kg (first frying) and then it decreased at second and third frying gradually while for Mustard oil a decrease in peroxide value from 0.830 (35°C) to 0.388 meq/kg (boiling point 170°C) and at three different frying the pattern were same as that in Corn oil was observed. The initial PV was found to have occurred around 2.5 to 5 meq/kg oil which indicates a relatively good quality of these oils. There is a successive decreased in PV when same oil was used for frying with a piece of potato. The peroxide value determines the extent to which the oil has undergone rancidity. The peroxide values ranged are closely related to the standard value of 10 meq/Kg specified by Standard Organization of Nigeria (SON) (2000) and Nigerian Industrial Standard (NIS) (1992).

3.3 Saponification value
Saponification value (SV) is an index of average molecular mass of fatty acid in oil sample. The SV value obtained for the oil samples in Table 1 showed 153.8 mg KOH/g for Corn oil and 125.6 mg KOH/g for Mustard oil. The values are below the expected range of 195 – 205 mg KOH/g of oil for edible palm oils as specified by SON (2000) and NIS (1992). The lower value of saponification values suggests that the mean molecular
weight of fatty acids is lower or that the number of ester bonds is less. This might imply that the fat molecules were not intact with each other (Denniston et al., 2004).

3.4 Iodine value

Iodine value (IV) measures the degree of unsaturation in a fat or vegetable oil. It determines the stability of oils to oxidation, and allows the overall unsaturation of the fat to be determined qualitatively (AOCS, 1993; Asuquo et al., 2012). It was observed that measured iodine values for Corn and Mustard oils are 15.96 g and 8.10 g respectively. These low iodine values may have contributed to its greater oxidative storage stability. The oxidative and chemical changes in oils during storage are characterized by increase in free fatty acid contents and a decrease in the total unsaturation of oils (Perkin, 1992).

All these physicochemical properties viscosity, density, peroxide value, iodine value, saponification values are qualitative properties of oils do not indicate the position of the double bonds or amount of olefinic carbon but rather it provides an overall status of unsaturation of the oils so it is not possible to point out the position of double bond(s) which are more susceptible to oxidation (Knothe and Dunn, 2003).

3.5 Spectral analysis

FT-IR spectroscopy is an excellent tool for analysis as the intensities of the bands in the spectrum are proportional to concentration. Mid IR spectra have been used to characterize edible oils and fats because they differentiate in the intensity and the exact frequency at which the max absorbance or transmittance of the band appears, according to the nature and composition of the sample (Guillen and Cabo, 2000). FT-IR spectra of Corn and Mustard oil samples showed that there exists notable difference in the band at room temperature, at boiling point and between the same oil used for three times frying with a piece of potato. The oil composition affects the exact positions of the band and yields shift when the proportion of the fatty acid changed. At room temperature Figures (1a) and (2a) the band around 3473 cm\(^{-1}\) assigned to O-H stretching vibration of hydroperoxide, 3006.8-3007.0 cm\(^{-1}\) as C-H stretching vibration of the cis-double bond (=C-H) and 2854.7-2925.8 cm\(^{-1}\) shows C-H asymmetric and symmetric stretching vibrations of the aliphatic CH\(_2\).
At different temperatures and during three times frying with a piece of potato, the percentage transmittance of almost all the peaks increased indicating the decrease in absorbance which may be due to hydrolysis of oil during frying and form free fatty acids and mono and diglycerides and these compounds accumulated in the frying oil with repeated use as the hydroperoxides also decrease which may be due to decomposition of hydroperoxides and secondary oxidation initiation.

At 35°C Figures 1(a) and 2(a) and at boiling point of Corn oil (140°C) and Mustard oils 170°C the region of double bond stretching shown at 1745.5 cm\(^{-1}\) which represents C=O ester carbonyl of triglycerides and 1654.0-1658.7 cm\(^{-1}\) indicates C=C stretching vibration of cis olefins as shown in Figures (1b) and (2b) respectively. The band trend is much more similar at first frying and third time frying with a piece of potato 1745-1747.5 cm\(^{-1}\) and 1660-1652.3 cm\(^{-1}\) respectively as in Figures 1(c and d) and 2(c and d). This observation shows the production of saturated aldehyde functional group or other secondary oxidation products that cause an absorbance at 1728 cm\(^{-1}\) which overlap with the stretching vibrations at 1746 cm\(^{-1}\) of the ester carbonyl functional group of the triglycerides this pattern is same at boiling point but in Mustard oil at boiling point Figure 2(b) and for one and three times frying Figures 2(c and d) there is also a peak 1705.0 cm\(^{-1}\) at the region of double bond’s stretching which is –C=O free fatty acids and the overall signal pattern looked similar with each other. As the spectral regions undergoes several changes during oxidation processes at the room temperature and at different temperatures oils showed some regions of other deformations and bending at 1460-1462 cm\(^{-1}\) of –C-H bending vibrations of the CH\(_2\) and CH\(_3\) aliphatic groups and at 1373.2- 1377 cm\(^{-1}\) of –C-H bending vibrations of CH\(_2\) group were observed while at 908.2-970.2 cm\(^{-1}\)of CH=CH shows trans unsaturation.

For the determination of oxidation processes, at boiling point and between three times frying of the Corn oil Figures 1(b-d) the value 2854.7 cm\(^{-1}\) frequency in the samples varies significantly from 2852.7-2926.0 cm\(^{-1}\). The 2926.0 cm\(^{-1}\) band is attributed to the symmetric stretching vibration of the aliphatic –CH\(_2\) group. For Mustard oil at boiling
point Figure 2(b), there is an additional peak at 3633.8 cm\(^{-1}\) which exhibits that the secondary oxidized product has been formed.

FT-IR capability using fingerprint as tool to make a first differentiation, representative fingerprint (1163.0-723.3 cm\(^{-1}\)) infrared spectra of two oils are shown in Figures 1(a) and 2(a). The major peaks in these spectra arise from stretching vibration of C-O at 1163.0 -1236.3 cm\(^{-1}\) and at 723.3 cm\(^{-1}\) represent (-CH\(_2\)), -CH=CH- overlapping of the CH\(_2\) rocking and the out of plane vibration of cis disubstituted olefins. As these changes in the spectral regions showed several changes during the oxidation process. The frequency of the 3007.0 cm\(^{-1}\) band depends on the oil composition as oil with high proportion of linoleic or linoleic acyl groups show higher frequency data at this band than oils with high proportion of oleic acyl group. The band at 2854 cm\(^{-1}\) and the shoulder at 2962 cm\(^{-1}\) increase their intensity but the band reduces its absorbance and increases percent transmittance.

The evaluated results of Mustard and Corn oils revealed that at the room temperature degree of unsaturation is low and there is trans hydroperoxides forms of esters present with primary oxidized products and as the sample treated at higher temperatures up to their respective boiling points with a piece of potato the decrease in %T indicates an increase in absorbance of peroxides. Secondary oxidation initiates the formation of secondary oxidation products and free fatty acids contents were also present. Thus each type of oil samples including fresh at room temperature and used (at different temperatures) showed very similar FT-IR spectra. However the heights of some specific bands were noticeable indicating the difference in quality of the two different oil samples used in this present study.
4. Conclusion

Deep frying and use of same oil for many times frying is a general practice mostly on commercial and sometimes in domestic cooking processes. This practice generates lipid peroxidation products that may be harmful for human health. Most of these compounds are non-volatile, so they remain in the frying medium and affect its physical properties at elevated temperatures in the presence of air and moisture causing the oxidative degradation of their amino acids and the partial conversion of these lipids to volatile chain-scission products, non-volatile oxidized derivatives and dimeric, polymeric or cyclic substances leading to the formation of toxic and/or carcinogenic compound.

The results of this particular study suggested that repeated heating gradually diminished the health-protective effects. As in Mustard oil at boiling point there is an additional peak at 3633.8 cm\(^{-1}\) which exhibits that the secondary oxidized product has been formed. The measurement of physicochemical properties by FT-IR spectroscopy, not only providing the benefit of rapid analysis but also avoiding the hidden disposal costs as well as the dangers associated with reagents used in the traditional chemical method. The present research may be forwarded in many aspects not only to enhance the quality of oil but also give public awareness not to expose edible oils to high temperature for long period for many times.

Acknowledgement

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<table>
<thead>
<tr>
<th>Properties</th>
<th>Corn Oil</th>
<th>Mustard Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/mL)</td>
<td>0.9223</td>
<td>0.9694</td>
</tr>
<tr>
<td>Viscosity (millipoise)</td>
<td>112.00</td>
<td>117.27</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>140.00</td>
<td>170.00</td>
</tr>
<tr>
<td>Saponification Value (mg)</td>
<td>153.8</td>
<td>125.6</td>
</tr>
<tr>
<td>Iodine Value (g)</td>
<td>15.96</td>
<td>8.10</td>
</tr>
<tr>
<td>Peroxide value (meq/Kg)</td>
<td>0.162</td>
<td>0.83</td>
</tr>
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</table>
Table 2
VISCOSITY, DENSITY AND PEROXIDE VALUES OF OILS AT BOILING POINT WITHOUT AND WITH FRYING WITH A PIECE OF FRESH POTATO FOR THREE TIMES USING SAME OIL.

<table>
<thead>
<tr>
<th>Trials At Boiling Point</th>
<th>Viscosity (millipoise)</th>
<th>Density (g/mL)</th>
<th>Peroxide Value (meq/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Corn Oil (B.P 140°C)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>At Boiling Point (Without Potato)</td>
<td>90.07</td>
<td>0.8632</td>
<td>0.538</td>
</tr>
<tr>
<td>1st Frying (With Potato)</td>
<td>90.60</td>
<td>0.8930</td>
<td>2.994</td>
</tr>
<tr>
<td>2nd Frying (With Potato)</td>
<td>92.24</td>
<td>0.8698</td>
<td>2.728</td>
</tr>
<tr>
<td>3rd Frying (With Potato)</td>
<td>94.36</td>
<td>0.8486</td>
<td>2.569</td>
</tr>
<tr>
<td><strong>Mustard Oil (B.P 170°C)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>At Boiling Point (Without Potato)</td>
<td>118.47</td>
<td>0.8764</td>
<td>0.388</td>
</tr>
<tr>
<td>1st Frying (With Potato)</td>
<td>121.60</td>
<td>0.8724</td>
<td>2.720</td>
</tr>
<tr>
<td>2nd Frying (With Potato)</td>
<td>120.25</td>
<td>0.8656</td>
<td>2.193</td>
</tr>
<tr>
<td>3rd Frying (With Potato)</td>
<td>115.10</td>
<td>0.8620</td>
<td>1.838</td>
</tr>
</tbody>
</table>
Figure 1 FT-IR SPECTRUM OF CORN OIL

a) At Room temperature (35 °C) b) Boiling Point c) First Frying d) 3rd Frying
Figure 2. FT-IR SPECTRUM OF MUSTARD OIL

a) At Room temperature (35 °C) b) Boiling Point c) First Frying d) 3rd Frying