

## Kinetic modelling and accelerated oxidation studies of groundnut (*Arachis hypogaea* L.) varieties for their shelf stability

Sai Kiran Chikkam, D D Wadikar\*, Dev Kumar Yadav, Atul Kumar, S Pandit Srihari and A D Semwal  
Grain Science & Technology Division, DRDO-Defence Food Research Laboratory, Siddhartha Nagar, Mysore, Karnataka 570011, India

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The present investigation aims to evaluate the oxidative stability of different high oleic and conventional groundnut varieties of Indian origin. A total of 6 groundnut varieties, including two high oleic varieties (Girnar-4 and Girnar-5) and four conventional varieties (GJG-22, GIG-HPS-1, GJG-31, KL-9), were analysed for fatty acid profiles, oxidative stability (accelerated oxidation), total phenols, antioxidant activities and prediction of their shelf life. Among the studied varieties, Girnar-4 and Girnar-5 had higher Oleic/Linoleic (O/L) ratios *viz.* 20 and 12, respectively. The induction times (IT) were significantly ( $P < 0.05$ ) reduced with the increase in temperatures (120, 130, and 140°C). Higher induction times were observed in Girnar-4 and Girnar-5; the lowest were in GJG-31. The highest activation energy ( $E_a$ ) of 107.05±0.15 kJ/mol was observed in Girnar-4. In addition, it was also found to have the longest predicted shelf life of 321.5±22 days at 37°C. Higher total phenols content and antioxidant activity were observed in Girnar-5. In conclusion, the high oleic varieties (Girnar-4 & Girnar-5) have shown greater oxidative stability, good phenolic content, and antioxidant activity. The higher oxidation resistance potentiality of these high oleic groundnut varieties ought to help in the development of value-added products with better stability.

**Keywords:** Arrhenius kinetics, High oleic, Induction time, Oxidative stability, Shelf-life

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### Introduction

Groundnut (*Arachis hypogaea* L.) is a well-known legume and oilseed due to its inherent oil content in the kernel. The diverse agroclimatic conditions of India make it the second-largest cultivator of groundnuts globally. Groundnuts are nutritionally dense, as they contain 45-50% fat, 25-30% protein, and a good amount of vitamin E, folic acid and minerals (potassium, calcium and iron)<sup>1</sup>. They are considered poor man's grain due to their availability, affordability, and nutritional strength. Growing demand for food security and nutrition leads to the development of potential groundnut varieties with high yield, improved pest resistance, and improved ability to grow in diverse agroclimatic conditions. The two high oleic acid varieties (Girnar-4 and Girnar-5) were released in the year 2020, having special characteristics of containing more than 78.5% oleic acid and resistant to stem rot and peanut bud necrosis. Other conventional varieties, namely KL-9, GJG-22, GJG-31, and GJG-HPS-1, were released in the following years: 2021, 2013, 2012 and 2010,

respectively. GJG-31 and KL-9 were high-yielding varieties with an average kernel yield of more than 2100 kg/ha and resistant to several pests and insects. GJG-22 and GJG-HPS-1 varieties were tolerant to specific diseases such as collar rot and peanut bud necrosis<sup>2</sup>.

Groundnut oil is rich in unsaturated fatty acids such as linoleic acid (35-40%) and oleic acid (45-50%). Owing to their higher unsaturation, groundnuts and their products are prone to oxidation, which negatively impacts their quality and shelf life<sup>1</sup>. During oil processing, several factors influence the oxidation process, such as the presence of free fatty acids, mono and di acyl glycerides, transition metals and photosensitisers. The free fatty acids are more prone to auto-oxidation and di acyl glycerides increase the surface area due to the presence of hydroxy and hydrocarbon groups, which facilitates the increase in the solubility of oxygen. These components can be reduced during the refining process. Transition metals such as iron and copper accelerate oxidation by the formation of lipid alkyl radicals and also help in the formation of singlet oxygen from triplet oxygen. Photosensitisers like chlorophyll help in the

\*Correspondent author  
E mail: ddwadikar@gmail.com

production of singlet oxygen, which in turn forms different reactive oxygen species in the presence of transitional metals. Photosensitisers can be eliminated during the bleaching process in refining<sup>3-5</sup>. Due to the majority of monomolecular reactions before the initiation step of fat auto-oxidation, the formation of lipid peroxides is limited, known as the induction period. It denotes the shelf life of oil and oil-rich foods with respect to oxidation<sup>3</sup>. Several factors, such as fatty acid composition, availability of oxygen and presence of natural or added antioxidants, influence the induction period. The probability of oxidation of oleate is less than linoleate. The researchers are developing groundnut varieties with high oleic content and less linoleic acid to get higher stable groundnuts and their products<sup>6,7</sup>. High oleic groundnuts have some health advantages as they have good hypocholesterolemic and anti-inflammatory activity<sup>8</sup>. The importance of high oleic peanut varieties is widespread, and the potentiality of these varieties has drawn interest from industrial stakeholders and led the path for research interventions to deliver more fruitful outcomes with respect to nutrition.

The kinetic behaviour of oils and mathematical modelling are useful to understand the scenario of the oxidation process, and it is well witnessed in several vegetable oils and their products through accelerated oxidation methods<sup>9,10</sup>. Accelerated oxidation methods are well used to determine the oxidative stability of oil. They are economical and produce quick results compared to conventional real-time analysis. Aktar and Adal<sup>9</sup> studied avocado oil in an accelerated method using rancimat and predicted the shelf life of avocado oil to be 250 days at 25°C. Similarly, several oils such as canola, sunflower, soybean, corn and olives were tested for oxidative stability using the rancimat method<sup>11</sup>. Other accelerated oxidation methods, such as the OXI apparatus and Rapid-oxy, were introduced to determine primary oxidation products in terms of induction time, which was found to be more effective and economical<sup>12,13</sup>.

There are meagre works carried out to understand the oxidation scenario of groundnut varieties of Indian (desi) origin, especially high oleic varieties. Therefore, the current research was undertaken to determine the kinetic parameters and oxidative stability of high oleic and conventional groundnut varieties of Indian origin.

## Material and Methods

### Collection of groundnut varieties

All six authentic varieties were procured from research stations and universities in September 2021. Two varieties, *i.e.*, GJG-HPS-1 and GJG-22, were procured from Junagadh Agricultural University, Gujarat. Three varieties, namely, GJG-31, Girnar-4 and Girnar-5, were collected from the Directorate of Groundnut Research, Junagadh, Gujarat, India. KL-9 was procured from the Regional Agricultural Research Station, ANGRAU, Kadiri, Andhra Pradesh. The collected varieties were packed in a laminated pouch and stored at <5°C until the analysis.

### Chemicals

The Fatty acid methyl esters mixture (FAME), n-hexane, Methanol, Boron trifluoride (BF<sub>3</sub>), DPPH (2,2-diphenyl-1-picrylhydrazyl), Gallic acid, Folin-Ciocalteu (FC) reagent were procured from Sigma-Aldrich, Merck, Quest International Pvt. Ltd, Bangalore, Karnataka, India. Other chemicals such as sodium hydroxide, sodium chloride, potassium iodide, sodium sulfate anhydrate, methanol, chloroform, glacial acetic acid, sodium thiosulfate and starch were all of analytical grade (SDFCL, LOBA chemicals) procured from Mysore pure chemicals Pvt. Ltd, Mysuru, Karnataka, India.

### Fatty acid profile

The samples were dried in a hot air oven for about 24 hours at 60°C; after that, the samples were ground and defatted with n-hexane in Soxhlet apparatus for 6 hours as per the method described in (AOAC)<sup>14</sup>. The extracted fat was methylated using the boron trifluoride (BF<sub>3</sub>) method adopted from (AOAC)<sup>15</sup>, with slight modifications. 200 mg of sample was taken into a reaction flask with 2-3 pumice stones, and 5 mL of methanolic KOH (5M) was added. The contents were refluxed in a boiling water bath for 5-10 minutes until the fat globules disappeared. Further, 5 mL of BF<sub>3</sub> solution was added through the top of the condenser, and the contents were allowed to boil for another 5 minutes. After that, 2-5 mL of n-hexane was added through the top of the condenser and boiled for another 2 minutes. Later, 15 mL of saturated NaCl was added while the contents in the flask were in lukewarm heat, followed by vigorous shaking for 15 sec. It was rested for 5 minutes to separate the hexane layer on top. The hexane layer with methylated fatty acid esters was collected, added with a pinch of anhydrous sodium sulfate, and stored at -20°C until

further analysis. The fatty acid methyl esters of samples were separated and quantified according to (AOAC)<sup>16</sup> by using a Gas chromatography system (M/s Agilent Technologies, 7890B) with a capillary column (Supelco SP2560, 100m x 0.25mm x 0.20m). The separation conditions were as follows: Oven temperature program: initial 140°C, hold for 5 minutes, ramp of 4.1°C/min till 240°C, hold for 30 minutes. The Flame Ionization Detector (FID) temperature was maintained at 300°C, and the injector port was maintained at 250°C. The carrier gas (N<sub>2</sub>) was maintained in the column at a flow rate of 1.2 mL/min, and a split injection mode (100:1) was applied. A total of 1 µL sample volume was injected into the column for separation. The sample peaks were identified from the retention time of the fatty acid methyl esters (FAME) standard mixture. The quantification was done and calculated based on the peak area of standards.

#### Determination of oxidative stability (Induction time)

Oxidative stability in terms of induction time (IT) was determined by the Induced oxidation method suggested by Pasqualone *et al.*<sup>12</sup>, with the Rapid Oxy 100 (Anton Paar, Germany) instrument installed with a microprocessor system. Approximately 5 g of sample (deskin split kernels) was weighed and kept in a sealable chamber equipped with a heating oven operating at a maximum temperature of up to 180°C. The induction times were estimated at three temperatures, *i.e.*, 120, 130, and 140°C adopted from Veloso *et al.*<sup>17</sup>. The chamber was filled with an initial oxygen pressure of 700 kPa, a 10% pressure drop from maximum pressure was considered as a stop criterion to determine the induction time (IT) of a sample.

#### Arrhenius kinetic parameters determination

The Arrhenius kinetic parameters were determined according to the methods described by Aktar and Adal<sup>9</sup>, Gagour *et al.*<sup>10</sup>, and Farhoosh *et al.*<sup>11</sup>. The reaction rate constant, *k* (h<sup>-1</sup>), was calculated as the reciprocal of induction time (h). The activation energy (*E<sub>a</sub>*) and the frequency factor, *A* (h<sup>-1</sup>), were calculated from the slope and intercepts of the linear regression equation (Arrhenius equation), obtained from the semi-logarithmic plot of reaction rate constant '*k*' versus temperature, *T* (1/K) and the equation as follows Equation 1:

$$\ln k = \ln A + \left( \frac{E_a}{RT} \right) \quad \dots (1)$$

Where '*k*' is the reaction rate constant (reciprocal of induction time (h)), '*R*' is the universal gas constant (8.314 J/mol K), and *T* is the temperature in K.

The values of predicted shelf life and temperature coefficient, *T<sub>c</sub>* (°C<sup>-1</sup>), were estimated from the slope '*a*' and intercept '*b*' between the log of induction time (h) versus temperature (°C) in Equation (2)

$$\log k = a(T) + b \quad \dots (2)$$

The *Q*<sub>10</sub> values were calculated from the values of slope '*a*' or Temperature coefficient *T<sub>c</sub>* of equation (2) by using the following Equation (3)

$$Q_{10} = -10^{10T_c} \quad \dots (3)$$

#### Peroxide value determination

Peroxide values (PV) of samples were determined by slight modifications of the method (AOAC)<sup>18</sup>. Fat was extracted with 3g of sample in 70 mL of chloroform for 2 hours using an orbital shaker. The fat content was determined by evaporating a known volume of chloroform extract (10 mL). 20 mL of chloroform extract was taken in an iodine flask, followed by an addition of 30 mL of glacial acetic acid. 1 mL of saturated KI solution was added to this mixture and allowed for incubation in the dark for 20 minutes. The reaction was arrested by slowly adding 50 mL of water through the stopper and 1 mL of 1% starch indicator solution. The liberated iodine was determined by titrating with 0.02 N standardised sodium thiosulfate till the blue colour turned to milky white. The PV was expressed as milli equivalence (meq) of O<sub>2</sub>/kg fat.

#### Extraction procedure for TPC and DPPH assays

The sample preparation and extraction procedure were adopted from Win *et al.*<sup>19</sup>, with minor modifications. The ground samples were defatted with n-hexane using the Soxhlet apparatus for 8 hours. The defatted samples were dried at ambient conditions, packed and stored at -20°C. Five grams of defatted samples were extracted with 100 mL of methanol for 3 hours with continuous shaking at room temperature. Then, the suspension was filtered, and the extraction was repeated thrice in the same manner. The total volumes of filtrate were pooled and further concentrated to a final volume of approx. 25 mL, under reduced pressure at 40°C using a rotary vacuum evaporator (Heidolph, Germany). The extracted volume was further diluted to a 1:4 ratio and used to analyse phenols and antioxidant activity.

**Determination of total phenol content**

The total phenols content (TPC) in different varieties of groundnut was determined by the Folin-Ciocalteu (FC) method described by Win *et al.*<sup>19</sup>. The methanolic extract of 0.4 mL was taken in a test tube and was mixed with 2 mL of FC reagent (1:10). After 5 minutes, 1.6 mL of sodium carbonate solution (7.5%) was added and mixed well using a vortex mixer. Further, the contents were incubated for 30 minutes at room temperature in the dark. The absorption was measured at 725 nm using a UV-visible spectrophotometer (Shimadzu, Japan). The standard curve for determining phenols of unknown samples was prepared using gallic acid at different concentrations. The results were expressed as mg GAE/g of the dry sample.

**Determination of Antioxidant activity (DPPH radical scavenging activity)**

The antioxidant activity of methanolic extracts of different groundnut varieties was determined by the method described by Win *et al.*<sup>19</sup>. 0.5 mL of methanolic extract of final dilution was taken in a test tube, and 2.5 mL of freshly prepared DPPH (2,2-diphenyl-1-picrylhydrazyl) solution (25 mg/L) was added. The mixture was incubated for 30 minutes in dark conditions. The absorption was measured at

625 nm using a UV-visible spectrophotometer (Shimadzu, Japan) against the methanol blank.

**Statistical analysis**

Statistically significant difference among the groups of observed data was determined through one-way ANOVA at a 5% significance level ( $P < 0.05$ ) using the Minitab 18 statistical tool. Tukey multiple comparison test was applied to compare groups with equal variance. In contrast, the Games-Howell test was applied for the data with unequal variance among the groups at a 5% significance level ( $P < 0.05$ ).

**Results and discussion****Fatty acid profile of different groundnut varieties**

The fatty acid composition of 6 different varieties of groundnuts is presented in Table 1. Palmitic, stearic, behenic, arachidic and lignoceric acids were the detected saturated fatty acids in all varieties. Among these, palmitic (3.30 to 5.69) and stearic acid (1.14 to 2.30) were the major predominant saturated fatty acids (g/100g), followed by behenic acid (0.94 to 1.28) and arachidic acid (0.52 to 0.74). In addition, two monounsaturated fatty acids (MUFA), *i.e.*, oleic acid and gadoleic acid<sup>20</sup>, were found in the range of 15.69 to 40.89 and 0.21 to 0.47 g/100g, respectively.

Table 1 — Characterization of fatty acid profiles of selected groundnut varieties

Fatty acids (g/100g)	Girnar-5	Girnar-4	GJG-31	KL-9	GJG-22	GJG-HPS-1
Palmitic acid (Hexadecenoic)	3.30±0.07 <sup>c</sup>	3.82±0.23 <sup>c</sup>	4.76±0.15 <sup>b</sup>	5.24±0.15 <sup>ab</sup>	5.69±0.44 <sup>a</sup>	3.75±0.12 <sup>c</sup>
Stearic acid (Octadecanoic)	1.14±0.14 <sup>d</sup>	1.59±0.07 <sup>bcd</sup>	1.93±0.07 <sup>ab</sup>	1.83±0.04 <sup>abc</sup>	2.3±0.34 <sup>a</sup>	1.27±0.07 <sup>cd</sup>
Arachidic acid (Eicosanoic)	0.55±0.03 <sup>bc</sup>	0.69±0.04 <sup>ab</sup>	0.69±0.03 <sup>ab</sup>	0.70±0.02 <sup>a</sup>	0.74±0.04 <sup>a</sup>	0.52±0.02 <sup>c</sup>
Behenic acid (Docosanoic)	0.97±0.03 <sup>cd</sup>	1.21±0.04 <sup>ab</sup>	1.04±0.02 <sup>cd</sup>	1.28±0.04 <sup>a</sup>	1.12±0.03 <sup>bc</sup>	0.94±0.04 <sup>d</sup>
Lignoceric acid (Tetracosanoic)	0.58±0.03 <sup>a</sup>	0.58±0.02 <sup>a</sup>	0.34±0.02 <sup>c</sup>	0.51±0.04 <sup>ab</sup>	0.43±0.02 <sup>bc</sup>	0.38±0.04 <sup>bc</sup>
Oleic acid (Octadecenoic)	30.61±0.50 <sup>b</sup>	40.89±0.10 <sup>a</sup>	15.69±0.12 <sup>e</sup>	17.55±0.44 <sup>d</sup>	29.28±0.38 <sup>b</sup>	20.78±0.28 <sup>c</sup>
Gadoleic acid (Eicosenoic)	ND	ND	0.21±0.00 <sup>c</sup>	0.34±0.02 <sup>b</sup>	0.47±0.02 <sup>a</sup>	0.38±0.02 <sup>b</sup>
Linoleic acid (Octadecadienoic)	2.39±0.04 <sup>d</sup>	2.01±0.03 <sup>d</sup>	12.74±0.2 <sup>a</sup>	13.85±0.18 <sup>a</sup>	9.64±0.79 <sup>b</sup>	7.83±0.08 <sup>c</sup>
SFA	6.56±0.09 <sup>d</sup>	7.89±0.19 <sup>cd</sup>	8.75±0.25 <sup>bc</sup>	9.57±0.23 <sup>ab</sup>	10.29±0.75 <sup>a</sup>	6.8±0.16 <sup>d</sup>
MUFA	30.61±0.59 <sup>b</sup>	40.89±0.10 <sup>a</sup>	15.90±0.13 <sup>e</sup>	17.89±0.41 <sup>d</sup>	29.75±0.4 <sup>b</sup>	21.16±0.2 <sup>c</sup>
PUFA	2.39±0.04 <sup>d</sup>	2.01±0.03 <sup>d</sup>	12.74±0.2 <sup>a</sup>	13.85±0.18 <sup>a</sup>	9.64±0.79 <sup>b</sup>	7.83±0.08 <sup>c</sup>
UFA/SFA	5.02±0.00 <sup>a</sup>	5.45±0.11 <sup>a</sup>	3.27±0.13 <sup>c</sup>	3.31±0.01 <sup>c</sup>	3.83±0.16 <sup>b</sup>	4.21±0.12 <sup>b</sup>
O/L	12.8±0.01 <sup>b</sup>	20.29±0.3 <sup>a</sup>	1.23±0.00 <sup>d</sup>	1.26±0.01 <sup>d</sup>	3.04±0.2 <sup>c</sup>	2.65±0.16 <sup>c</sup>

ND=Not detected. The values are mean ± SD (Standard deviation) of (n=3) observations. The values in each row with a different superscript are significantly different ( $P < 0.05$ ).

SFA- Saturated Fatty Acid; MUFA- Monounsaturated Fatty Acid; PUFA- Polyunsaturated Fatty Acid; UFA/SFA- Ratio of unsaturated fatty acid to saturated fatty acid; O/L- Oleic to linoleic ratio.

However, the latter one was not identified in Girnar-4 and Girnar-5. Linoleic acid is the only polyunsaturated fatty acid (PUFA) detected among all the varieties, with the highest extent in KL-9 (13.85 g/100g) and the lowest extent in Girnar-4 (2.01 g/100g). The two varieties, Girnar-4 and Girnar-5, were found to have significantly ( $P < 0.05$ ) higher oleic acid contents (40.89 and 30.61 g/100g, respectively). In contrast, both were found with significantly ( $P < 0.05$ ) lower quantities of linoleic acid (2.01 and 2.39 g/100g). Other varieties have similar fatty acid profiles with distinct variability, which may be attributed to the genetic makeup and agronomic factors<sup>20</sup>. Some of the derived indicators from fatty acid profiles, such as oleic/linoleic acid (O/L) ratio, unsaturated /saturated (UFA/SFA) ratio and omega-3/omega-6 ( $\omega$ -3/ $\omega$ -6) ratio, are important indicators for nutritional quality as well as oxidative stability. In groundnuts, an O/L ratio of  $\geq 9$  is referred to as high oleic, 3 to 9 as medium oleic and 1 to 2 as normal variety<sup>7</sup>. The O/L ratio for all varieties was calculated and depicted in Table 1. Girnar-4 has significantly ( $P < 0.05$ ) the highest O/L ratio (20.29), followed by Girnar-5 (12.8). Whereas other varieties have O/L ratios in order as follows: GJG-HPS-1 (2.65), GJG-22 (3.04), KL-9 (1.26), and GJG-31 (1.23), respectively. Generally, in high oleic varieties, the activity of the oleic desaturase enzyme is suppressed, which is essential for the conversion of oleate to linoleate during seed maturation<sup>6</sup>. Several studies have reported that groundnuts with high O/L ratio were found effective in delaying the onset of peroxidation compared to normal varieties with lower O/L ratio<sup>21,22</sup>, and this was attributed to the relatively lower oxidation rate of oleic acid (10-12 times) than linoleic acid<sup>23</sup>.

#### Evaluation of accelerated oxidative stability

The oxidative stability, in terms of induction time of groundnut varieties, was analysed at three temperature levels (Table 2). The observed induction times were reduced with increased temperature, affirmed by regression coefficient values ( $R^2 > 0.996$ ). A similar decreasing trend of induction time with temperature was observed in different vegetable oils through the rancimat technique<sup>24</sup>. The Girnar-4 variety has shown the significantly ( $P < 0.05$ ) highest induction time of 672 minutes, followed by the Girnar-5 variety of 600.25 minutes at 120°C. Whereas, in other varieties, *i.e.*, GJG-22, GJG-HPS, KL-9 and GJG-31, induction times were as follows:

389, 299, 200.85 and 164.78 minutes at 120°C. A similar trend in the order was observed at 130°C and 140°C for all varieties. The higher induction times of Girnar-4 and Girnar-5 were due to the high oleic acid content and corresponding O/L ratio. The resistance of the fat to auto-oxidation is influenced by several factors such as fatty acid composition and availability of oxygen to propagate the chain reaction; thereby, monounsaturated fatty acids like oleic acid have a lesser tendency to auto-oxidation process<sup>25,26</sup>. Higher induction times and oxidative stability of high oleic acid peanuts were reported by Okeffe *et al.*<sup>27</sup> and Huang *et al.*<sup>28</sup>. Similarly, along with fatty acid composition, other contributing factors, *i.e.*, phenols and tocopherols, were reported to hinder the oxidation process to some extent<sup>29,30</sup>.

#### Kinetic parameters of different groundnut varieties

The fat oxidation process in fat-rich agro products, especially groundnuts, during transport and storage follows a complex reaction profile. The Arrhenius kinetic model was applied to determine the stability and quality of groundnut varieties for the best fit with respect to recorded data.

The Arrhenius kinetic parameters, *i.e.*, activation energy  $E_a$  (kJ/mol), pre-exponential or frequency factor  $A$  ( $h^{-1}$ ), along with the reaction rate constant  $k$  ( $h^{-1}$ ) and their respective regression coefficient values, were calculated and depicted in Table 3. It was observed that reaction rate constants were increased with the temperature with well-acceptable regression coefficients (0.987 to 0.999). This means the fatty acids get oxidised linearly by a rise in temperature. Similar findings of increased reaction rates with temperature were recorded previously in avocado and olive oil through rancimat analysis<sup>9,10</sup>. The resistance of fatty acids to oxidation can be known through the Arrhenius activation energy, as it was described, the minimum energy required for the bond scission to initiate the reaction<sup>11</sup>. Polyunsaturated fatty acids

Table 2 — Oxidative stability (min) of selected groundnut varieties

Variety	Induction time (min)		
	120°C	130°C	140°C
GJG-HPS-1	299±1.41 <sup>d</sup>	165.25±0.77 <sup>c</sup>	88.22±0.48 <sup>d</sup>
Girnar-4	672±1.41 <sup>a</sup>	256.47±0.67 <sup>a</sup>	138.75±0.35 <sup>a</sup>
Girnar-5	600.25±0.35 <sup>b</sup>	238.94±0.78 <sup>b</sup>	127.72±0.39 <sup>b</sup>
GJG-31	164.78±0.31 <sup>f</sup>	89.46±0.76 <sup>f</sup>	56.41±0.58 <sup>f</sup>
GJG-22	389±0.24 <sup>c</sup>	160.80±0.82 <sup>d</sup>	92.14±0.19 <sup>c</sup>
KL-9	200.85±1.20 <sup>e</sup>	112.75±1.34 <sup>e</sup>	67.50±0.70 <sup>e</sup>

The values are mean±SD (Standard deviation) of (n=3) observations, The values in each column with a different superscript are significantly different ( $P < 0.05$ ).

Table 3 — Reaction rates and Arrhenius parameters of selected groundnut varieties

Variety	Reaction rate constant $k$ ( $\text{h}^{-1}$ )			$E_a$ (kJ/mol)	$A \times (10^{10})$ ( $\text{h}^{-1}$ )	Regression coefficient $R^2$
	120°C	130°C	140°C			
GJG-HPS-1	0.200±0.000 <sup>c</sup>	0.363±0.000 <sup>c</sup>	0.679±0.003 <sup>c</sup>	82.33±0.02 <sup>d</sup>	1.85±0.20 <sup>c</sup>	0.999
Girnar-4	0.089±0.000 <sup>f</sup>	0.233±0.000 <sup>e</sup>	0.433±0.002 <sup>f</sup>	107.05±0.15 <sup>a</sup>	1700±42 <sup>a</sup>	0.987
Girnar-5	0.099±0.000 <sup>e</sup>	0.251±0.000 <sup>d</sup>	0.469±0.001 <sup>e</sup>	104.64±0.25 <sup>b</sup>	840±56.6 <sup>b</sup>	0.991
GJG-31	0.363±0.002 <sup>a</sup>	0.670±0.005 <sup>a</sup>	1.062±0.013 <sup>a</sup>	72.49±0.34 <sup>e</sup>	0.14±0.05 <sup>c</sup>	0.995
GJG-22	0.154±0.002 <sup>d</sup>	0.373±0.001 <sup>c</sup>	0.648±0.005 <sup>d</sup>	97.16±0.74 <sup>c</sup>	155±36 <sup>c</sup>	0.989
KL-9	0.299±0.001 <sup>b</sup>	0.526±0.006 <sup>b</sup>	0.764±0.006 <sup>b</sup>	73.45±0.41 <sup>e</sup>	0.205±0.007 <sup>c</sup>	0.998

The values are mean±SD (Standard deviation) of (n=3) observations. The values in each column with a different superscript are significantly different ( $P < 0.05$ ).

$E_a$ =activation energy,  $A$ =pre-exponential factor or frequency factor.

usually require lower activation energies than monounsaturated and saturated fatty acids<sup>31</sup>. Girnar-4 variety was observed with significantly ( $P < 0.05$ ) highest activation energy (107.05 kJ/mol) followed by Girnar-5 (104.64 kJ/mol). Whereas the remaining conventional varieties had widely variable ( $P < 0.05$ ) activation energy values in the following range of 72.49 to 97.16 kJ/mol. These observed ranges for conventional varieties were found to be in line with the activation energies observed for roasted peanut oils at different temperatures reported by Ciou *et al.*<sup>32</sup>. The higher activation energies of Girnar-4 and Girnar-5 were due to the high monounsaturated fatty acid content and the findings were similar to the activation energies observed in olive and avocado oils with rancimat method, owing to both similar fatty acid composition and O/L ratio<sup>10,31</sup>. Furthermore, the activation energies can also be increased by the presence of natural antioxidants, *i.e.*, phenols, tocopherols and also by other addition of synthetic antioxidants, thereby positively influencing the oxidative stability of extracted oil and products<sup>29,30</sup>. Along with this, Arrhenius kinetic parameter, also known as the frequency factor, refers to the occurrence of molecular collisions and orientation changes responsible for chemical reactions, such as fat oxidation, in the present context. The frequency factors also linearly increased with activation energy, and a similar trend was observed for other oils with rancimat studies<sup>10,11</sup>. This probably explains the results that, Girnar-4 ( $17 \times 10^{12}$ ) and Girnar-5 ( $8.4 \times 10^{12}$ ) have been observed with higher frequency factors. Similarly, GJG-31 has shown a lower frequency factor value of  $1.4 \times 10^9$  with the least activation energy recorded among varieties. Frequency factor values were meant to be more temperature sensitive; smaller changes in temperature and activation energy induce greater variation in frequency factor values<sup>11,30</sup>. Moreover, higher values of activation

energy and frequency factor indicate the dependency of oxidation on temperature; hence, slight temperature variations may produce significant changes in fat oxidation rate<sup>30</sup>. The effect of temperature on fat oxidation can be understood by temperature acceleration factor,  $Q_{10}$  and temperature coefficient,  $T_c$  ( $^{\circ}\text{C}^{-1}$ ). The significant ( $P < 0.05$ ) variability in  $Q_{10}$  value was observed among the varieties in the range from 1.71 to 2.20. The highest  $Q_{10}$  value of 2.2 was observed in Girnar-4, followed by 2.16 in Girnar-5, which indicates the decline in stability or increase in the rate of lipid oxidation by almost twofold at every 10°C increase in temperature<sup>11,30</sup>. Whereas other varieties have  $Q_{10}$  values as follows: GJG-22 (2.05), GJG-HPS-1 (1.84), KL-9 (1.72) and GJG-31 (1.71), respectively. Higher  $Q_{10}$  values of Girnar-4 and Girnar-5 were in accordance with the previous finding in different vegetable oils, *i.e.*, soybean (2.18), sunflower (2.15), canola (2.13), and corn (2.10)<sup>11</sup>. It was also found that  $Q_{10}$  values were in trend with activation energies, and similar findings were also observed in different vegetable oils<sup>11,23</sup>. In most of the cases, products with the highest  $Q_{10}$  values were found with longer predicted shelf life<sup>12,33</sup>. Similarly, Prakash K *et al.*<sup>23</sup> also observed that macadamia oil with a  $Q_{10}$  value of 2.15 has also shown the highest predicted shelf life of 15 months through rancimat study. Some studies found that the added antioxidants increased the  $Q_{10}$  values significantly in oils and their related products<sup>11,30</sup>. The temperature coefficient is an indicative parameter for the rate of oxidation, with co-ordinance of temperature, which was calculated from the slope of log (IT) vs temperature ( $^{\circ}\text{C}$ ). The temperature coefficients have maintained the trend with  $Q_{10}$  numbers. Girnar-4 has a higher  $T_c$  value of 3.4 and the lowest values were observed as 2.3 in both GJG-31 and KL-9. The remaining varieties, *i.e.*, Girnar-5, GJG-22, and GJG-HPS-1, have temperature coefficient values as follows: 3.3, 3.1, and 2.6,

respectively. These findings were in agreement with previous studies on different olive oil varieties<sup>34</sup>. The acceleration and temperature coefficient factors were likely to depend on the activity of pro-oxidants, the presence of natural and synthetic antioxidants and the solubility of the oxygen<sup>29,34</sup>.

#### Shelf-life Prediction

The shelf-life predictions of different varieties of groundnuts were calculated for 37°C from the log of induction time (h) versus temperature (°C) according to equation (2). It was observed that the Girnar-4 variety had shown a longer shelf life of 321.5 days, followed by Girnar-5 (244), GJG-22 (99.23), GJG-HPS-1 (32.94), KL-9 (12.66) and GJG-31 (9.6) respectively. The predicted shelf life of varieties has shown a good linearity range ( $R^2 = 0.98-0.99$ ). The observed shelf life of some of the conventional varieties, *i.e.*, GJG-HPS-1, KL-9, and GJG-31, was in line with previous findings in groundnut oil, which was found to be 18 days at 25°C and 45 days at 30°C<sup>35,36</sup>. The longer predicted shelf life of Girnar-4 and Girnar-5 is due to the higher O/L ratio. The results were further affirmed by good correlations observed between predicted shelf life with O/L ratio ( $R=0.998$ ) and induction time ( $R=0.996$ ). The previous findings of Davis *et al.*<sup>7</sup>, Ana *et al.*<sup>22</sup>, and O'Keefe *et al.*<sup>27</sup> showed that a higher O/L ratio improved the stability of peanuts and their products, and longer shelf life was observed than the normal varieties with a lower O/L ratio. This is attributed to the relatively lesser unsaturation (double bonds); thereby, limited sites were available for oxygen to

react majorly during storage and transport. However, the GJG-31 variety has been observed to have a shorter shelf life due to the higher unsaturation (less O/L ratio). These predictions of shelf life are based on the oxidized conditions, which are indicative of grain stability. However, in practical storage, the shelf life of nuts and oil seeds would be affected or influenced by grain freshness, moisture, packing and storage conditions.

#### Other Chemical Characteristics Influencing Stability

The peroxide value is generally considered an essential quality parameter, indicating the degree of primary oxidation reaction pertaining to fat oxidation, especially in foods. The peroxide values of oxidized samples are depicted in Fig. 1. The results showed that, initially, raw samples have negligible peroxide values. It was observed that there was a wide variation in peroxide values across the three different accelerated temperatures, which is attributed to the temperature and unsaturation that supports peroxide development<sup>37</sup>. Besides, high temperature also destroys the heat-labile antioxidant components, *i.e.*, phenols, vitamin C and vitamin E; thereby, the probability of auto-oxidation and generation of oxidation by-products becomes high<sup>37</sup>. It was noticed that varieties with less O/L ratio have been found to have higher peroxide values, *i.e.*, 349.4 in GJG-31 at 130°C, 324.93 in KL-9 at 140°C, and 303.19 meq O<sub>2</sub>/kg of oil in GJG-31 at 140°C. This may be due to the higher number of double bonds, resulting in more reactive sites for oxygen to react<sup>38</sup>. In contrast, the high oleic acid groundnuts have comparatively lesser

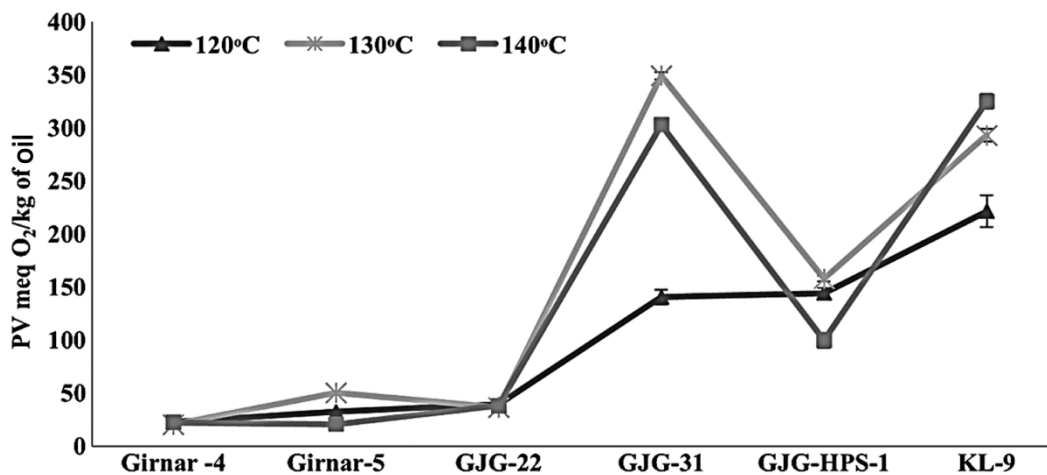


Fig. 1 — Peroxide values (PV) of oxidized samples (deskinmed split kernels) of all varieties at three different temperatures (120°C, 130°C and 140°C). The peroxide values were expressed in milli equivalence (meq) of O<sub>2</sub>/kg of oil. The values are means and error bars indicating the standard deviation (n=3) observations.

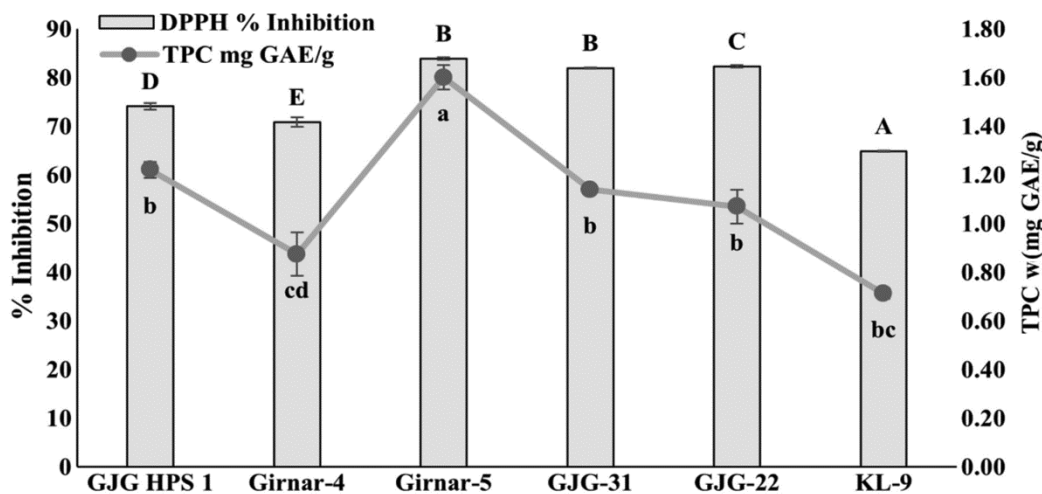


Fig. 2 — The antioxidant activity and total phenolic content (TPC) of different varieties of groundnuts (de-skinned whole kernels) on a dry mass basis. TPC was expressed as gallic acid equivalence (GAE) per gram, and DPPH (2,2-diphenyl-1-picrylhydrazyl) was expressed as percentage inhibition. The values are means and error bars indicating the standard deviation ( $n=3$ ). Different letters (lowercase for TPC and uppercase for DPPH activity) indicate a significant difference at ( $P < 0.05$ ).

peroxide values, *i.e.*, 22.75, 20.52, and 22.57 meq  $O_2$ /kg of oil at 120, 130, and 140°C in Girnar-4. Meanwhile, in Girnar-5, the values are as follows: 32, 50.27, and 20.92 meq  $O_2$ /kg of oil at 120, 130, and 140°C respectively. Similarly, O'keefe *et al.*<sup>27</sup> also observed that the development of peroxides was considerably low in high oleic peanuts with longer induction times compared to the normal varieties.

The total phenol and antioxidant activities of different varieties of groundnut are illustrated in Fig. 2. The results showed that total phenol contents ranged from 0.71 to 1.6 mg GAE/g, and the highest phenolic content of 1.6 mg GAE/g was observed in the Girnar-5 variety. The observed variability in total phenol content among the varieties may be attributed to the genetic makeup, post-harvest handling, etc<sup>39</sup>. The ranges of total phenolic contents were found to correlate with the previous findings reported in groundnut kernels without skin<sup>19</sup>. The antioxidant activity was also highest for the Girnar-5 variety (84%). In addition, a good correlation ( $R=0.863$ ) was observed between TPC and antioxidant activity. The lowest TPC and antioxidant activity values were observed in the KL-9 variety (64.92%).

## Conclusion

The characterisation with respect to fatty acids and factors influencing the stability of groundnuts were studied. The accelerated oxidative stability studies revealed that the two high oleic groundnuts, Girnar-4 and Girnar-5, showed excellent potential to sustain

the oxidation process. Other parameters, such as antioxidant activity, had a minor effect on stability, which may correlate with the natural oxidation process. The crucial kinetic parameters, *i.e.*, activation energy and frequency factors, were found to be variably higher for the high oleic varieties than other conventional varieties. Moreover, the following research output might draw out a realistic perspective of oxidation as the samples taken for analysis were whole kernels, and the research findings will be useful in exploring the product or confections based on groundnuts with higher shelf-life.

## Conflict of interest

The authors declare that they have no known conflicting interests that could have appeared to influence the work reported in this paper.

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