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Assessment of Physico-Chemical Characteristic Deterioration of Lipids by FTIR Spectra for Successively Used Soy Bean and Sunflower Oils in Frying Spice Food Stuffs

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Abstract: *The quality of edible oils is an emerging factor to decide the quality of fried foods. Elevated temperature favours lipid oxidation. The edible oil is repeatedly used for deep frying at 190^0C to 200^0C, the physico-chemical characteristics of the edible oil get deteriorated. A critical evaluation of the degree of lipid oxidation and deterioration in the quality of oil is informative to use fried foods as hygienic or not. The present work mainly focused on the determination of the variation of peroxide value (PV) and p- anisidine value (p-AV) in correlation with FTIR spectra of frying oils used for frying chicken kebab and potato chips at $200^0C \pm 3^0C$ which contributes to the rancidity of frying oils. High peroxide value (soybean;20.96 meq / kg, sun flower; 21.05 meq / kg) and p- anisidine value(soybean; 0.15, sun flower; 0.16) with -OH stretching frequency 3470 $cm^{-1}$of hydro peroxide contributes to the lipid oxidation product (Hydro peroxide). When the same oil was used fourth or fifth frying, the fried chicken and potato chips become dark in colour and absorbed more oil which leads digestive offsets. In the same time, fried potato chips sustain more oil within it and get rancid soon. The physico-chemical characteristics and FTIR spectra of frying oils decide the quality of oil to use for frying or liable to discard.*

Keywords: *Edible oils, lipid oxidation, peroxide value, p-anisidine value, FTIR spectra.*

I. Introduction

Oxidative stability of oil and fat is mainly affected by processing conditions that imply the application of high temperature, oxidants, enzymes (such as lipoxygenase), moisture and light [1, 2]. The peroxide index is the most common parameter used to characterize oils and fats. A product with peroxide value between one and five meq/kg is classified at low oxidation state that between 5 and 10 meq / kg is classified at high oxidation state. To decide the quality of oil, the peroxide value is one of the parameter which could be determined iodometrically applying standard method [3]. The p-anisidine value measures carbonyl content in the oil and fat [3].The total oxidation value (TOTOX) ensures the oxidative deterioration of lipids. The TOTOX value is given by “2PV+p-AV” [4]. The oxidative stability of oil or fat can also be determined by recording the vibrational frequency of functional groups using FTIR spectrum [4]. A secondary oxidation product of oils and fats is determined by thiobarbituric acid (TBA) test [5]. The most widely used procedure employs the oxidative capacity of lipid (Hydro) peroxides to produce iodine from potassium iodide [6,7].

A detailed critical evaluation of methods for measurement of oxidative rancidity in vegetable oils was carried out by Marc Pignitter and Veronika Somoza [8]. Frying oils used continuously or repeatedly at high temperatures in the presence of oxygen from the air and water from the food being fried are subjected to a series of degradation reactions, producing a variety of decomposition compounds. Methods of chemical analysis of these decomposition compounds in deep frying oils are reliable [9]. Among the chemical methods, the measurement of total polar compounds (TPC) in frying oils is the most reliable and common method used [10]. The determination of carbonyl compounds (known as carbonyl value, CV) in frying oils is a very important chemical method for evaluating the quality of frying oils, because these compounds often contribute to rancid and unpleasant flavours, and reduce the nutritional value of fried foods [11]. However, these chemical methods are time consuming, costly and usually require reasonable analytical expertise. Among the several accelerated techniques most commonly used for assessment of the oxidative stability of edible fats and oils and fat-containing foods, the Rancimat test has gained acceptance because of its ease of use and reproducibility [12].

Lipid oxidation has a negative impact on the functionality of raw materials, sensory and nutritional quality of food, and causes economic losses [13]. The most noticeable result of lipid oxidation is the appearance of an unpleasant flavour often referred to rancid, which modifies the sensory characteristics of the food, so its assessment by the consumer [14-17]. Lipid oxidation also led to a change in colour and sometimes texture, as well as the loss of essential nutrients and micronutrients [16]. Finally, lipid oxidation can lead to the formation of potentially toxic oxidation products (oxycholesterol, malonaldehyde, endoperoxides, acrolein, polymeric peroxides) [17, 18]. Objective of the present work is to measure density, peroxide value and p-anisidine value in correlation with FTIR spectra of frying oils (soy bean and sun flower) on frying potato chips and chicken kebab. The same oil samples were repeatedly used five times for frying and determination has been carried out for each frying.

II. Materials And Methods

2.1. Chemicals:

The chemicals used are of analytical and HPLC grade. Glacial acetic acid (AR), Chloroform (AR), Potassium iodide (AR), Sodium thiosulfate (LR), Potassium dichromate (AR), Soluble starch (CP), Isooctane (HPLC) and Anisidine (AR). These chemicals are used to determine peroxide value and p- anisidine value.

2.2. Sample preparation:

Commercially available soy bean and sunflower oil from local market were purchased. The commercial sun flower oil and soy bean oil under study were heated to 190-200^{0}C for each determination on frying potato chips and chicken kebab. The oil samples were allowed to room temperature for determination of physico-chemical characteristics.

2.3. Physico-chemical Characteristics:

Density:

The densities (in g /ml) of commercial soy bean oil and sunflower oil were determined by viscosity method. The experiment was conducted using thermostat maintaining the temperature at 28^{0}C for frying oils and the variation of densities against number of frying times at frying temperature 200^{0}C was plotted.

Peroxide Value (PV):

PV (in meq / kg) was determined iodometrically according to standard method for the oil analysis. PV of the soy bean and sun flower oils were determined before and after frying and plotted against number of frying times.

P-Anisidine Value (p-AV):

The carbonyl content in oils was determined by standard method according to AOCS. It measures the reactiveness of the aldehydes carbonyl bond on the p-anisidine amine group forming a Schiff's base which absorbs at 350 nm. 2g (W) of each soy bean and sun flower oil was dissolved in 25 ml isooctane and absorbance A_1 was measured at 350nm against a blank isooctane. An aliquot (5ml) of this solution, respectively 5 ml of isooctane (as blank) was transferred to each of two test tubes of 10ml and 1ml anisidine solution (0.25% g/v glacial acetic acid) was added to each. After 10 minute the absorbance A_2 was measured at 350nm against isooctane containing p-anisidine. The p-AV is determined as; p-AV = 25 x 1.2 x (A_2-A_1) / W.

FTIR Spectra:

Nicolet- 5700 FTIR spectrophotometer was used to record IR spectrum. A small drop of oil sample was rubbed on KBr pellet under the specification Thermospectra-Tech, KBr disc 32x3mm drilled 7000-467.

III. Results And Discussion

Density of frying oils is a direct measure of the quality of edible oils. Densities of frying soy bean and sunflower oils are measured against the number of times used for frying are as shown in the Table 1. Frying temperature was fixed at 195-200^{0}C.

Table 1: Densities of soy bean and sun flower oils at frying temperature 200^{0}C

No. of frying times	0	1	2	3	4	5
Density of soy bean oil (g/ml)	0.9081	0.9301	0.9558	0.9751	0.9980	1.0312
Density of sun flower oil (g/ml)	0.9071	0.9285	0.9452	0.9672	0.9901	1.0180

The plot of density against number of frying times is given in the Figure 1, which explains the variation of density with rancidity. The gradual increase in density of frying oils with number of frying times justifies the presence of some added mass such as water molecules, carbonyls and polymerized product of oils. These molecules are responsible for rancidity of oils. As the result, rancidity varies with density.

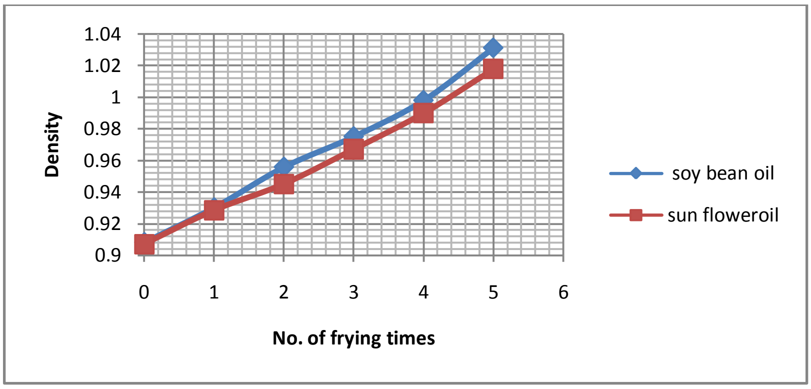

Figure 1: Densities of frying soy bean and Sun flower oils.

The peroxide value of soy bean and sun flower oils at frying temperature 195-200^{0}C was determined with number of frying times were recorded as shown in the Table 2. The variation in the peroxide value was plotted against number of frying times (Fig. 2).

Table 2: Peroxide Value of soy bean and sun flower oils at frying temperature 200^{0}C.

No. of frying times	0	1	2	3	4	5
PV of soy bean oil (in meq / kg)	1.72	4.52	8.23	13.42	16.12	29.96
PV of sun flower oil(in meq / kg)	1.81	4.63	8.41	12.98	16.56	21.05

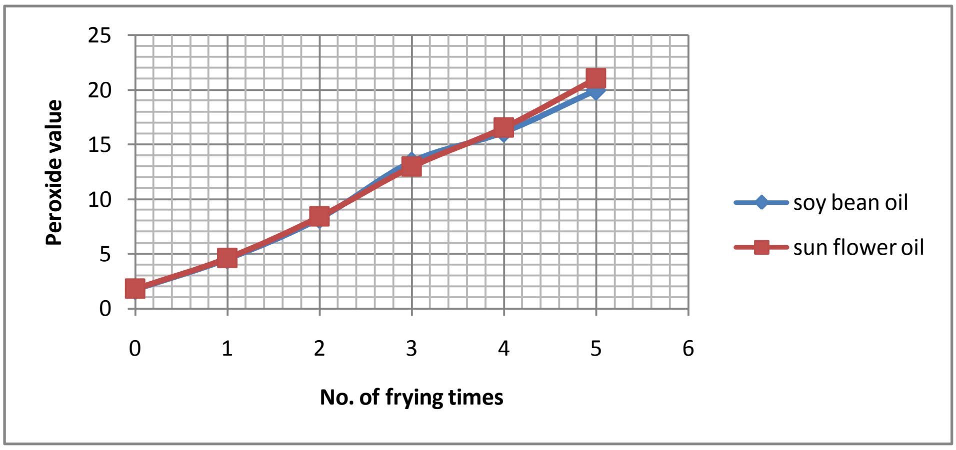

Figure 2: Peroxide Values of frying soy bean and Sun flower oils.

The plot clearly explains gradual increase of peroxide value with the number of frying times as shown in Figure 2. This increase is due to the formation of peroxide at double bond which on simultaneous cleavage results in formation of aldehydes and ketones.

The rancidity is a direct cause of carbonyls in turn the quality of foods will be affected. Thus as the number of frying times increases the deterioration in quality of potato chips and chicken kebab also increases.

Secondary oxidation can be measured by p-anisidine value. It measures high molecular weight saturated and unsaturated carbonyl compounds in triacylglycerols [4]. The range of p-anisidine values with number of frying times were listed in Table 3.

Table 3: p-Anisidine Value of soy bean and sun flower oils at frying temperature 200^{0}C.

No.of frying times	0	1	2	3	4	5
p-AV of soy bean oil(in meq / kg)	0.01	0.03	0.06	0.09	0.12	0.15
p-AV of sun flower oil(in meq / kg)	0.01	0.03	0.05	0.10	0.13	0.16

The plot of p-anisidine value against number of frying times shows gradual increase as indicated in the Figure 3. The rancidity is also increase in same trend. Successively used frying oils spoils the quality of potato chips and chicken kebab and imparts undesirable colour to the fried foods.

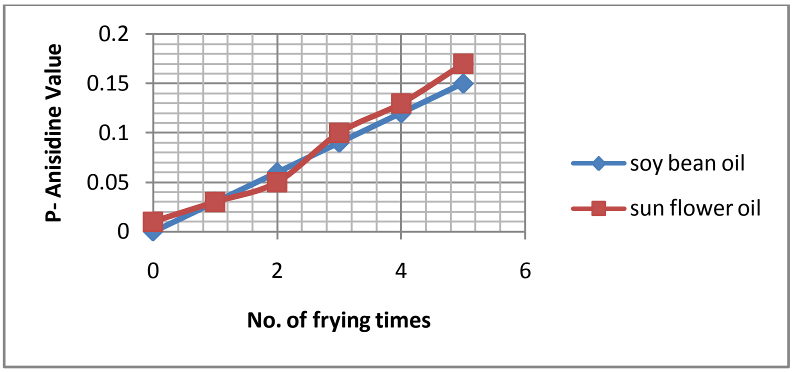

Figure 3: p-Anisidine Values of frying soy bean and Sun flower oils.

IR Spectra:

The IR- spectra clearly gives the frequency and percentage transmission of relevant functional groups frying oil samples. The spectra obtained have strong C-H absorption between 3010 and 2850 cm^{-1}. The Figure 4 clearly showed separate band with asymmetrical CH stretching (CH_2) at 2925 cm^{-1} and symmetrical C-H stretching (CH_2) at 2855 cm^{-1} with weak peak at 3008 cm^{-1} due to methylene asymmetrical stretching band. Frying oil samples gave strong bands at 1746, 1464 and 1163 cm^{-1} that corresponds to C=O (ester) stretching, C-H bending (Scissoring) and CO, CH_2 stretching, bending respectively.

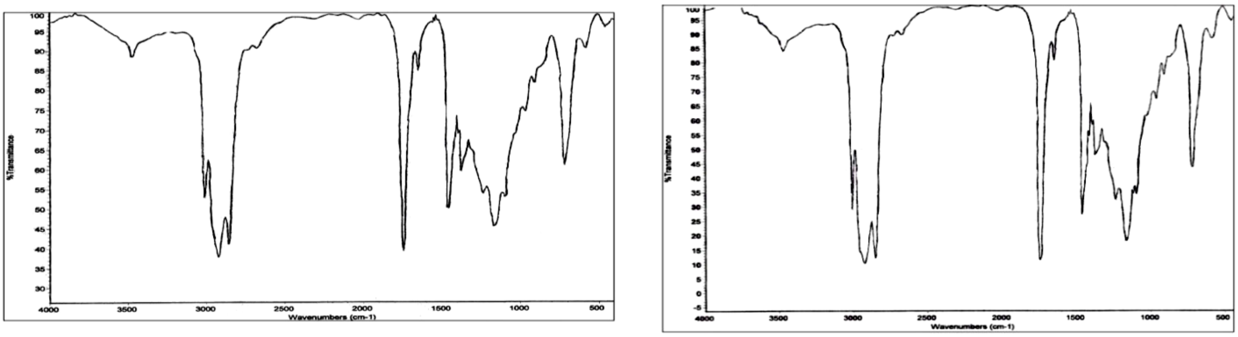

Fig. 4: IR spectra of sun flower oil and soy bean oil

Normally, the critical absorption bands associated with common oxidation end products from frying process could be observed in the region 3800-3200 cm^{-1}, -OH stretching region [19]. The peak at 3470 cm^{-1}has been reported to be associated with the -OH stretching frequency of hydro peroxide. On relating the frequency 3470 cm^{-1} with peroxide value and p-anisidine value, evidently clear that the quality deterioration of the frying oil samples. The high values of PV (soy bean; 29.96, sun flower; 21.05) and p-AV (soy bean; 0.15, sun flower; 0.16) were evidently proved by IR spectra.

IV. Conclusion

Based on the present results, the density, peroxide value and p-anisidine value in correlation with FTIR spectra of frying soy bean and sun flower oils are significantly increased during repeated use for frying. The physico-chemical oxidation of oils at frying temperature 200^0C was increased to more than 20 meq / kg which evidenced by FTIR spectra (3470 cm^{-1}). This attributes to the rancidity of frying oils. So, repeated usage of same frying oil for more than five times, the rancidity is notably increased. Thus, the increased rancidity spoils the quality of food and on eating such food causes many acute problems on health like diarrheal diseases, gastric, ulcer etc.

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