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Determination of Thermal Degradation in Palm Oil Using Viscosity and FTIR Analysis

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ABSTRACT

Fried food products have unique organoleptic and sensorial properties, including flavor, texture and appearance largely enjoyed by the customer. The high temperatures used during frying, in the presence of oxygen, induce chemical changes of the oils inevitably reducing their shelf life and affecting the quality of the fried food. Thermal degradation of edible oils occurs in three stages, related to the decomposition of polyunsaturated, monounsaturated and saturated fatty acids. In this work kinematic viscosity is measured for heated and unheated palm oil using Redwood viscometer. The oil is studied by heating it four cycles to frying condition and the variation of viscosity is measured from 30°C to 90 °C and it is noted that r square value ranges from 0.986 to 0.995 for the dependable parameter viscosity. The oxidative deterioration of the oils heated to 210°C for 0.5, 1, 1.5 and 2 hours is also studied. FTIR spectroscopy is used to non-invasively measure the degradation of frying oil caused by heating. It is an effective tool for the determination of the degree of saturation of heated and unheated palm oil.
Keywords: Kinematic viscosity, Redwood viscometer, thermal degradation, FTIR spectroscopy.

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INTRODUCTION

Oils and fats are an imperative part of the human diet and greater than 91% of worldwide production is used as food or as constituents in food products, Oil is considered as the highest basis of energy, that are nutritionally requisite and their purposeful and textural distinctiveness add to the flavors and adequacy of numerous natural and processed foods [1]. Oils start its fester from the instant they are extracted from their natural resources causing a unpleasant taste and smell.

Thermal degradation is the deterioration of the material by heat, characterized by molecular scission. It occurs at the temperature at which some components of the material separated and react with one another to modify the macro or microstructures of unsaturated fatty acids. Viscosity of vegetable oil increases with diverges in the chain lengths of triglyceride fatty acids and dwindles with raise in hydrogenation and oxidation, which exhibits its degree of saturation. Therefore it is implied that viscosity is a function of molecular dimension and orientation. Physical property like viscosity of pure triglycerides depends on the short chain length as the compounds interact among themselves [2].

Palm oil is a suitable vegetable oil extracted from the fruit of the palm tree. During 19^{th} to 20^{th} century palm oil was the second-most widely produced edible oil, after soybean oil. Palm oil is one of the 17 major oils produced and traded in the world today. The nutritional attributes of *trans*- fatty acids have been a subject of concern among food scientist, nutritionists and consumers. In natural vegetable oils, unsaturated acids are present in the *cis*-form. However during heating *cis*-unsaturated fatty acids are partly converted to *trans*-isomer. This *trans*- fatty acids affect cholesterol levels in much the same ways as saturated fatty acids [3].

Fried food is one of the inevitable and highly preferable diets in the home and industry, and the prolonged heating of oil for this purpose causes changes in its chemical and physical properties. Frying and heating at high temperature hastens the oxidative rancidity resulting thermal degradation with the production of composite like peroxides, free fatty acids and hydroxylic compounds which are very detrimental to human health [4]. During deep frying many volatile and non-volatile products are produced which are toxic. The Oxidative deterioration is directly related with the removal of double bond functional groups in fatty acids and lipids which are in superfluous nutrient in the development of human tissue [5].

Crude palm oil is considered the richest natural source of carotenoids (about 15 times more than in carrots). Antioxidant carotenoids are used as Vitamin A which enhances eye health of human body. Carotenoids also play an important potential role by acting as biological antioxidants, protecting cells and tissues from the damaging effect of free radicals, which could cause cancer [6]. Boiling the oil few minutes destroys the carotenoids. Studies also suggest that carotenoids enhance immune function by a variety of mechanisms, and improve cardiovascular health. Tocotrienols an antioxidant in the oil have been demonstrated to lower blood cholesterol levels, by reacting with certain enzymes in the liver which produces cholesterol. Its

antioxidant properties bring many benefits to the human body, such as preventing skin aging, preventing fat oxidation, reducing blood pressure and many more [7]. High dietary intake of oils and fats that consist of large amount of fatty acids that has more than one double bond accelerates the oxidation of lipoproteins that leads to Atherosclerosis, Hypertension, Coronary artery disease, stroke, etc., saturated fatty acids are converted into diacyl glycerol which alter colonic epithelial cells leading to colon cancer [8].

In the present work the study of the formation of saturated fatty acid composition of palm oil is studied using kinematic viscosity of oils that is observed before and after four cycles of heating to frying temperature and the structural changes are studied using FTIR spectrum analyses. Analytic and spectroscopic studies can be employed to evaluate degradation in oils subjected to intense heat.

MATERIALS AND METHODS

Materials

Refined as well as branded palm oil which is the most commonly used for cooking in South India, was purchased from the local commerce. Fifty milliliter of sample oil is placed in a copper beaker and heated by means of an electric heater and is stirred manually with glass rod. A microcontroller based temperature controller has been designed and is used to monitor the temperature of the sample oil. To mimic the oil oxidation process during frying, the sample is heated up to 210°C for five times.

Sample preparation for FTIR analysis

Perkin Elmer Fourier transforms infrared spectrometer with deuterated triglycin sulphate (DTGS) as a detector is used for the analysis. The liquid sample is placed between two KBr pellets with the help of capillary tube. Each pellet is made of 0.2mm thickness and it is placed in the path of the sample beam. The spectra are recorded from 4000 to 450cm^{-1}, the number of scans being 256 at a resolution of 4cm^{-1}. Scan speed is 0.20cm/s. Data acquisition and processing software spectrum for windows, Perkin Elmer.

Method

Redwood viscometer specification No.1 was selected as the standard viscosity measurement device to provide the actual kinematic viscosity of edible oil at different temperature. Redwood viscometer is based on the principle of laminar flow through capillary tube. The viscometer consists of an oil cup furnished with a pointer, which ensures a constant head and orifice at the center of the base of inner cylinder. The orifice is closed with a ball, which is lifted to allow the flow of oil during the experiment [1, 9]. The cylinder is surrounded by a water bath, which can maintain temperature of the liquid to be tested at required temperature. Electric heater heats the water bath. The cylinder, which is filled up to fixed

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height with liquid whose viscosity is to be determined is heated by water bath to the desired temperature. The orifice is opened and the time required collecting 50cc of oil is measured.

The kinematic viscosity is calculated from the following relation:

$$(\nu) = (A^* t - B/t) \times 10^{-4} \ m^2/s$$

A & B are constants.

The copper cup in the viscometer is washed with CCl_4 after each observation. Each reading is taken from the average of three trials.

RESULTS AND DISCUSSION

Behavior of unheated palm oil

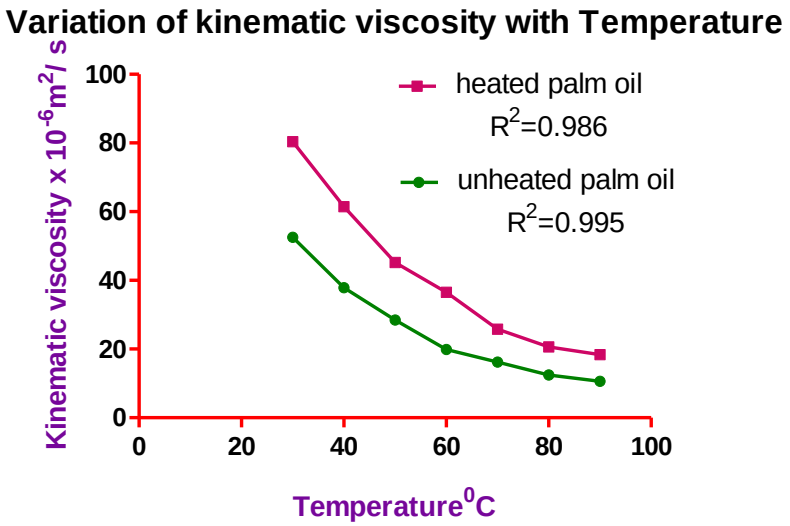

Figure 1: Variation of viscosity with temperature of palm oil

Figure 1 show the variation in kinematic viscosity of edible oils within the temperature range of 30°C to 90°C. Kinematic viscosity is premeditated from the redwood seconds in the step increase of 10°C using the above formula. From the graph it is experiential that the viscosity decreases with increase in temperature. The decrease is due to the elevated thermal movements amid molecules that reduce intermolecular forces, making surge among them easier and reducing viscosity. The presence of double bonds in fatty acid that exist in *cis* configuration form, produces "kinks" in the geometry of the molecules [10]. This prevents the chains coming close together to form intermolecular contacts, resulting in an increased capability of the oil to flow. The variation of viscosity of the unheated oils between the temperatures 30°C to 90°C is studied for heating and cooling and is found to be the same, to say that there is no degradation in this temperature range.

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Viscosity is correlated to related to the content of large amount of fatty acids that is made up of more than one double bond (polyunsaturated) compared to single double bond (monounsaturated) chains because of π bonds, which makes bonding more inflexible and decrease the rotation between C-C bonds [2, 11]. For low viscosity of the oil it has substantial large amount of polyunsaturated fatty acids. A more extended chain makes flow easier and viscosity smaller [12].

Behaviour of heated palm oil

Palm oil contains relatively high (50%) saturated fats (such as coconut oil) and thus semi-solid at room temperature [13]. To study about the degree of unsaturation of unheated and heated palm oil of household origin, which has been used for frying different types of food, are selected and characterized. Rheological behavior of palm oil after frying condition is studied from figure 1. It is found that viscosity of unheated oil is lesser than that of heated oil. It is known that certain properties of fatty acid residues in the molecule of triglycerol have important effects on the fluidity of the oil. Most of the bonds in the hydrocarbon chain of fatty acids are single bonds. The linear "zig-zag" organization of bonding nature in fatty acids facilitates the chains to be lined up close to each other and intermolecular Vander Waals force of interaction will take place [14]. This structure restrains the flow of oil, resulting in the relatively high viscosity of the oils.

Thermal degradation study of palm oil

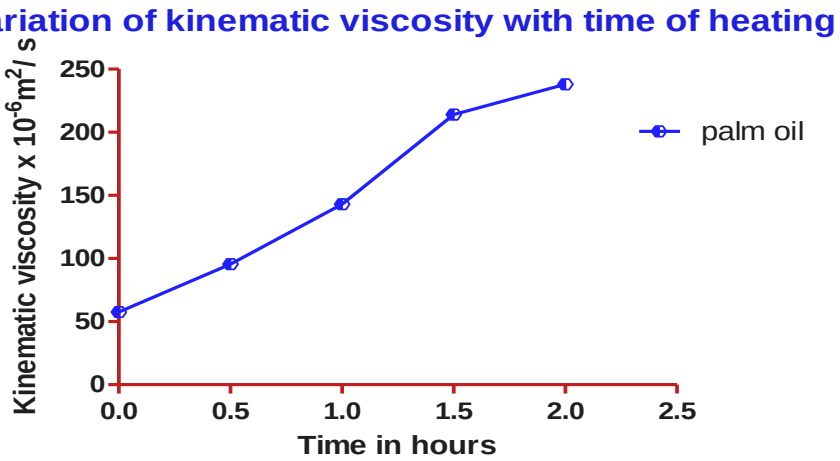

Figure 2: Variation of kinematic viscosity with time of heating

Heating the oil to the frying temperature up to 210°C for 0.5hr, 1hr, 1.5hrs, and 2hrs carries out the study of thermal degradation of the oil. After heating to preferred time, viscosity is calculated at room temperature. From figure 2, it is found viscosity increases with frying time. This might be due to oxidation and polymerization reaction that leads to degradation of oil. Oxidation reaction leads to the formation of carbonyl and hydroxyl groups bonded to carbon chain. This oxygen leads to the formation of hydrogen bonds that enhance intermolecular

forces, making flux among molecules to increase viscosity [2, 15]. During deep frying many volatile and non-volatile products are produced which are toxic. From the graph it is found that the effect of antioxidant decreases on four times of heating and then the viscosity increases sharply depending on saturation. The change in volume is caused by the compositional and structural changes of the fatty acids in the oil on repeated heating.

FTIR Analysis

FTIR provides a quick and accurate way of evaluating structural changes of edible oil subjected to intense heat, equivalent to that used in the preparation of food. The determination of unsaturation in oils makes it possible to classify them and evaluate their oxidative deterioration which is directly related with the degradation of polyunsaturated fatty acids in the lipids and which are indispensable nutrients in human tissue development [16].

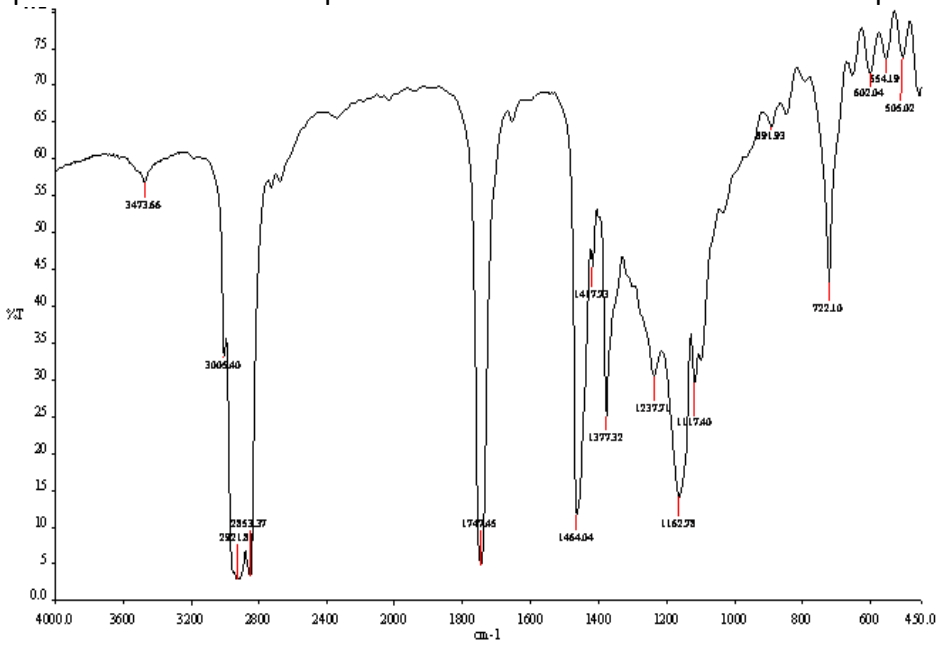

Figure 3 FTIR spectrum of unheated Palm oil

Unsaturated compounds are more chemically reactive than saturates. The double bonds can be broken and new atoms attached without disrupting the existing skeleton of the hydrocarbon. Fig.3 and Fig.4 shows the spectra of heated and unheated palm oil. Shift in transmission from 3473 cm $^{-1}$ to 3376 cm $^{-1}$ has been observed mention the formation of hydroperoxide band of the sample [17]. Band at 2920.27 and 2854.85 cm^{-1} appears after heating at elevated temperatures due to symmetric and asymmetric stretching vibration of CH_2 group [18]. Triglyceride esters and ketones have a strong absorption band at 1747.08cm^{-1} due to stretching vibration of carbonyl group [19]. A spectrum at 1417.78cm-1 is due to rocking vibration of CH bond. The 1634.90cm^{-1} band show C=C stretching vibration of *cis*-olefins [20]. Bands formed in the range of wave number 1300-1100cm^{-1} give the formation of ketones. Absorption at 892 cm^{-1}which is found in unused oil is absent in used oil shows the degree of saturation [21].

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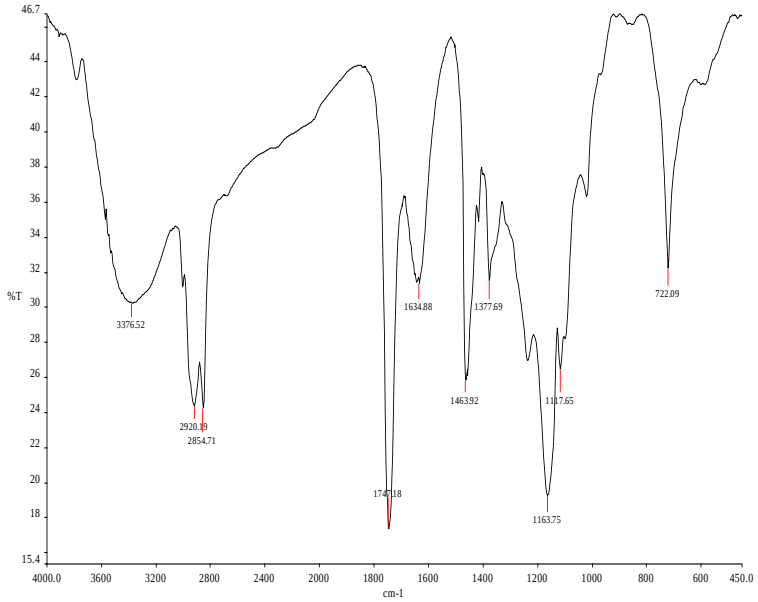

Figure 4 FTIR spectrum of heated Palm oil

Statistical analysis

Table 1: Regression coefficient for the measured parameter

Sample	R^2 value	F	Std error
Palm oil unheated	.9949	991	0.03201
Palm heated	.9859	473	0.080

Statistical analysis was made using software SPSS version 12. The data analysis is studied for the calculated viscosity (dependent) with rise in temperature (independent), as shown in Table 1. It is found that the exponential function to be the best curve fit with minimum error if the rsq value approach 1.It is noted that rsq value ranges from 0.986 to 0.995. The most important part of the result is F-ratio and the associated significance value. Larger the F-ratio larger would be the chance of occurrence. Therefore one can conclude that our regression model result is significantly better prediction of accuracy. Fig.1 shows the regression curve fit for the variation of viscosity with temperature.

CONCLUSION

Kinematic viscosity is measured for unheated and heated palm oil at the range of temperature 30°C - 90°C. The variation of viscosity at different temperatures can be used to indicate the changes in the composition of the oil on heating. The viscosity of heated oil is found to be greater than unused oil that shows the thermal degradation. They exhibit the Newtonian behaviour even after heating. The determination of unsaturation in oils makes it possible to classify them and evaluate their oxidative deterioration which is directly related with the degradation of polyunsaturated fatty acids in the lipids and which are indispensable

nutrients in human tissue. The variation in the structure is confirmed by FTIR analysis. The oil becomes dark, high viscous with unpleasant smell. Significant variation occurs in the physicochemical and structural (saturation and unsaturation) characteristics of palm oil which may affect the digestion capability of human, when they are repeatedly heated to frying temperature.

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