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Study of Rheological Behaviour and Thermal Degradation in Vegetable Oils on Heating

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Study of viscosity of vegetable oils is an important engineering parameter for designing processing equipment. The rheological and thermal degradation in unheated and heated rice bran oil, mustard oil, sesame oil and groundnut oil is studied as a function of temperature (30 to 90 ºC) using temperature controlled redwood viscometer. The viscosity decreased with increasing temperature at different rates depending on the saturated and unsaturated fatty acid composition of the oils. Some experimental relations that describe the temperature dependence of viscosity are fitted to experimental data and correlation constants are studied. The amount of polyunsaturated chains is better correlated ($R^2 = 0.896$) with viscosity than monounsaturated chains. The content of unsaturated fatty acids has good correlation ($R^2 = 0.867$) with viscosity than saturated fatty acids ($R^2 = 0.747$) for unheated oils and heated oils. It is observed that the viscosity of heated (to smoke point 210 - 250 ºC) oil sample is greater than unheated oil due to increase in the content of saturated composite in the oil on heating.

Key Words: Vegetable oils, Viscosity, Thermal degradation, GC-MS.

INTRODUCTION

In food industry and processing applications, the physical properties of foods play an important role in the analysis of quality, process, design and fabrication of processing equipment. Vegetable oils undergo extensive oxidative deterioration due during deep frying, storage, marketing and hydrogenation[1]. The main factors influencing the entity of these transformations are represented by the temperature of the treatment, the nature of foods being fried, the presence of metals that catalyze the oxidation phenomena and the composition of the frying oil[2]. It is known that fats and oils, when subjected to prolonged heating for frying, are subjected to a series of physico-chemical modifications, the effects of which can be observed in the variation of the sensory and nutritional characteristics[3]. Hydro-peroxide is the major oxidation product, decomposes to secondary products, such as esters, aldehydes, alcohols, ketones, lactones and hydrocarbons[4]. These secondary products adversely affect flavour, aroma, taste, nutritional value and overall quality of foods[3]. These heated oils get biologically degraded before disposal.

Physical parameter of vegetable oils like viscosity is essential for designing processing system in food industry[5]. In vegetable oils, viscosity increases with chain lengths of triglyceride fatty acids and decreases with unsaturation (monounsaturated or polyunsaturated fatty acids) composition in the oil[6]. Change in the fatty acid composition on heating changes the physical property, which is necessary to predict processing variation, predict processing equipment and thermal degradation in oils[7]. Hence viscosity is a function of molecular dimension and orientation used to estimate the quality deterioration in the oil that causes great economic losses to the food industry[8,9]. Viscosity is the marker of thermal degradation is also an index for thermal stability of antioxidants in edible oils[10].

In present study the viscosity of unheated and heated rice bran oil, mustard oil, sesame oil and groundnut oil is measured using microcontroller based instrument in the temperature range[11] from 30 to 90 ºC. From the variation of viscosity with temperature the thermal degradation in the heated oil with respect to unheated is studied. Empirical relations that relates kinematic viscosity and temperature is used to find the coefficient R^2, variance and standard error. The relationship between the viscosity and fatty acids for heated and unheated oils using GC-MS results are also premeditated.

EXPERIMENTAL

Commonly available and popular branded rice bran oil, sesame oil, groundnut oil and mustard oil has been collected from a local grocery shop located in Thanjavur district of Tamilnadu, India to assess the thermal effect and possibility of usage of repeatedly heated oil by the society. To get sample for heated oils 100 mL of sample has been placed in a copper beaker and heated on an electric device, stirring manually with glass rod. A microcontroller based temperature controller has been designed and has been used to monitor the sample temperature. To mimic the oil oxidation process during frying, the sample has been heated up to 250 ºC for five times. In order to ensure that the sample has been heated to the temperature greater than its smoke point, it has been exposed to successive heating.

Microcontroller based the redwood viscometer is used to measure the viscosity in Laminar flow method. The microcontroller based instrument is used to measure temperature and time taken for the collection of 50 cc of sample[11]. The temperature is maintained by a temperature controller which has a very good accuracy of ± 1 % of error. The kinematic viscosity is calculated from the following relation:

$$(\nu) = (A^* \, t - B/t) \times 10^{-6} \ m^2/s \qquad (1)$$

where, A and B are constants that are calculated from the diameter and height of the orifice; t = redwood time, which measure the rate of flow in seconds. When t > 34, A = 0.26 and B = 172.

The redwood seconds were ramped from 50 to 250 s at temperatures of 30 to 90 ºC. The copper cup in the viscometer is washed with CCl_4 after each observation. Each reading is taken from the average of three trials.

For the fatty acid compositional variation determination, an Agilent gas chromatograph from Hewlett-Packard (Palo Alto, CA, USA) equipped with a HP 5971 MS detector was used. Separations were carried out on an Agilent-Hewlet Packard fused silica capillary column HP-5 (30 m × 0.25 mm I.D. column coated with a 0.25 µm film thickness) (Folsom, CA, USA). The GC-MS interface temperature was maintained at 250 ºC. 1 µL of both heated and unheated oil samples were injected manually in splitless mode with injector port temperature at 250 ºC. The helium carrier gas flow rate was 1 mL/min. The column temperature program was as follows: 95 ºC held for 1 min, 12 ºC min^{-1} to 150 ºC, held for 1 min, 2 ºC min^{-1} to 230 ºC, held for 3 min, 10 ºC min^{-1} to 250 ºC, held for 25 min. The selective ion mode was used in the analysis. Mass charge range was between 50-500 amu. Oven temperature programmed to 50-250 ºC.

RESULTS AND DISCUSSION

The variation of viscosity of unheated and heated rice bran oil, mustard oil, groundnut oil and sesame oil with temperature are depicted in Figs. 1-4. It is observed that the viscosity of oils decreases with increase in temperature. This is due to the high thermal movements among molecules reducing intermolecular forces, making flow among them easier and reducing viscosity. The presence of double bonds in fatty acid that exist in *cis* configurational form, produces kinks in the geometry of the molecules[7,12]. This prevents the chains coming close together to form intermolecular contacts, resulting in an increased capability of the oil to flow[13].

Fig. 1 shows the variation of viscosity of unheated oil and heated rice bran oil in the temperatures range of 30 to 90 ºC. It is observed at 30 ºC, the viscosity of heated oil is 45 % greater than unheated oil, whereas at 90 ºC the viscosity varies by only 6 % that exemplify the thermal degradation in the oil is low and antioxidant stability is appreciable. Fig. 2 shows the change in viscosity of heated mustard oil is 24 % greater than unheated mustard oil at 30 ºC, the variation at 90 ºC is nearly 30 %, which do not show much variation and support its antioxidant activity. Fig. 3 illustrates the difference between the viscosity of unheated groundnut oil and heated groundnut oil at 30 ºC is found to be 25 % and it increases to 35 % at 90 ºC. Fig. 4 confirms the variation in viscosity of unheated sesame oil and heated sesame oil. The modification at 30 ºC is found to be 41 % whereas at 90 ºC it is 55 % shows degradation in the oil.

On comparing the viscosity change at 90 ºC, mustard oil, groundnut oil and sesame oil shows more difference between unheated oil and heated oil than rice bran oil. This exemplifies that the percentage of thermal degradation in the oils. The viscosities at 30 ºC are about to the maximum of 6-fold greater than those at 90 ºC. This disparity produce significant effect on the power required to pump the oil at desired temperatures as well as in choosing pipe of definite radius.

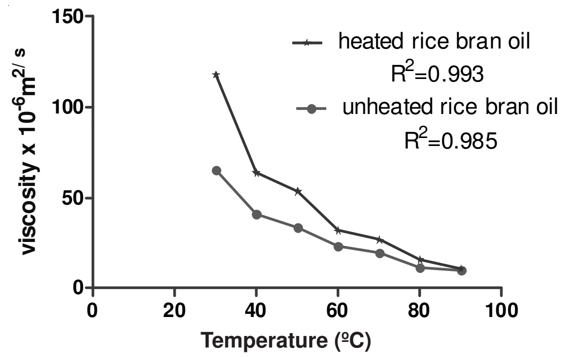

Fig. 1. Variation of viscosity of rice bran oil with temperature

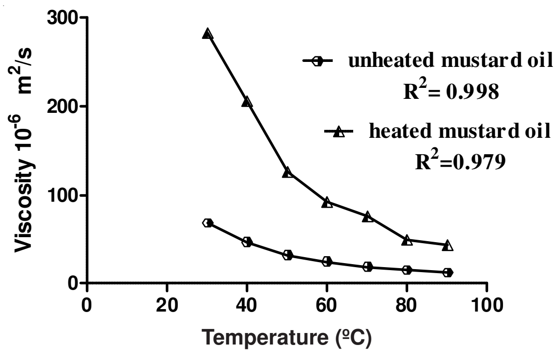

Fig. 2. Variation of viscosity of mustard oil with temperature

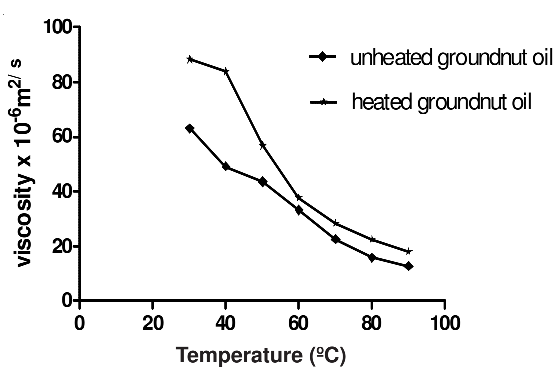

Fig. 3. Variation of viscosity of groundnut oil with temperature

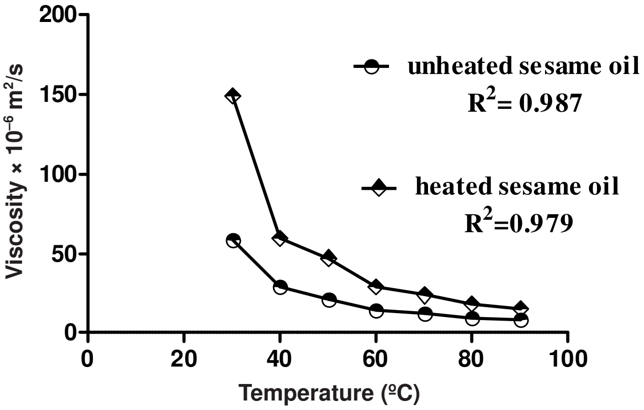

Fig. 4. Variation of viscosity of sesame oil with temperature

The changing of viscosity with temperature relation is modeled using eqns. 2-4. Eqn. 2 is the Arrhenius model where viscosity varies exponentially with temperature. This is used by the researchers to characterize Newtonian and non-Newtonian liquids[14]. Eqn. 3 shows viscosity relationship in power law model. The logarithmic variation of viscosity with temperature is given in Williams-Landel-Ferry model eqn. 4.

Arrhenius model:

$$\eta = A\exp\left[E/\left(T - T_0\right)\right]$$

$$\eta = A\exp\left[E_a/RT\right] \quad (2)$$

where, E_a in the equation is the activation energy with unit kJ/kg, R is universal gas constant (8.314 kJ/kg mol K), T is absolute temperature ºC and A is a pre exponential constant.

(i) Power law model:

$$\eta = C\left(T - T_{ref}\right)^n \quad (3)$$

where, C and n are constants, T_{ref} is the value of reference temperature 273 K.

(ii) Modified Williams-Landel-Ferry model:

$$\ln\left(\eta\right) = \frac{pT}{q + T} \quad (4)$$

where, p and q are the constants. Constants A, C, n, p and q in eqns. (2-4) were calculated using nonlinear regression procedure the values of the constants are illustrated in Tables 1-3.

The quantities of saturated fatty acids and unsaturated fatty acids are calculated from the results obtained using GC-MS analysis[15]. Fig. 5 shows the variation of viscosity with unsaturated fatty acids of unheated oils. The correlation between

TABLE-1
EXPONENTIAL (ARRHENIUS MODEL) FUNCTION

Oil sample	Specifications	R^2	Significance	Constants		SEE
				A	Ea	
Rice bran oil	Unheated	0.999	0.0001	161.9	31.9	0.080
	Heated	0.993	0.0004	150.1	25.2	0.109
Mustard oil	Unheated	0.995	0.0000	172.5	36.4	0.065
	Heated	0.996	0.0000	198.5	38.6	0.050
Ground nut oil	Unheated	0.989	0.0000	180.2	35.3	0.054
	Heated	0.993	0.0001	187.0	34.3	0.084
Sesame oil	Unheated	0.998	0.0000	169.7	35.8	0.037
	Heated	0.999	0.0002	161.1	31.50	0.037

TABLE-2
POWER LAW MODEL

Oil sample	Specifications	R^2	Significance	Constants		SEE
				k	n	
Rice bran oil	Unheated	0.986	0.0009	353.75	-0.576	0.072
	Heated	0.974	0.0021	282.71	-0.452	0.097
Mustard oil	Unheated	0.988	0.0001	436.36	-0.664	0.037
	Heated	0.993	0.0009	692.69	-0.699	0.053
Ground nut oil	Unheated	0.959	0.0165	468.519	-0.623	0.021
	Heated	0.976	0.0002	546.558	-0.614	0.094
Sesame oil	Unheated	0.991	0.0004	407.312	-0.646	0.055
	Heated	0.992	0.0002	349.224	-0.567	0.053

TABLE-3
LOGARITHMIC (WLF) MODEL

Oil sample	Specifications	R^2	Significance	Constants		SEE
				a	b	
Rice bran oil	Unheated	0.982	0.0000	100.71	-0.0198	0.063
	Heated	0.967	0.0000	97.69	-0.0101	0.057
Mustard oil	Unheated	0.996	0.0000	107.41	-0.0253	0.047
	Heated	0.989	0.0000	113.41	-0.0169	0.042
Ground nut oil	Unheated	0.977	0.0000	115.92	-0.0209	0.054
	Heated	0.980	0.0000	107.29	-0.0135	0.053
Sesame oil	Unheated	0.983	0.0000	113.307	-0.0278	0.038
	Heated	0.985	0.0000	107.614	-0.0316	0.033

monounsaturated fatty acids and viscosity is less than that of polyunsaturated fatty acid (PUFA) for the correlation is R^2 = 0.896 a more extended chain makes viscosity smaller and flow easier[16]. Fig. 6 shows the variation of viscosity with saturated fatty acid and unsaturated fatty acid and it is observed unsaturated fatty acids are highly correlated with viscosity ($R^2 > 0.87$) than saturated fatty acids which characterizes the chain length of fatty acids. The viscosities of oils are better related to the concentration of polyunsaturated (more than one double bond) chain length than to monounsaturated fatty acids (has only one double bond) like oleic acid. This is due to the increase in the amount of π bonds that makes bonding more rigid by decreasing rotation between C - C bonds[6,17]. The viscosity is negatively correlated with polyunsaturated fatty acid shows decrease in viscosity due to the presence of unsaturated fatty acids like linoleic acid of this type as the unsaturation increases. Fig. 7 indicates the disparity of viscosity of heated oils with fatty acid composition calculated from the analysis. It is found from the result of correlation analysis ($R^2 << 1$) between viscosity of heated oil with the amount of saturated fatty acids, which is very poor. Thus the thermal degradation in mustard oil and groundnut oil is substantiated.

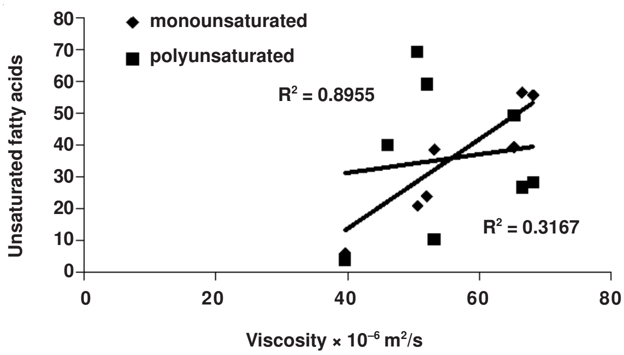

Fig. 5. Variation of viscosity of unheated edible oil with unsaturated fatty acids

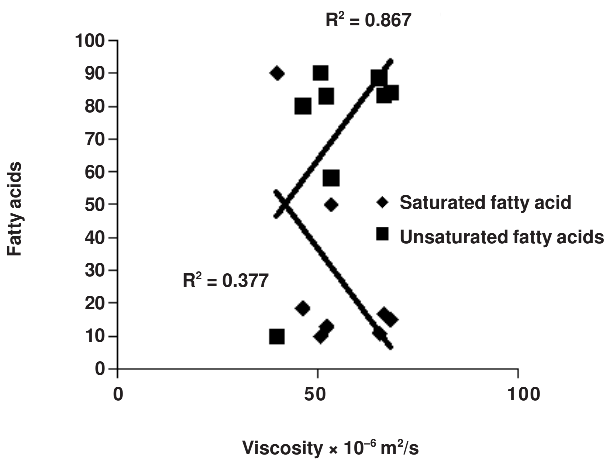

Fig. 6. Variation of viscosity of unheated edible oil with fatty acids

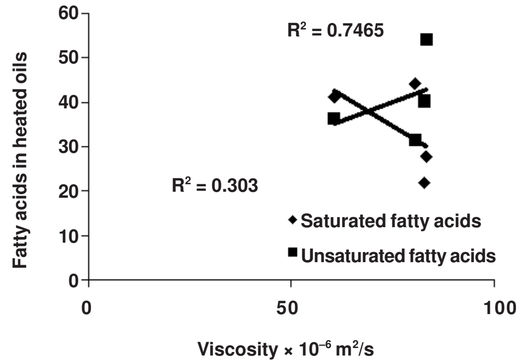

Fig. 7. Variation of viscosity of heated edible oil with fatty acids

Conclusion

The variations of viscosity with temperature of unheated oil and heated oil are studied and thermal degradation is found to be occurred more in mustard oil and groundnut oil compared to rice bran oil and sesame oil. The increase in viscosity of oil submitted to frying condition may be due formation of undesirable compounds caused by polymerization reaction. The study of variation in viscosity with temperature is found to fit more in Arrhenius model which can help to predict viscosity at any temperature within the range. The GC-MS analysis confirms the change in viscosity is due to the composition of more percentage of polyunsaturated fatty acids and increase in viscosity due to saturated fatty acids. From the correlation analysis it is observed that there is increase in the saturation of compounds in the oil on heating.

REFERENCES

1. F.T. Orthoefer, in ed.: Y.H. Hui, Vegetable Oils, in Bailey's Industrial Oil and Fat Products, 5th edn., Vol.1, John Wiley & Sons, New York (1996).
2. M.C.M.M. Moreno, D.M. Olivares, F.J. Amezquita, J.V.G. Adelantado and F.B. Reig, *Talanta*, **50**, 267 (1999).
3. M.C.M.M. Moreno, D.M. Olivares, F.J.A. Lopez, V.P. Martinez and F.B. Reig, *J. Molecul. Struc.*, 557 (1999).
4. Y.H. Hui, Bailey's Edible oil & Fat Products, Vol 2, A Wiley-Interscience Publication, New York (1996).
5. F.A. Valdes and A.B. Garcia, *Food Chem.*, **8**, 214 (2005).
6. J.C.O. Santos, I.M.G. Santos and A.G. Souza, *J. Food Eng.*, **67**, 401 (2004).
7. H. Abramovic and C. Klofutar, *Acta Chem. Slov.*, **45**, 69 (1998).
8. O.O. Fasina, H. Hallman, M. Craig Schmidt and C. Clements, *JAOCS*, **83**, 899 (2006).
9. A. Srivastava and Prasad, *Indian J. Chem. Tech.*, **8**, 473 (2001).
10. S.R. Valantina, P. Neelameagam and K. Gayathri, *Asian J. Chem.*, **21**, 4325 (2009).
11. P. Neelameagam, S.R. Valantina and K. Muruganantham, *Sens. Transducers*, **3**, 45 (2009).
12. D.B. Min and E.O. Choe, *J. Food Sci. Biotech.*, 582 (2003).
13. M.A. Rao, *J. Tenure Studies*, 135 (1997).
14. A. Mukherjee, S. Bhattacharyya and B. Bagchi, *J. Chem. Phy.*, **116**, 4577 (2002).
15. W.W. Christie, Gas Chromatography and Lipids, The Oily Press Ltd., Dundee, Scotland, (1989).
16. A.H.A. Tarmizi and R. Ismail, *J. Am. Oil Chem. Soc.*, **85**, 254 (2008).
17. E. Choe, J.Y. Lee and D.B. Min, in ed.: C. Akoh. Chemistry of Oxidative Stabilities of Edible Oils, Healthful Lipids, Am. Oil Chem. Soc. Press, Champaign, IL, USA, pp. 558-590. (2005).