Regular Article

PHYSICAL CHEMISTRY RESEARCH
Published by the
Iranian Chemical Society
www.physchemres.org
info@physchemres.org

Phys. Chem. Res., Vol. 8, No. 3, 417-427, September 2020
DOI: 10.22036/pcr.2020.221177.1737

Viscosity-Temperature Stability, Chemical Characterization, and Fatty Acid Profiles of some Brands of Refined Vegetable Oil

M. Abdul-Hammed[a,*], S. Adewale Adegboyega[a], I. Abdulwahab[a] and A. Olakunle Jaji[a,b]

[a]*Department of Pure and Applied Chemistry, Ladoke Akintola University of Technology, Ogbomoso, Nigeria*

[b]*Department of Science Laboratory Technology, Kwara State Polytechnic, Ilorin, Nigeria*

(Received 30 January 2020, Accepted 28 March 2020)

Oils of vegetable origin are of great importance in food, soap, and cosmetic industries which are sometimes used as lubricants and raw materials for biodiesel production depending on their viscosity and thermal stability. This work provides insight into the fatty acid components, physicochemical properties and thermal stability of some refined vegetable oils. The Saponification values, peroxide values, acid values, iodine values and refractive index of these oils range from 185.38 to 209.26 mg g^{-1} KOH, 2.00 to 37.00 meq O_2/kg, 2.50 to 5.50 mg KOH/g, 31.09 to 89.46 g/100g and 1.441 to 1.488, respectively The activation energies obtained from Arrhenius-type equation vary from 11.32 to 3.85 kJ mol^{-1}, while the enthalpy ($\Delta H^{\#}$) and entropy ($\Delta S^{\#}$) of activation obtained from Eyring-type equation range from 6.852 to 14.317 kJ mol^{-1} and -31.85 to -29.06 J mol^{-1} K^{-1}, respectively. The Gibbs free energy of activation ($\Delta G^{\#}$) ranges from 15.51 to 23.81 kJ mol^{-1}. The P_w oil brand has the highest thermal stability and resistance to shear stress due to its high activation energy and a low degree of unsaturation. The heat was absorbed during the process, the reaction mechanism was associative and the entire process was non-spontaneous.

Keywords: Viscosity, Fatty acids, Eyring-type equation, Arrhenius-type equation, Activation energy

INTTRODUCTION

Studies have shown the functional health benefits of vegetable oils as a result of their components ranging from several oil-soluble vitamins, essential fatty acids, phytonutrients, antioxidants, antimicrobial and antibacterial activities. These oil components are useful for immune regulation and prevention of various diseases and the oils serve as surpassing source of energy when compared to carbohydrates and proteins which are also important constituents of our diets [1-3].

The compositions and operating temperature of a particular vegetable oil dictates the physical and chemical properties of such oil as well as the quality of the oil for human consumption [4-6]. Oils exposed to high temperatures might encounter peroxidation after a long period, and the consequences of this could be to induce oxidative stress in endothelial cells when such oils are consumed [7,8]. Similarly, presence of excess polar compound in the frying oils which are reused repeatedly could result in high risk of hypertension when consumed, it could also raise the total lipid serum with low lipoprotein density [9,10]. The main focus of this work is to investigate the stability of brand vegetable oils which are commercially available by studying their thermophysical and physicochemical properties. Therefore, physical and chemical properties, temperature stability, viscosity as well as and the fatty acid compositions of the vegetable oils were investigated.

*Corresponding author. E-mail: mabdul-hammed@lautech.edu.ng

MATERIALS AND METHODS

Sample Collections

Seven different brands of commercial vegetable oils (G_n, P_w, M_d, L_d, B_m, K_g and G_y with brand names Gino, Power, Mamador, Lahda, Bimoli, Kings and Goya oils respectively) were purchased from different supermarkets within Ogbomoso; Nigeria (Latitude 8°8′N, Longitude 4°16′E) and Lagos metropolis, Nigeria (Latitude 6°35'N, Longitude 3°45'E). The oils were stored at room temperature in a dark cupboard to prevent exposure to light before usage.

Analysis of Chemical and Physical Properties of the Oils

Chemical analysis. Determinations of saponification value, peroxide value, free fatty acid, and iodine value for the seven samples were carried out using AOAC methods.

Saponification value. About 5 g of the oil was weighed into a flask (250 ml Erlenmeyer Flask) connected to a reflux condenser to gently boil the sample on a water bath. About 50 ml of alcoholic KOH was added and the mixture was shaken until a clear homogeneous solution was obtained after about 30-60 min indicating a complete saponification. The sample was then allowed to cool to room temperature. 0.5 N HCl was titrated against the sample using a phenolphthalein indicator until the pink color of the indicator disappeared. Replicate titration was performed to obtain the average value. The blank titration was carried out similarly with only 50 ml of alcoholic KOH without the oil sample. The saponification value was calculated using the equation below

$$Saponification = \frac{(B-S)\times N\times 56.1}{W} \quad (1)$$

where B is the average volume (ml) of HCl obtained from blank titration, S is the volume obtained from titration HCl against the sample, *N* is the normality of HCl (mmol ml^{-1}), W is the weight (g) of the sample and 56.1 is molecular weight (MW) of KOH (mg $mmol^{-1}$). The saponification value is expressed as mg KOH per g of sample.

Peroxide value. About 30 ml acetic acid-chloroform solution was added to 5 g of oil in a 250 ml glass-stoppered Erlenmeyer flask, the mixture was swirled to dissolve the oil. About 0.5 ml of saturated KI was added to the mixture, it was then allowed to stand for few minutes with occasional shaken at an interval of 1 minute, after which 30 ml distilled water was added. Sodium thiosulphate (0.1 N) was titrated against the solution with vigorous shaking until a yellow color almost disappeared. 1% Starch solution (0.5 ml) was added giving a blue color, and the titration process continued until the blue color just disappeared. The average volume of titrant used was taking after repeated titrations. The blank titration was conducted following the same procedure but without the oil sample. The peroxide value was obtained from titration as follows:

$$Peroxide\ value = \frac{(S-B)\times N}{W}\times 1000 \quad (2)$$

The peroxide value is expressed as meq peroxide per kg of sample, S is the volume of titrant (ml) used for the solution containing the sample, B is the volume of titrant (ml) used for the blank solution, N is the normality of $Na_2S_2O_3$ solution (meq ml^{-1}) 1000 is the conversion units (from g to kg) and W is the mass of the weighted sample.

Free fatty acid. About 100 ml of neutralized alcohol and 2 ml of phenolphthalein was added to 5 g of the oil sample in a 250 ml Erlenmeyer flask and was shaken. NaOH (0.1 N) was titrated against the mixture with thorough shaking until the endpoint was achieved giving a slight pink coloration which only persists for a few seconds. The average volume of sodium hydroxide used was obtained after 3 replicate titrations. The free fatty acid value was calculated as follows:

$$\%FFA\ (as\ oleic\ acid) = \frac{V\times N\times 282}{W}\times 100 \quad (3)$$

where %FFA is percent free fatty acid (g/100 g) which is expressed as oleic acid, V is the volume of NaOH (ml) used during titration, N is the normality of NaOH (M, 000 ml), 282 is the molecular weight of oleic acid (g mol^{-1}) and W is the mass of the oil (g). The acid value could be obtained from free fatty acids by multiplying with a factor of two.

Iodine value. 10 ml of chloroform was added to 0.5 g of oil sample in a 500 ml stoppered flask. 25 ml of Hanus iodine solution was pipette into the flask and the mixture was allowed to stand for about 30 min in the dark with occasional shakes then, 20 ml of saturated potassium iodide solution was added to the mixture. 100 ml of freshly boiled and cooled water was added to wash down any free iodine on the stoppered flask. The standard solution of sodium thiosulphate (0.1 N) was gradually titrated against the iodine solution in the flask with constant shaking until yellow color almost disappears. About 2 ml of starch indicator was then added and the titration continued until the blue color entirely disappeared. The volume of titrant was recorded and the Iodine value was calculated as follows:

$$Iodine\ value = \frac{(B - S) \times N \times 126.9}{W} \tag{4}$$

where B is the volume of blank titrant (ml), S is the volume of titrant titrated with sample (ml), N is the normality of $Na_2S_2O_3$ (mol/1000 ml), 126.9 is the molecular weight of iodine (g mol^{-1}) and W is the sample mass (g). The Iodine value mass (g) of Iodine absorbed per 100 g of sample.

Physical Measurement

Specific gravity and refractive index measurement. 10 ml of distilled water was measured into a clean and dry density bottle and was weighed; the bottle was dried and cleaned. The same volume of oil samples was measured into the same bottle and was weighed. The values obtained for the two parameters were then compared with the weight of the empty density bottle to obtain the actual weight of the oil as well as that of water. The specific gravity of the oil was obtained using the formula

$$Specific\ gravity\ \frac{density\ of\ oil\ sample}{density\ of\ water} \tag{5}$$

Refractive indices were measured using an ATC refractometer. The sensor point of the refractometer was cleaned and a little portion of the oil was introduced on the sensor and the lid was closed. Then readings were then recorded as the angle of refraction (θ) and the refractive indices (n) were obtained.

Viscosity measurements. The oil samples were heated to temperatures of 60, 70, 80, 90, 100 and 120 °C and the viscosity of the heated oil was determined on a viscometer with an adjusted speed of 6, 12, 30, 60 rpm, starting with the least speed. The sample was loaded into the spindle, and the results were read in millipascal seconds (mPa s).

Viscosity-temperature dependency. The relationship between the viscosity and temperature had previously been shown in an Arrhenius-type equation [11], and this is expressed in Eq. (6) as follows:

$$\eta = \eta_0 \exp\left(\frac{E_a}{RT}\right) \tag{6}$$

Equation 6 can further be linearized by taking the natural log of both sides resulting in Eq. (7) below:

$$\ln\eta = \ln\eta_0 + \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \tag{7}$$

where η is the viscosity in mPa.s, η_0 is the Arrhenius (pre-exponential) constant, R is the gas constant given as 8.314 J k^{-1} mol^{-1}, T is the absolute temperature in Kelvin and E_a is the activation energy in kJ mol^{-1} and this could be obtained from the slope of a plot of lnη against 1/T.

However, the enthalpy, entropy and Gibbs free energy of activation were calculated from Eyring-type equation (Eq. (8)), this is similar to the Arrhenius-type equation but is based on transition state theory;

$$\eta = \frac{k_B T}{h}\exp\left(\frac{\Delta H^{\mp}}{R}\right)\exp\left(\frac{\Delta S^{\mp}}{R}\right) \tag{8}$$

where $\Delta H^{\#}$, $\Delta S^{\#}$, k_B, and h represent enthalpy of activation, the entropy of activation, Boltzmann constant (1.38×10^{-23} J K^{-1}) and Planck's constant (6.6×10^{-34} J s), respectively.

The linearized form of the equation is given as Eq. (9)

$$\ln\left(\frac{\eta}{T}\right) = \left(\frac{\Delta H^{\mp}}{R}\right)\left(\frac{1}{T}\right) + \left\{\ln\left(\frac{k_B}{h}\right) + \left(\frac{\Delta S^{\mp}}{R}\right)\right\} \tag{9}$$

The enthalpy of activation $\Delta H^{\#}$ and entropy of activation $\Delta S^{\#}$ were obtained as the slope and intercept respectively when ln(η/T) is a plotted against (1/T); Gibb's free energy of activation ($\Delta G^{\#}$) was obtained from enthalpy and entropy of activation using the equation below:

$$\Delta G^{\mp} = \Delta H^{\mp} - T\Delta S^{\mp} \quad (10)$$

Fatty Acid Analysis and Quantification

Methylation of the sample oil (seven samples) was done using the already established procedure [12]. The oil samples were homogenized by heat for the formation of methyl esters and the fatty acid analysis was carried out as described previously with some modifications. 1 ml of 0.5 N KOH in methanol and 1 ml of boron trifluoride in methanol were added to 100 mg of each oil sample in different tubes, the tubes were shaken in a vortex mixer and transferred to a COD reactor for 1hr at 100 °C. The tubes were then allowed to cool and 2 ml of salt 10% v/v NaCl and 2 ml of hexane were added, the mixture was shaken vigorously and left to settle for the separation of phases subsequently.

An aliquot of 1 ml was taken from the supernatant, deposited in a hermetically sealed amber vial with 9 ml of hexane and was frozen at -26 °C until injection into the Gas Chromatograph/Mass Spectrometer. The composition of fatty acid was analyzed using GC-MS (Model 7693, Agilent Technologies, with auto sampler) equipped with a flame ionization detector (FID). HP5 wax capillary column (30 m long by 0.25 mm, internal diameter and 0.25 μm phase thickness) was used. The temperatures of the injection and detector were 26 °C and 27 °C, respectively. The flow rate of the carrier gas (N_2) was 2 ml min^{-1}. Oven temperature programming was as follows: 100 °C (initial) to 180 °C (5 °C min^{-1}) which finally increased to 220 °C (0.8 °C min^{-1}). Injection volume was 0.5 μl of each sample; fatty acid methyl ester (FAME) peaks were identified by comparison of retention times to the standard mixtures (GLC-10, GLC-20, GLC-40) and GLC-80 sep ms (St Lous, MO, USA). The peak areas were computed and the percentage of FAME was obtained as area percentages by direct normalization data and is expressed as normalized peak area percent of all identified FAME.

RESULTS AND DISCUSSION

Table 1 shows the physicochemical properties of the vegetable oils. The measurement of saponification, peroxide, free fatty acid, and iodine values as well as refractive index, specific gravity and viscosity remain an important approach (among others) to assess the qualities of fats and oils, their suitability for human consumption and industrial applications [13].

The relationship between saponification value, SV (mg of KOH per g of fat) and average molecular weight of triglycerides of fats and oils has been established, and the mechanism is based on the interaction between the fatty acid chain and the potassium hydroxide. Oils with higher SV are suggested to contain low to medium-chain fatty acids [14-16]. The saponification values obtained for the seven brands of vegetable oils under study indicate that the vegetable oil G_n has the highest SV (209.26 mg g^{-1} KOH) and L_d has the lowest value (185.38 mg g^{-1} KOH). The SV which varying from 185.38 to 209.26 mg g^{-1} KOH for the seven brands of oils were in close range with those reported as standard (186 to 209 mg g^{-1} KOH) by Codex [17] for crude vegetable oils such as peanut, palm, maize, cotton, grape, sesame seed oils and soya bean oil [17].

Fats and oils, as important as they are to human survival, are susceptible to oxidation, the state which is referred to as rancidity. This deterioration in the quality of fats or oils could be monitored by evaluating the peroxide value (PV) of such oil. The chemistry behind this oxidative rancidity is a continuous oxidation of olefin bonds that are present in the unsaturated fatty acids to form peroxides or hydro-peroxides with final products as aldehydes, ketones as well as acids with low molecular weights [13]. The PV of the seven brands of oils (Table 1) ranges from 2.00-37.00 meq O_2/kg. A very low PV has been recommended for oils most especially edible oils, and in case of storage, a higher PV is a negative indication showing that the oils would be finally unsuitable and unusable for human consumption. Following several standards by countries and regulatory organizations; Germany has recommended a PV of 10 meq O_2/kg and 5 meq O_2/kg for virgin oils and refined fats and oils, respectively [6], similarly [17] , had earlier recommended that a PV be limited to 15 meq O_2/kg oil and

10 meq O_2/kg oil for virgin oils and refined fats and oils, respectively. Going by the recommendations above, only P_w, M_d, L_d, B_m and K_g oils with PV of 4.50, 2.00, 3.00, 3.00 and 2.50 meq O_2/kg respectively, may be considered suitable for human consumption, whereas G_n and G_y oils with outrageous PV of 15.0 and 37.0 meq O_2/kg oil respectively may be considered to be rancid and hence not suitable for human consumption, they may, however, serve other purposes such as for lubrication.

The free fatty acids and peroxide value have been jointly implicated in the peroxidation and rancidity of edible oils; high values of these parameters are responsible for a defect in the flavor of oils and influencing the organoleptic properties of the oils negatively. Free fatty acids in oils represent fatty acids that have been dissociated from the triacylglyceride molecules and this is a product of high level of degradation and quality deterioration [4,18]. The free fatty acid values of the oils (Table 1) ranged from 1.30-2.80% with the highest value in K_g, while the acid values ranged from 2.50-5.50 mg KOH/g. The standard acid value according to Codex [17] was given to be between 0.6 to 10.0 mg KOH/g from refined and virgin palm oils. The higher acid values obtained for these oils indicate that the oxidation process might have just been initiated due to poor storage conditions or other environmental factors.

One of the important interests for food scientists dealing with oils is the composition of fatty acids present in the oil, whether saturated or unsaturated, as this factor is used in screening the suitability of the oils for consumption, unsaturated fatty acid is of greater interest when it gets to health benefits and iodine value is an important parameter in oil analysis because it gives a direct measure of the level of unsaturation of fatty acids in the oil. Industrial processing of oil such as hydrogenation also takes advantage of this parameter. The decrease in iodine value is an indication of double bonds destruction by oxidation, disintegration or polymerization [13,15,19-21]. As shown in Table 1, the range of iodine values for the seven brands of oils under study were from 31.09 to 89.46 g I_2/100 g of oil. These iodine values were higher than the range reported for babassu (10-18 g I_2/100 g), coconut (6.3-10.60 g I_2/100 g), red palm (50.00-55.00 g I_2/100 g) and palm kernel (14.10-21.00 g I_2/100 g) oils [17]. Comparing the level of unsaturation of the oils under study, it could be inferred that the level of unsaturation of the oils is in the order $L_d > G_y > G_n > B_m > M_d > P_w > K_g$. The K_g oil with the lowest iodine value consists mostly of saturated fatty acids and the level of unsaturation of fatty acids in L_d is the highest.

The refractive index and specific gravity play important roles in the determination of the purity of oils, with a high refractive index associated with a high degree of unsaturation in fatty acids and an increase in double bond conjugation was reported to be responsible for the increase in refractive index. It relates directly with specific gravity which is also dependent on temperature. The relationship between the refractive index and iodine value has also been reported for fresh/virgin oil [22-25]. From the refractive indices reported in Table 1, L_d oil has the highest refractive index (1.488) and G_n has the least value (1.441). However, the range of refractive index values obtained for the oils is in parallel with 1.47 value reported by Walia *et al*. (2013) [24], and also within the range of 1.4677-1.4707 for virgin, refined and refined-pomace oils as reported by Codex [17]. A similar trend was observed for the specific gravity of the oils reported in this work.

Viscosity in fluid is a factor of molecular cohesion and adhesions, as well as intermolecular friction which results in resistance to fluid flow and deformation in shear. Viscosity of seed oil is a function of its chemical and fatty acid compositions, the higher the degree of unsaturation in the fatty acid components of vegetable oils, the lower the viscosity of the oils. Temperature variation is one of the physical conditions clarifying whether the viscosity of a liquid decreases, increases or remains fairly constant [26,27]. To determine the rheological properties of the vegetable oils, the influence of temperature on their viscosities was studied. As the temperature increases, the viscosities of the vegetable oils decrease exponentially (Fig. 1), confirming previous assertions about the oil viscosity-temperature relationship [28].

Activation energy determination remains one of the approaches to the identification of the thermal stability of the vegetable oils. However, the activation energy of the process, the energy required to change the oil viscosity,

Table 1. Chemical and Physical Properties of the Selected Refined Brand of the Vegetable Oils

Chemical properties	G_n	P_w	M_d	L_d	B_m	K_g	G_y
Peroxide value (Meq/kg)	15.00 ± 0.45	4.50 ± 0.09	2.00 ± 0.02	3.00 ± 0.06	3.00 ± 0.09	2.50 ± 0.08	37.00 ± 1.11
Acid value (mg KOH/g)	5.50 ± 0.17	3.00 ± 0.06	4.00 ± 0.04	2.50 ± 0.05	3.50 ± 0.14	5.50 ± 0.22	3.00 ± 0.12
Free fatty acid (%)	2.80 ± 0.08	1.50 ± 0.03	2.00 ± 0.02	1.30 ± 0.03	1.80 ± 0.02	2.80 ± 0.03	1.50 ± 0.02
Iodine value (g/100 g)	46.70 ± 1.40	38.58 ± 0.77	43.90 ± 0.44	89.46 ± 1.79	45.68 ± 0.91	31.09 ± 0.62	70.68 ± 1.41
Saponification value (mg g^{-1} KOH)	209.26 ± 2.09	202.44 ± 2.02	193.34 ± 1.93	185.38 ± 1.85	187.34 ± 1.87	194.64 ± 1.95	191.44 ± 1.91
Physical properties							
Refractive index	1.441 ± 0.040	1.487 ± 0.030	1.457 ± 0.010	1.488 ± 0.029	1.456 ± 0.058	1.445 ± 0.058	1.472 ± 0.059
Specific gravity	0.92 ± 0.03	0.95 ± 0.01	0.93 ± 0.01	0.95 ± 0.02	0.93 ± 0.04	0.92 ± 0.04	0.94 ± 0.03
Viscosity (mPa s)	18.19 ± 0.55	14.88 ± 0.30	19.38 ± 0.19	17.95 ± 0.36	17.19 ± 0.52	16.62 ± 0.50	20.17 ± 0.60

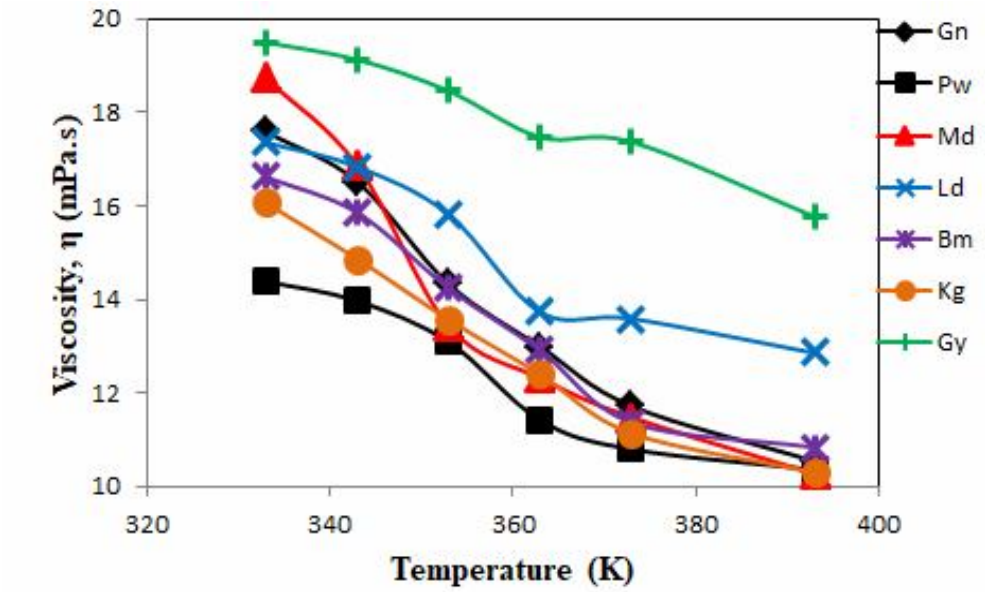

Fig. 1. The viscosities of the vegetable oils decrease exponentially with increasing temperature.

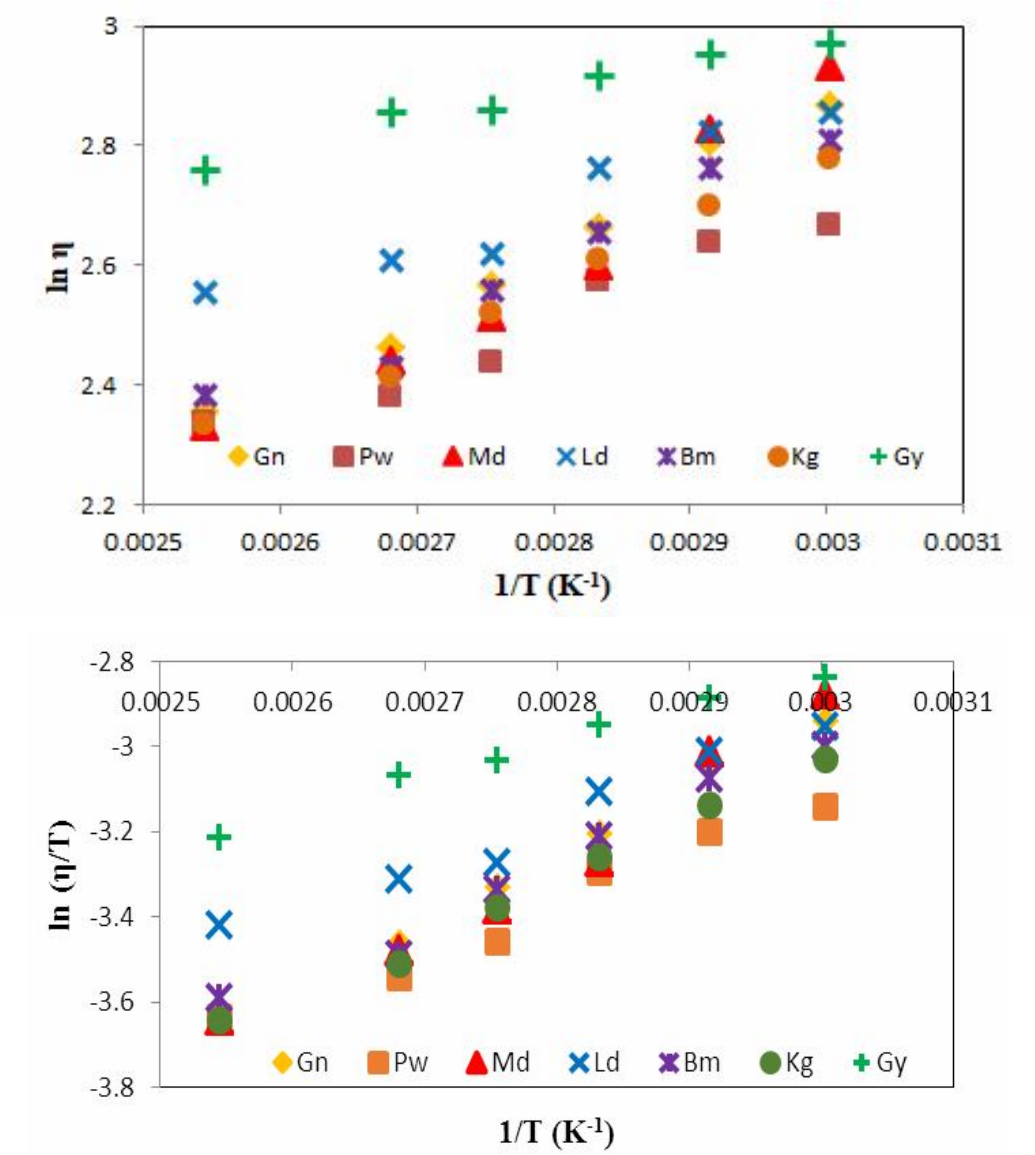

Fig. 2. (A) Arrhenius-like; (B) Eyring-like plots for the viscosity-temperature changes in the refined brand vegetable oils.

such as crossing the activation barrier was extrapolated from the Arrhenius-type equation (Eq. (7)) (Fig. 2A). The activation energies of the seven refined brand vegetable oils, G_n, P_w, M_d, L_d, B_m, K_g and G_y, were 9.87, 6.76, 11.32, 6.07, 8.58, 8.50 and 3.85 kJ mol^{-1}, with the model correlation coefficients (R^2 values) ranging between 0.923 and 0.985, respectively (Table 2). When the activation energy is high, greater energy would be required to effect a viscosity change. Hence, the thermal stability of the oil would be high. Oils with high activation energy may be said to have high thermal stability and may also be characterized by a low degree of unsaturation in the fatty acid chain. The results obtained (Fig. 2A), showed that the vegetable oil brand P_w with activation energy of 11.32 kJ mol^{-1} may mainly consist of fatty acids with lower degree of unsaturation, conversely, the oil brand G_y with least value

Table 2. Kinetic and Thermodynamic Properties of some Vegetable Oil Brands in Nigeria

	Parameters from Eyring-type plot			
	Enthalpy of activation	Entropy of activation	Gibb's free energy of activation	R^2
Oil samples	$\Delta H^{\#}$ (J mol^{-1})	$\Delta S^{\#}$ (J mol^{-1} K^{-1})	$\Delta G^{\#}$ at 298 K (kJ mol^{-1})	
Gn	12870	-31.35	22.21	0.991
Pw	9769	-30.42	18.83	0.969
Md	14317	-31.85	23.81	0.984
Ld	9071	-29.99	18.01	0.965
Bm	11598	-30.94	20.82	0.978
Kg	11507	-30.95	20.73	0.992
Gy	6852	-29.06	15.51	0.987
	Parameters from Arrhenius-type plot			
	E_a	Viscosity		R^2
	(kJ)	Pre-exponential factor (mPa s)		
Gn	9.87	0.50		0.984
Pw	6.77	1.26		0.936
Md	11.32	0.30		0.948
Ld	6.07	1.95		0.923
Bm	8.59	0.75		0.96
Kg	8.50	0.97		0.985
Gy	3.85	4.92		0.966

of activation energy of 3.85 kJ mol^{-1} in this study is most likely to contain fatty acids with higher level of unsaturation than other brands, as confirmed later from the reports of the fatty acids (Table 3).

The thermodynamic parameters such as enthalpy of activation, ($\Delta H^{\#}$) and entropy, ($\Delta S^{\#}$) of activation were obtained during the process of viscosity changes with increasing temperature as shown in Fig. 2B, using the Eyring-type equation as a model, and the Gibbs free energy of activation, ($\Delta G^{\#}$) were obtained by the substitution of enthalpy and entropy values into Gibbs free energy equation (Eq. (10)). The thermodynamic activation parameters for $\Delta H^{\#}$ were 12.87, 9.77, 14.32, 9.07, 11.60, 11.51 and 6.85 kJ mol^{-1}, that of $\Delta S^{\#}$ values were -31.35, -30.42, -31.85, -29.99, -30.94, -30.95 and -29.06 J mol^{-1} K^{-1} and the $\Delta G^{\#}$ values were 22.21, 18.83, 23.81, 18.01, 20.82, 20.73, 15.51 kJ mol^{-1} for the oil brands G_n, P_w, M_d, L_d, B_m, K_g and G_y respectively, as presented in Table 2. The positive values

Table 3. Fatty Acid Composition of some of Selected Brands of Vegetable Oils

Fatty acids content (%)	G_n	P_w	M_d	L_d	B_m	K_g	G_y
Myristic acid ($C_{14:0}$)	0.85 ± 0.01	1.21± 0.01	1.62 ± 0.02	0.01 ± 0.00	1.58 ± 0.02	0.71 ± 0.01	-
Palmitic acid ($C_{16:0}$)	36.75 ± 0.11	36.08 ± 0.11	34.08 ± 0.10	7.61 ± 0.02	38.91 ± 0.12	46.08 ± 0.14	14.28 ± 0.04
Stearic acid ($C_{18:0}$)	3.81 ± 0.01	4.84 ± 0.01	4.72 ± 0.01	2.19 ± 0.01	1.05 ± 0.00	2.84 ± 0.01	1.81 0.01
Total Saturated	41.41 ± 0.13	42.13 ± 0.13	40.42 ± 0.13	9.81 ± 0.03	41.54 ± 0.14	49.63 ± 0.16	16.09 ± 0.05
Oleic acid ($C_{18:1}$)	46.80 ± 0.09	42.54 ± 0.08	44.80 ± 0.09	26.52 ± 0.05	42.12 ± 0.08	37.86 ± 0.07	73.17 ± 0.14
Linoleic acid ($C_{18.2}$)	7.41 ± 0.15	13.08 ± 0.26	13.50 ± 0.27	60.67 ± 1.21	12.33 0.25	7.86 ± 0.16	7.01 ± 0.14
Total unsaturated	54.21 ± 0.24	55.62 ± 0.34	58.3 ± 0.36	87.19 ± 1.26	54.45 ± 0.33	45.72 ± 0.23	80.18 ± 0.28
Other compounds/Minor components	4.38 ± 0.37	2.25 ± 0.47	1.28 ± 0.49	3 .00 ± 1.29	4.01 ± 0.47	4.65 ± 0.39	3.73 ± 0.33

of $\Delta H^{\#}$ indicate that the process was endothermic while the negative values of $\Delta S^{\#}$ indicate a decrease in entropy upon the formation of the transition state. This is an attribute of an associative mechanism in which the combining molecules form a single activated complex [29]. The positive $\Delta G^{\#}$ values showed the non-spontaneity of the reaction process implying that the oils would resist, to a reasonable extent, the shear deformation over a specific range of temperature.

The fatty acid profile from GC-MS analysis (Table 3) reveals different proportions of saturated (myristic ($C_{14:0}$), palmitic ($C_{16:0}$) and stearic ($C_{18:0}$)) fatty acids as well as the unsaturated (Oleic ($C_{18.1}$) and linoleic acid ($C_{18.2}$)) fatty acids contents of the oils. The data reveals that L_d oil brand possessed the highest total unsaturated fatty acid contents (87.19%) among the vegetable oils understudy with linoleic acid (60.67%) being the most prominent fatty acid. Similarly, G_y vegetable oil brand has total unsaturated fatty acid (80.18%), with oleic acid (73.17%) being the most prominent unsaturated fatty acid therein. However, other brands of the oils contain total saturated and unsaturated fatty acids at closer proportions with palmitic acid and oleic acid being generally prominent in the total saturated and unsaturated fatty acids, respectively. This result is in agreement with the trends obtained from various physicochemical characterizations of the oil brands reported earlier in this study.

CONCLUSIONS

Various investigations on the physical and chemical properties of some commercially available vegetable oil brands have revealed their compositions, stability to some physical factors, susceptibility to environmentally induced

chemical deterioration and suitability for human consumption. The brands G_n and G_y were considered not suitable for human consumption at the time of analysis due to their high susceptibility to rancidity; however, they could serve other purposes such as for lubrication. The L_d, G_y and G_n brands were characterized with contain higher saturated fatty acids than all other brands investigated. The thermal stabilities of the oils correspond inversely to the heating temperature increase. However, the high thermal stability of the P_w oil brand was due to its high activation energy (in terms of resistance to shear stress) and a low degree of unsaturation. The thermodynamic parameters indicate that heat was absorbed during the process (endothermic), the reaction mechanism was associative and the entire process was non-spontaneously feasible.

ACKNOWLEDGMENTS

The authors are greatly indebted to the Abdus Salam International Centre for Theoretical Physics (ICTP), Italy for the award of Junior Associate to Dr. Abdul-Hammed, M. and for the use of the institutional facilities which aid the preparation of this manuscript.

REFERENCES

[1] Olanrewaju, A. S.; Moriyike, O. E., Physicochemical characteristics and the effect of packaging materials on the storage stability of selected cucurbits oils. *Am. J. Food Nutr.* **2013**, *1*, 34-37. DOI: 10.12691/ajfn-1-3-3.

[2] Aremu, M. O.; Ibrahim, H.; Bamidele, T. O., Physicochemical characteristics of the oils extracted from some nigerian plant foods -A review. *Chem. Process Eng. Res.* **2015**, *32*, 36-52.

[3] Owen, R. W.; Giacosa, A.; Hull, W. E.; Haubner, R.; Spiegelhalder, B.; Bartsch, H., The antioxidant/anticancer potential of phenolic compounds isolated from olive oil. *Eur. J. Cancer* **2000**, *36*, 1235-1247. DOI: 10.1016/S0959-8049(00)00103-9.

[4] Wiesman, Z., Olive-oil quality biotechnologies. In desert olive oil cultivation; Academic Press, 2009; pp. 257-302. DOI: 10.1016/b978-0-12-374257-5.00011-7.

[5] Crockett, S. L., Allanblackia oil : Phytochemistry and use as a functional food. *Int. J. Mol. Sci.* **2015**, *16*, 22333-22349. DOI: 10.3390/ijms160922333.

[6] Matthäus, B., Oxidation of Edible Oils. In Oxidation in Foods and Beverages and Antioxidant Applications; Decker, E. A.; Elias, R. J.; McClements, D. J., Eds.; Woodhead Publishing Limited: Max Rubner-Institute, Federal Research Institute for Nutrition and Food, Department for Lipid Research, Piusallee 68/76, 48147 Münster, Germany 2010; pp. 183-238. DOI: 10.1533/9780857090331.2.183.

[7] Williams, M. J. A.; Sutherland, W. H. F.; McCormick, M. P.; De Jong, S. A.; Walker, R. J.; Wilkins, G. T., Impaired endothelial function following a meal rich in used cooking fat. *J. Am. Coll. Cardiol.* **1999**, *33*, 1050-1055. DOI: 10.1016 S0735-1097(98)00681-0.

[8] Lapointe, A.; Couillard, C.; Lemieux, S. Effects of Dietary Factors on Oxidation of Low-Density Lipoprotein Particles. *J. Nutr. Biochem.* **2006**, *17*, 645–658. DOI: 10.1016/j.jnutbio.2006.01.001.

[9] Soriguer, F.; Rojo-Martínez, G.; Dobarganes, M. C.; García Almeida, J. M.; Esteva, I.; Beltrán, M.; Ruiz De Adana, M. S.; Tinahones, F.; Gómez-Zumaquero, J. M.; García-Fuentes, E.; *et al.*, Hypertension is related to the degradation of dietary frying oils. *Am. J. Clin. Nutr.* **2003**, *78*, 1092-1097. DOI: 10.1093/ajcn/78.6.1092.

[10] Katragadda, R. H.; Fullana, A.; Sidhu, S.; Carbonell-barrachina, Á. A., Emissions of volatile aldehydes from heated cooking oils. *Food Chem.* **2010**, *120*, 59-65. DOI: 10.1016/j.foodchem.2009.09.070.

[11] Singh, R. P.; Heldman, D. R., Introduction to food engineering, fourth.; Taylor, S. L., Ed.; Elsevier Inc.: USA 2012; Vol. 33. DOI: 10.1073/pnas.0703993104.

[12] AOAC. Official Methods of Analysis, 16th ed.; Association of official analytical chemists: Washington DC, USA, 1995.

[13] Baião, N.; Lara, L., Oil, and fat in broiler nutrition. *Rev. Bras. Ciência Avícola* **2005**, *7*, 129-141. DOI: 10.1590/s1516-635x2005000300001.

[14] Patterson, H. B. W., Quality and Control. In Hydrogenation of Fats and Oils: Theory and Practice: Second Edition; AOCS Press, 2010; pp. 329-350. DOI: 10.1016/B978-1-893997-93-6.50018-X.

[15] Bockisch, M., Analytical Methods. In Fats and Oils Handbook; Bockisch, M., Ed.; Academic Press and AOCS Press: Hamburg, Germany 1998; pp. 803-808. DOI: 10.1016/B978-0-9818936-0-0.50014-7.

[16] Przybylski, R.; Eskin, N. A. M., Oil Composition and Properties. In Canola: Chemistry, Production, Processing, and Utilization; AOCS Press, 2011; pp. 245-280. DOI: 10.1016/B978-0-9818936-5-5.50011-5.

[17] Codex, A., Codex Standard for Named Vegetable Oils. In Joint FAO/Who Food Standards Programme Codex AlimenTAtarius Commission. 2001; Vol. 8, pp. 11-25.

[18] Şenel, E.; Atamer, M., Yayik Butter Profiles from Different Species of Mammals' Milk. In Processing and Impact on Active Components in Food; Elsevier 2014; pp. 215-221. DOI: 10.1016/B978-0-12-404699-3.00026-3.

[19] Otunola, G. A.; Africa, S.; Adebayo, G. B., Evaluation of some physicochemical parameters of selected brands of vegetable oils sold in ilorin metropolis. *Int. J. Phys. Sci.* **2009**, *4*, 327-329.

[20] Orthoefer, F. T.; List, G. R. Dynamics of Frying. In Deep Frying: Chemistry, Nutrition, and Practical Applications; AOCS Press 2007; pp. 253-275. DOI: 10.1016/B978-1-893997-92-9.50018-9.

[21] Kyriakidis, N. B.; Katsiloulis, T., ABSTRACT: A New Calculation Method For. *J. Am. Oil Chem. Soc.* **2000**, *77*, 1235-1238.

[22] Anwar, F.; Mohammad, N. O. R. A.; Othman, F.; Saari, N., Inter-varieta variation in the composition of seeds and seed oils from winter melon [benincasa hispida (Thunb.) Cogn.] fruit. *Pakistan J. Bot.* **2011**, *43*, 2029-2037.

[23] Ogungbenle, H. N.; Sanusi, D. S., Extraction, physicochemical, phytosterols and fatty acid of celosia spicata leaves. *Br. J. Res.* **2015**, *2*, 009-020.

[24] Walia, M.; Rawat, K.; Bhushan, S., Fatty acid composition, physicochemical properties, antioxidant and cytotoxic activity of apple seed oil obtained from apple pomace. *J. Sci. Food Agric.* **2013**, *94*, 929-934. DOI: 10.1002/jsfa.6337.

[25] Simpson, B. W.; Hamilton, D. J., Oil quality analyzer. *Queesl. Agric. J.* **1982**, 283-285.

[26] Hollebone, B., Measurement of Oil Physical Properties; Elsevier Inc., 2011. DOI: 10.1016/B978-1-85617-943-0.10004-8.

[27] Williams, L.; Stapleton, F.; Carnt, N., Microbiology, Lens Care and Maintenance. In Contact Lenses; Elsevier Inc., 2004; pp. 65-96. DOI: 10.1016/B978-0-7020-7168-3.00004-0.

[28] Fasina, O. O.; Colley, Z., Viscosity and specific heat of vegetable oils as a function of temperature: 35 °C to 180 °C. *Int. J. Food Prop.* **2008**, *11*, 738-746. DOI: 10.1080/10942910701586273.

[29] Espenson, J. H., Chemical Kinetics and Reaction Mechanisms, 2nd Editio.; McGraw-Hill Education: New York, 2002.