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A Study of rheological behavior and oxidative stability of rice bran and corn oil using FTIR spectra

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Abstract

In the food industry, rheological behavior and thermal degradation is the important parameters required to determine the quality and stability of food system. In this paper, the rheological behavior and thermal degradation of rice bran and corn oil, is investigated. Redwood viscometer is used to measure viscosity at various temperatures. A 16F88 microcontroller based temperature controller is designed to measure and to keep the temperature of the oil at the desired temperature. The rice bran and corn oil exhibit Newtonian behavior during heating and cooling in the temperature range 30º to 90°C.. The oils also exhibit Newtonian behavior even after heating to the frying temperature. A non-Newtonian characteristic is observed in sunflower oil due to rancidity that changes the complex chemical composition of oil. To characterize the cooking oils the structural study is carried out using FTIR spectra analysis and it is observed that the antioxidant activity is stronger in rice bran oil. The performance of Microcontroller based temperature controller is studied.

Keywords: rheology, Newtonian, non-Newtonian, thermal degradation, redwood viscometer, kinematic viscosity, FTIR, microcontroller.

Introduction

Rheology is defined as the study of the change in the form and the flow of viscosity, elasticity and plasticity. Rheological measurement is much useful behavioral and predictive information for product consistency and quality [1]. It also has important applications in engineering, geophysics, pharmaceutics and physiology. In particular, hemorheology, the study of blood flow, has an enormous medical significance. In engineering, rheology has had its predominant application in the development and use of polymeric materials. Temperature is an important parameter in the study of rheological behaviour [2]. In the food industry, viscosity is one of the most important parameters required to determine the quality and stability of food system. Edible oils represent one of the primary constituents in the formulation and manufacture of products by food industry [3]. Viscosity simply means the resistance of one part of the fluid to move relative to another one. Therefore, viscosity is closely correlated with the structural parameters of the fluid particles [1]. The oil viscosity has a direct relationship with some chemical characteristics of the liquids, such as the degree of unsaturation and the chain length of the fatty acids that constitute the triglycerides [4]. Viscosity slightly decreases with increased degree of unsaturation and rapidly increases with polymerization that led to the development of the idea to use edible oils as bio-diesel fuel [1]. When the oil is heated to the frying condition the unsaturation decreases and it becomes saturated due to oxidation. Edible oils are complex mixtures of many triglycerides with different chain lengths [4].

Oxidation is accelerated by exposure of heat, light, amount of oxygen available and humidity. The intense frying of oils causes an oxidizing thermal degradation with the formation of decomposition, such as aldehydes, ketones, free fatty acids and hydroxyl compounds that in high levels can be harmful to human health [5]. When the oil is heated to the frying condition the unsaturation decreases and it becomes saturated due to oxidation. Mid FT-IR spectra have been used to characterize edible oils and fats because it differentiates the intensity and the exact frequency at which the maximum transmission of the bands appears, according to the nature and composition of the sample [5]. Moreover infra red spectra show differences in the profile, maximum intensity and position of transmission bands according to the oil composition. Hence infrared spectral analysis is used to study the structural changes of edible oils [6].

Corn oil has 13% of unsaturated, 25.8%monounsaturated and 61.2% polyunsaturated fatty acids. This implies that a quantity of antioxidant essence in corn oil like propyl gallate, α-Tocopherol , β-sitosterol sterols – 1%, sitostanyl ferulate which lowers LDL, γ-oryzanol, ester of sterol 5 – 9%, free sterols -2.1% [7].gets evaporated. Rice bran oil is the oil extracted from the inner husk of rice. It is notable for its very high smoke point of 490° F (254° C) and its mild flavor, making it suitable for high-temperature cooking methods such as stir frying and deep frying. Rice bran oil contains a range of fats, with 47% of its monounsaturated, 37% polyunsaturated, and 20% saturated. The oil may also offer some health benefits, as it contains oryzanol, an antioxidant that help to prevent heart attacks; phytosterols, compounds believed to help lower cholesterol absorption; and relatively high amounts of vitamin E [8].

High dietary intake of polyunsaturated fatty acids increases 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. In this work the study of Newtonian and non-Newtonian nature of oils and its oxidative stability on heating is studied. An FTIR Spectroscopic method is employed to evaluate degradation in oils subjected to intense heat.

Experimental

Materials

Edible oils like rice bran and corn oils are purchased in local commerce.

Sample preparation for FTIR analysis

Perkin Elmer Fourier transform 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.

Method

The Redwood viscometer manufactured by Associated Instrument manufacturers India Private limited; New Delhi (India) is used for the measurements. Redwood viscometer specification No.1 and flow time of 30 to 2000sec is selected as the standard viscosity measurement device to provide the actual kinematic viscosity of edible oil at different temperature. Kinematic viscosity (ν) is defined as the ratio of absolute viscosity (η) to mass density. 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 can be lifted to allow the flow of oil during the experiment. The cylinder, is filled up to a fixed height with liquid whose viscosity is to be determined. The cylinder is surrounded by a water bath. To maintain the water bath at the desired temperature a dedicated PIC16F88 microcontroller based temperature controller is designed for the measurement and to control of temperature.

The Block diagram for the temperature controller is shown in Fig 1. The Temperature control hardware consists of K- type thermocouple, signal conditioning circuit, solid state power controller and PIC 16F88 microcontroller. The PIC16F88 microcontroller (18 pin DIP) in Block B is the heart of the measurement system that is a low power, high performance RISC CPU 8-bit microcontroller with 4 K Words of flash programmable and erasable memory and 368 bytes of RAM and 256 bytes of EEPROM. It has two 8-bit and one 16-bit timer/counters, two capture, comparators and pulse width modulation (PWM) modules, a full duplex serial port, 2 parallel ports, an on-chip oscillator, a programmable code protection, and a 7 channel 10- bit A/D converter. To measure the temperature of the sample a chromel alumel thermocouple in Block A is used. The emf generated by the thermocouple is amplified (gain 250) by an operational amplifier [Block A]. The analog temperature in the form of voltage is digitized by the inbuilt A/D converter in the microcontroller. Port A is used to get analog input voltages from the temperature sensor and to activate temperature control circuit. The solid-state power controller in block C is built with optocoupler (MOC3040), Triac (BT136) and other components are used to control the power of the electric heater in Block D . An LCD display is interfaced with the microcontroller through Port B to display the measured temperature. Keys are provided to give data to microcontroller. Software is developed in C language to initialize the ports, to read set temperature, to measure temperature, to display the temperature and to control the temperature of the sample liquid.

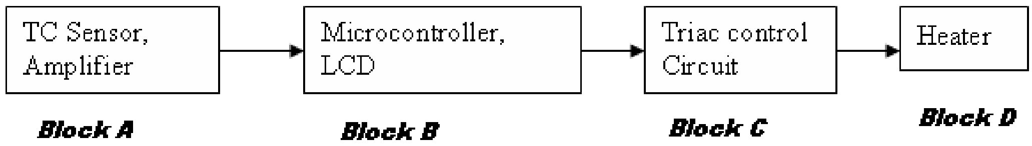

Figure 1 : Block Diagram of Temperature Controller

The copper cup in the viscometer is washed with CCl_4 after each observation. The sample is taken in the copper cup and after the desired temperature is maintained the orifice is opened and the time required for collecting 50cc of oil is measured. The experiment is repeated and the average of three trials is taken for measurement of time and kinematic viscosity is calculated using the following relation:

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

t = redwood time which measure the rate of flow in seconds.

A & B are constants

A = 0.0026 & B = 1.175 when, $t < 34$ and

A = 0.26 & B = 172 when, $t > 34$

To study the Newtonian behavior and non-degradation of oil, the sample is kept at various temperatures (in steps of 10°C from 30°C to 90°C) and the viscosity is measured during heating and cooling. To study of thermal degradation and non-Newtonian behavior, the sample is kept at 210° C (frying temperature) for the duration (1, 2, 3, 4 &5hrs.). After heating to desired time, viscosity of the sample is measured at 30°C

Results and Discussion

Fig.2. Shows the variation of kinematic viscosity of rice bran and corn oils with temperature and it is observed that the viscosity of oils decreases as the temperature increases. This is due to the high thermal movements among molecules reduces intermolecular forces, making flow 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 [1]. This prevents the chains coming close together to form intermolecular contacts, resulting in an increased capability of the oil to flow. The flow of oil is related to the concentration of polyunsaturated chains than monounsaturated chains because of π bonds, which makes bonding more rigid, decreasing rotation between C-C bonds [3]. For low viscosity of the oil it has appreciable amount of polyunsaturated fatty acids. A more extended chain makes flow easier and viscosity smaller. It is observed that the variation of viscosity of the oils between the temperatures range 30°C to 90°C is same for heating and cooling and

is found that there is no degradation and the oil has Newtonian behavoiur in this temperature range.

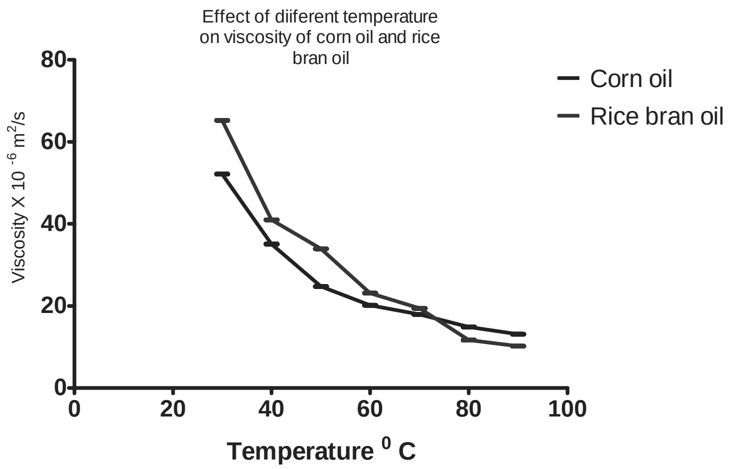

Figure 2 : Variation of viscosity with temperature

Thermal degradation of sunflower, rice bran oil and corn oil

The figure 3 shows the variation of viscosity with time to study of thermal degradation and non-Newtonian behavior of the samples. From the figure, it is seen that viscosity of corn and rice bran oil is almost constant with time whereas the viscosity of sunflower oil increases. The constant value of viscosity of corn and rice bran oil can be due to antioxidants in the oil that prevents oxidation and no saturation occurs with time. Antioxidants are molecules that slow or prevent the oxidation of other molecules. The increase in viscosity of sunflower with frying time shows that unsaturated hydrocarbons become saturated as the antioxidants get evaporated. Edible oil repeatedly used in frying is degraded by oxidative reaction with air and water. Oxidation leads to the formation hydrogen bonds that increase intermolecular forces, making flux among molecules that increases viscosity. Sunflower oil is not suitable for high temperature cooking because polyunsaturated fat would turn into *trans*- fats after cooking at high temperature [3]. The antioxidant tertiary butyl hydroquinone that is added to the oil gets evaporated on successive heating.

From the figure 3 it is observed that there is least variation in the viscosity of corn oil as it has higher composition of antioxidants. Heating to a very high temperature for long duration causes degradation in the oil due to high percentage of polyunsaturated fatty acids. Thermal degradation in the oil is further confirmed in FTIR analysis.

The flow rate of rice bran oil is also constant in fig.3, due to the large composition of antioxidants in the oil. It retains the Newtonian behavoiur of the oil. The percentage of polyunsaturated fatty acids is less compared to corn oil hence it shows less degradation of oil in FTIR analysis. The latest findings from Mohammad Minhajuddin, Ph.D., and colleagues, are reported in the May 2005 Food and Chemical

Toxicology journal. They show that total cholesterol levels in animals dropped by 42 percent, and LDL or "bad cholesterol" levels dropped up to 62 percent, after their diets are supplemented with a concentrated form of Vitamin E called tocotrienol rich fraction isolated from rice bran oil.

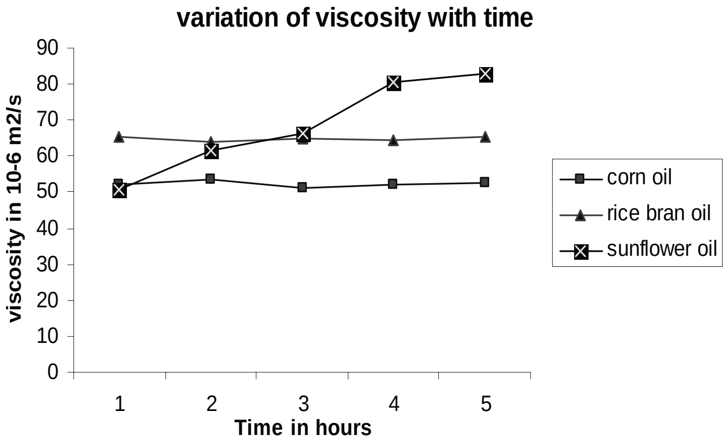

Figure 3 : Variation of viscosity with time

Structural analysis using FTIR

Fourier transform spectroscopy is a measurement technique whereby spectra are collected based on measurements of the temporal coherence of an irradiative source. It provides a quick and accurate way of evaluating thermal degradation 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.

FTIR spectrum of corn oil

Fig 4 shows the FTIR spectra of unheated corn oil. To study the thermal degradation the oil is heated for one hour and the process is repeated 5 timed and it is shown in fig.5. From the figures it is observed that the transmission at 3008, 2924, 2854, 1463, 1378, 1237, 1163, 1099, 722 cm $^{-1}$ exist. The presence of the same wavelength in both cases reveal that most of the compounds can maintain stability due to the presence of antioxidants Also it is observed from the fig 5 that the transmission 1417 cm $^{-1}$ 1746 cm $^{-1,}$ 3471 cm $^{-1}$ are changed due to partial thermal degradation of oil. The presence of transmission 1417 cm $^{-1}$ in Fig 5 may be due to rocking vibrations of -CH bonds of *cis* disubstituted olefins [9]. Also the broadening of transmission at 1746 cm $^{-1}$ in fig.5 is due to the production of saturated aldehydes functional groups or other secondary oxidation products that cause a transmission at 1728 cm $^{-1}$ that overlaps with the stretching vibration at 1746 cm $^{-1}$ of the ester carbonyl functional group of the triglycerides. This results correlate with the earlier reference [9]. When new carbonyls are formed from initial aldehydes and ketones compounds, the maximum absorbance is in the region between 1700 and 1726 cm $^{-1}$ resulting in a broadening of carbonyl region [9]. The 1651.57cm^{-1} band show C=C stretching vibration of *cis*-olefins [10]. It is also observed that the valley between 2925 and 2854 cm $^{-1}$ has found to be deepened during heating. This may be due to the change in the characteristic of oregano [11]. Shift in transmission from 3448 cm $^{-1}$ to 3471 cm $^{-1}$ has been observed. Hamed and Mousa A.Allam (2006) have mentioned that hydroperoxide band of the sample without antioxidant is much higher than that of sample containing antioxidants. In our present study, the hydroperoxide band showed increased transmission while heating. This possibly will be due to the loss of various antioxidants during heating. The transmission 915 cm $^{-1}$ has been formed due to –CH=CH_2 (in unsaturated fatty acids) out of plane bending [10]. Unsaturated bonds are reactive and new atoms attached without disrupting the existing skeleton of the hydrocarbon, though a large majority of lipids are fatty acid tri-esters of glycerol.

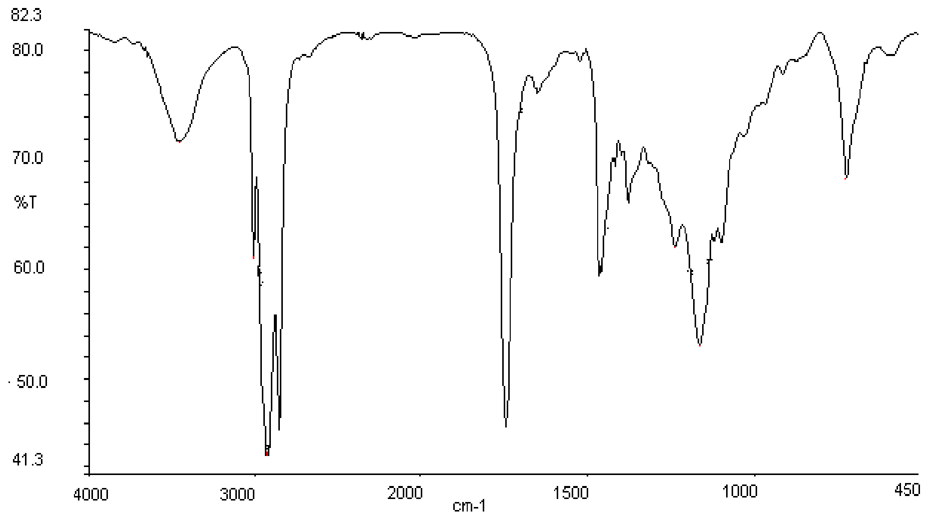

Figure 4 : FTIR spectra of corn oil (unheated)

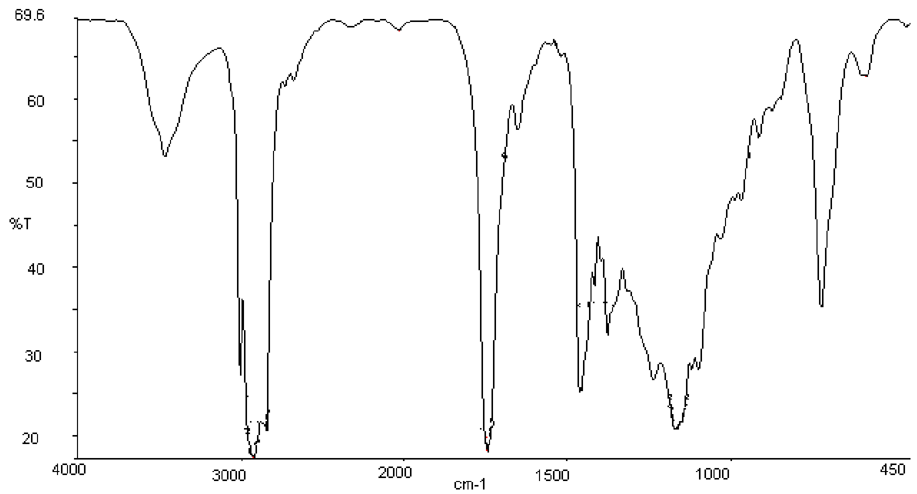

Figure 5 : FTIR spectra of corn oil (heated)

FTIR Spectrum of rice bran oil

Figs 6 and 7 show the FTIR spectra of unheated and heated rice bran oil. Almost all the transmissions are found to be the same. The decrease in transmission from 3465cm $^{-1}$ (fig.5) to 3432cm $^{-1}$ (fig.7) reveals the lack of formation of hydroperoxide [10]. This might be due to the presence of 2417ppm of antioxidants in RBO[8]. Transmission at 3008 cm $^{-1}$ shows the higher presence of Linoleic and linolenic acyl groups [5]. 2854 cm -1 has been formed due to symmetric and asymmetric stretching of $-CH_2$ group [11]. The broadening of 1743 to 1744 cm $^{-1}$ may be due to production of saturated aldehydes functional groups [9].

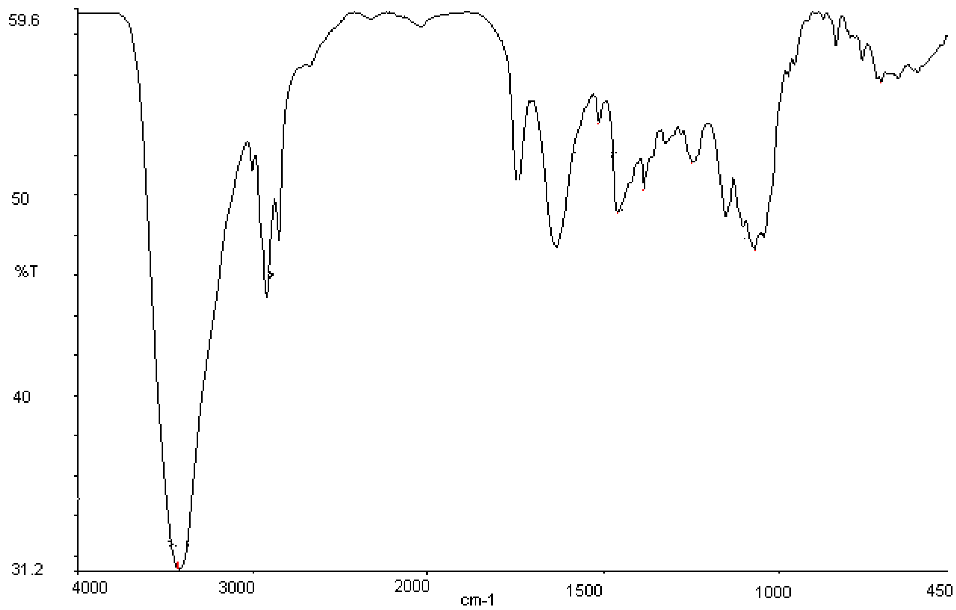

Figure 6 : FTIR spectra of rice bran oil (unheated)

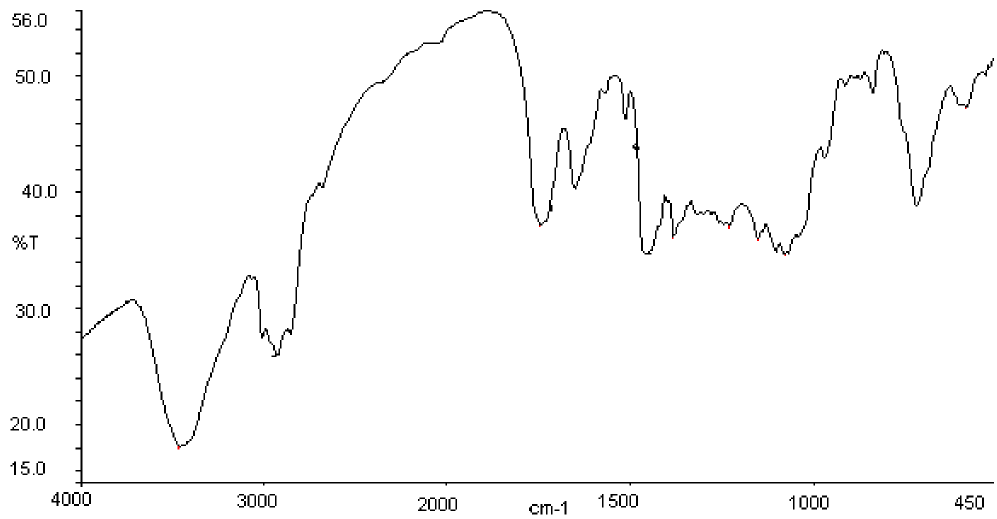

Figure 7 : FTIR spectra of rice bran oil (heated)

Conclusion

Kinematic viscosity is measured for the edible oils at different temperatures ranging from 30°C - 90°C. A low cost microcontroller based temperature controller is designed and fabricated for thermal degradation study of oils. The error in measurement of temperature is found to be less than 1%. The Study of viscosity with time for rice bran and corn oil reveals that they are Newtonian liquids in the temperature range (30°C - 90°C); Thermal degradation studies reveal sunflower is non-Newtonian at high temperature 210°C. FTIR studies show that corn oil has more structural change in the composition in the oils compared to rice bran oil. From the study of FTIR and viscosity measurement it is observed that rice bran is the best for deep-frying.

References

[1] Santos, J.C.O., Santos, I.M.G., & Souza, A.G., (2004). Effect of heating and cooling on Rheological parameters of edible vegetable oils. *Journal of food engineering,* 401 - 405.

[2] Abramovic, H., & Klofutar, C. (1998). The Temperature Dependence of Dynamic viscosity for some vegetable oil, Actat Chem. Slov, 69-77.

[3] Adolfo F.Valdes, Ana B.Garcia. (2005). Study of the evolution of the physicochemical and structural characteristics of olive and sunflower oil after heating at frying temperatures. *Food chemistry,* (8), 214-219.

[4] Arnold, R.G., & Hartung, T.E. (1971). Infrared spectroscopy determination of the degree of unsaturation of fats and oils. *Journal of food science, (*36), 166-168.

[5] Moya Moreno, M.C.M., Menndoza Olivares, D., Amezquita, F.J.,Gimeno Adelantado, J.V., Bosch Reig, F.(1999). Analytical evaluation of polyunsaturated fatty acids degradation during thermal oxidation of edible oils by FTIR *Journal of talanta, (50),* 267-275.

[6] Moya Moreno, M.C.M., Menndoza Olivares, D., Amezquita, F.J., Peris, V., Bosch Reig, F., (1999).Study of the formation of carbonyl compounds in edible oils and fats by H-NMR and FTIR. *Journal of molecular structure,* 557-561.

[7] Hui, Y.H., *Bailey's Industrial oil & Fat Products.* (Vol 2), *Edible oil & Fat Products*, 603-675.A Wiley- Interscience Publication, New York.

[8] C. Rukmini and T. C. Raghuram, Nutritional and Biochemical Aspects of the Hypolipidemic Action of Rice Bran Oil: A Review. Jour. of the ACN. 10(6) (1991) 593.

[9] Hamed S F and Mousa A.Allam, Application of FTIR Spectroscopy in the determination of antioxidant efficiency in sunflower oil, JASR, 2(1), 27 – 33, 2006.

[10] Jag Mohan, (2001) *Organic spectroscopy principles and applications,* (2nd ed., pp29-95). Narosa Publishing House. New Delhi.

[11] N. Vlachos, Y. Skopelitis, M. Psaroudaki, V. Konstantinidou, A. Chatzilazarou and E. Tegou, Application of Fourier Transform Infrared Spectroscopy to edible oils, Analytica. Chemica. Acta, pp. 573-574, (2006) pp. 459-465.