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## THERMAL OXIDATION KINETIC OF SESAME OIL (*Sesamum indicum* L.) BY <sup>1</sup>H NMR

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### ABSTRACT

This study aims to investigate by <sup>1</sup>H NMR the thermal oxidation kinetics of sesame oil (SO) and commercial sesame oil (CSO) obtained from roasted and unroasted seeds, respectively. The samples were heated at 180°C by 8 hours/day for 15 days. The <sup>1</sup>H NMR data analysis indicated that the hydrogen concentration decreases during 96 h of heating, remaining at 69.51%, 60.63% and 42.69% of allylic (E), vinylic (V) and bis-allylic (G) hydrogen in SO, and 49.29%, 38.51%, 18.58% in CSO, respectively. Behaving as the first order oxidation kinetics, SO average rate constant ( $k = \text{mol.L}^{-1}.\text{h}^{-1}$ ) was:  $k_G = 0.088 > k_V = 0.0052 > k_E = 0.0037$  and half-life period (h),  $t_{1/2}(E) = 188.37 > t_{1/2}(V) = 134.56 > t_{1/2}(G) = 79.04$ . To CSO,  $k_G = 0.0169 > k_V = 0.0101 > k_E = 0.0074$  and  $t_{1/2}(E) = 94.18 > t_{1/2}(V) = 68.49 > t_{1/2}(G) = 41.12$ . These results indicated that SO is more resistant to thermal oxidation [ $<k, >t_{1/2}$ ] than CSO [ $>k, <t_{1/2}$ ]. The study allowed to conclude that sesame oil obtained from unroasted samples has higher thermal-stability than commercial sesame oil from roasted seeds and that their cannot be used after 14.3 and 3.6 hours, respectively, for deep-frying purposes at 180°C.

**Keywords:** Kinetic reaction; thermal oxidation, sesame oil; <sup>1</sup>H NMR

### INTRODUCTION

Knowledge of the benefits that functional foods have on health has increased the consumption of vegetable oils with high levels of essential fatty acids, creating the need for more effective quality control. One of the main causes for food degradation is the oxidation of unsaturated fatty acids, that starts when lipids are exposed to environmental factors such air, light, temperature and catalyst, producing undesirable flavors (rancid odor), discoloration and nutritional changes (Silva, Borges and Ferreira, 1999). Oils with a high degree of unsaturation, like sesame oil, meet the requirements of functional foods having beneficial properties for health and nutrition (Moraes and Colla, 2006).

Sesame (*Sesamum indicum* L.) is an oleaginous vegetal highly used in the food, pharmaceutical and cosmetic industries. Its seeds provide approximately 50% of oil with a high concentration of unsaturated fatty acids (mainly linoleic and oleic acids). The total unsaturated fatty acids in the oil is approximately 85% and also contains phytosterols and lignans (Yoshida, et al, 2007; Reshma et al. 2010). Sesame oil contains significant levels of natural antioxidants like sesamine and sesamolone, which give high oxidative stability (Abou-Gharbia et al. 1997; Kim and Choe, 2005; Ghafoorunissa, 2007; Sukumar, Armboor and Arumughan, 2008; Lee et al. (2009).

Oils with a high degree of unsaturation are susceptible to oxidation but sesame oil has reserves of endogenous antioxidants, which interfere with the oxidation reactions. During oxidation the number of unsaturations decrease, and can be investigated as iodine values, being converted to primary and secondary oxidation products. Monitoring these unsaturations presents triacylglycerol (TAG), fatty acid acyl fragments, in a time interval, characterize the oil oxidation kinetics (Berchmans, Morishita and Takarada, 2010). Thermal oxidation kinetics studies in vegetable oils are usually performed by monitoring the iodine, peroxides and acidity values at different oxidation times. Nzikou et al. (2010), studying sesame oil, obtained good correlation between iodine and peroxides values, determining kinetic parameters like rate constant and activation energy. Currently, thermal analysis such as DSC, PDSC, CSDP and DTG methods are popular in studies involving oxidative stabilities determination of vegetable oils (Nzikou et al., 2010). Studies conducted by Tan, et al (2001) with 10 vegetable oils, found that rate constant and activation energy were determined by DSC data Adhvaryu, et al (2000); Santos et al., (2004); Yu, Chen and Gong, 2010).

Nevertheless, there are few studies that discuss the utilization of spectroscopic techniques like high resolution NMR, especially <sup>1</sup>H and <sup>13</sup>C NMR, as a potential tool to provide insights into the chemical structure of TAG molecules and the nature of unsaturation in the fatty acid chain (Adhvaryu, et al,

2000). In this sense, <sup>1</sup>H NMR spectroscopy has much to contribute because this technique can monitor the hydrogen concentration of vinyl, bis-allyl, allyl and alkyl groups at any reaction time. The spectra show the structural changes caused by oxidation reactions and NMR- derived structural parameters can explain the thermal, oxidative and kinetic behavior of vegetable oils.

Therefore <sup>1</sup>H NMR use in oils oxidation studies, fats and foods tend to increase due to the large amount of information that NMR can offer in a short period of time, with a reduced amount of sample sample (Guillén and Ruiz, 2008).

This work uses <sup>1</sup>H NMR spectroscopy to study the thermal oxidation kinetics of sesame oils by monitoring the concentration of allylic, bis-allylic and vinylic hydrogen.

### MATERIAL AND METHODS

#### Extraction of Sesame Oil

Unroasted white raw sesame seeds were acquired locally. The seeds were dried at 50°C for 8 h, crushed and subjected to continuous extraction for 8 hours in a Soxhlet apparatus using hexane as solvent. After solvent removal in a rotary evaporator, the crude oil was centrifuged at 3000 rpm, yielding a translucent yellow oil supernatant that was decanted and used in the experiments.

#### Thermoxidation Oils

Two oils were used, one commercial extra virgin sesame oil (Sesame Real brand) purchased in the local market, previously obtained from roasted seeds (240°C for 20 min) and another, extracted from white unroasted seeds, using hexane as solvent. The oils were heated on a heating plate containing 100 mL of each oil, in 250 ml of Becker, at 180 °C (this is the common temperature of deep-frying process) for 8 h/day during 15 days in a discontinuous manner. The bottles remained open and exposed to light in the cupboard during this period. Samples of 0.7 mL were collected after 8 h of heating and their <sup>1</sup>H NMR spectra recorded.

#### <sup>1</sup>H NMR spectra

A 100 mg of each oil sample was dissolved in 0.7 mL of CDCl<sub>3</sub> and their NMR spectra recorded in a Varian-300 MHz spectrometer, Mercuri model, operating in the FT mode at room temperature. The spectra were obtained for <sup>1</sup>H

nuclei at 300.057 MHz using 16 K points, spectral width of 14 ppm, acquisition time 3.3 s, relaxation time of 1.0 s, pulse width 45°, number of scans 16 and total time about 1.12 minutes. <sup>1</sup>H NMR simulated spectrum was performed by using ACD/labs 12.0/ChemSketch program.

RESULTS AND DISCUSSION

All the hydrogen can be monitored during the thermal oxidation process in the integrated spectrum. Bis-allylic hydrogen is present in linolenic and linoleic acyl fragments; vinylic and allylic hydrogen are present in linolenic, linoleic and oleic acyl fragments (Guillén and Goicoechea, 2009).

The bis-allylic, vinylic and allylic hydrogen concentrations for the sesame oils are shown in Table 1, as obtained from <sup>1</sup>H NMR spectra integrated under thermal oxidation process.

Table 1 Allylic (E), vinylic (V) and bis-allylic (G) hydrogen concentrations as obtained from integrated <sup>1</sup>H NMR spectra of sesame oils under thermal oxidation.

period*	Sesame oil (%)			Commercial sesame oil (%)		
	E	V	G	E	V	G
0	9.84	7.52	2.60	9.94	7.66	2.69
16	9.59	7.23	2.44	8.93	6.62	2.15
32	9.74	7.23	2.36	7.75	5.42	1.55
48	8.93	6.55	2.09	6.92	4.62	1.16
64	8.36	6.00	1.82	6.08	3.91	0.87
80	7.73	5.33	1.46	5.64	3.50	0.68
96	6.84	4.53	1.11	4.90	2.95	0.50
112	6.31	4.06	0.91	-	-	-

(\*): heating time (h) at 180 °C.

The data analysis shown in Table 1 indicates that allylic, vinylic and bis-allylic hydrogen concentration decreased with oxidation time. Comparing data from the two oils it was observed that sesame oil (SO), obtained from the unroasted seeds was more resistant to oxidation than commercial sesame oil

(CSO) obtained from roasted seeds. After 96 hours of heating higher hydrogen concentration to sesame oil was observed (Figure 1).

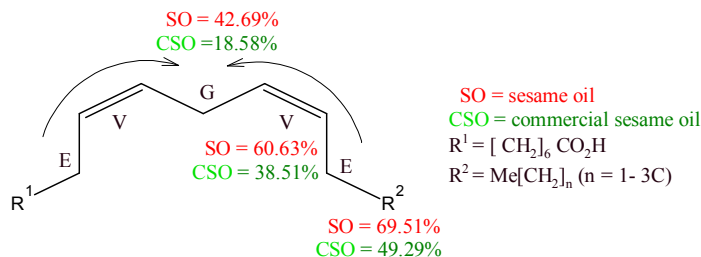


Figure 1 Fatty acid acyl fragments in sesame oil indicating the most affected positions under thermal oxidation conditions (96 h at 180°C).

Figure 1 and Table 1 data analysis shows that bis-allylic, vinylic and allylic hydrogen were the most consumed, respectively. This is strong evidence to support the radical mechanism in vegetable oil under thermal stress that begins with bis-allylic hydrogen abstraction. Hydrogen of the bis-allylic methylene groups is highly susceptible to rapid radical attack and it initiates oxidative degradation of the TAG molecules.

Thermal oxidation involves oxygen reaction with unsaturated acyl fragments in TAG, the major oil component (≥ 95%). Although the reaction was conducted in an open environment with good oxygenation, the kinetics can be treated as first-order, depending only on TAG concentration, especially by their unsaturated acyl groups, monitorable by G, K, E peaks in the <sup>1</sup>H NMR spectra. The kinetic rate constants and half-life period for bis-allylic, vinylic and allylic hydrogen can be accessed by using Equations 1 and 2. Results are presented in Table 2:

$$\ln [A_0] / [A] = k t$$

$$(1)$$

$$t_{1/2} = \ln 2 / k$$

$$(2)$$

Where: Ln, natural logarithm; [A<sub>0</sub>] and [A] the hydrogen molar concentrations at the beginning and at determined periods of time, from <sup>1</sup>H NMR integrated spectra; k, the rate constant; t the oxidation time elapsed and t<sub>1/2</sub> the half-life period.

Table 2 Kinetic parameters of sesame oils (Sesamum indicum L.) in thermal oxidation

Period*	Sesame oil			Commercial sesame oil		
	k <sub>E</sub>	k <sub>V</sub>	k <sub>G</sub>	k <sub>E</sub>	k <sub>V</sub>	k <sub>G</sub>
0	0.0016	0.0025	0.0040	0.0067	0.0091	0.0140
16	0.0003	0.0012	0.0030	0.0078	0.0108	0.0172
32	0.0020	0.0029	0.0045	0.0075	0.0105	0.0175
48	0.0025	0.0035	0.0056	0.0077	0.0105	0.0176
64	<b>0.0030</b>	<b>0.0043</b>	<b>0.0072</b>	0.0071	0.0098	0.0172
80	<b>0.0038</b>	<b>0.0053</b>	<b>0.0089</b>	0.0074	0.0099	0.0175
96	<b>0.0040</b>	<b>0.0055</b>	<b>0.0094</b>	0.0067	0.0091	0.0140
112	<b>0.0039</b>	<b>0.0055</b>	<b>0.0096</b>	-	-	-
k <sub>average</sub>	0.0037	0.0052	0.0088	0.0074	0.0101	0.0169
t <sub>1/2</sub>	188.3660	134.5621	79.0434	94.1762	68.4996	41.1230

(\*): heating time (h) at 180°C. k<sub>E</sub>, k<sub>V</sub>, k<sub>G</sub> = rate constant (mol. L<sup>-1</sup>. h<sup>-1</sup>) as determined from allylic (E), vinylic (V) and bis-allylic (G) hydrogen present in acyl fragments of TAG; t<sub>1/2</sub> = half-life period (h) of allylic, vinylic and bis-allylic hydrogen.

Oxidation is a very complex process leading to numerous oxidation products involving various intermediates. These intermediate compounds have their own rate constants. Complex reactions also involving endogenous antioxidants present in sesame oil affect the first-order kinetic, so the rate constant is not regular during the first 48 hours of thermal oxidation. After the consumption of antioxidants the reactions follow first-order kinetics, showing similar k values, from which average rate constants and half-life periods were determined (Figures 2 and 3).

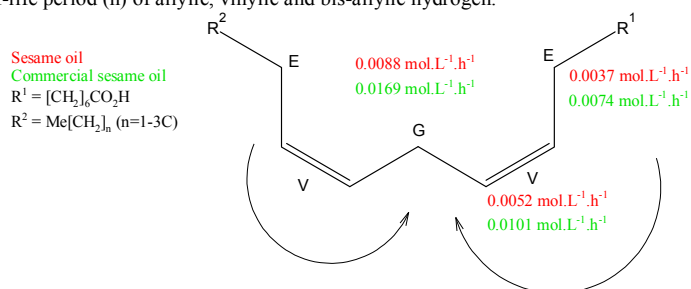
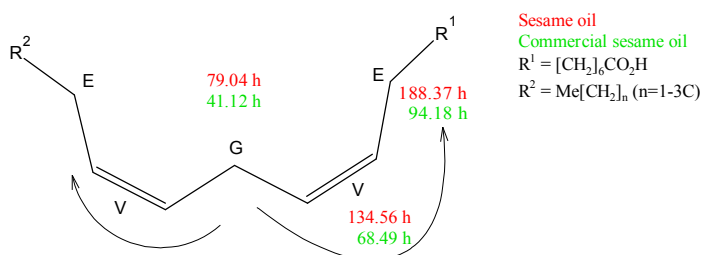


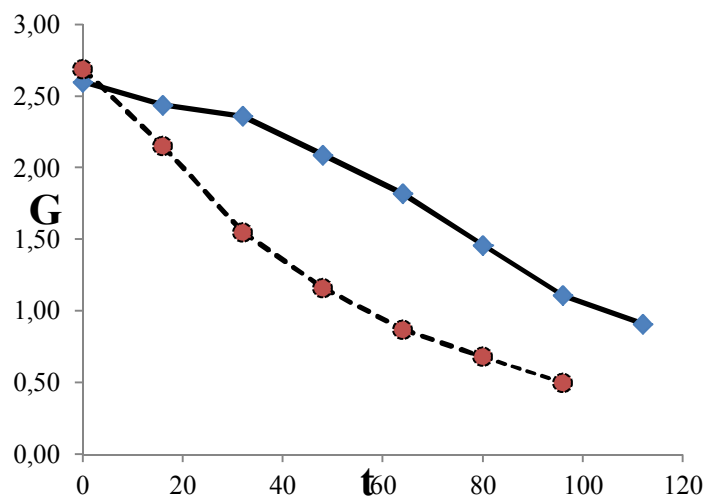
Figure 2 Average rate constant of allylic (E), vinylic (V) and bis-allylic (G) hydrogen as determined from <sup>1</sup>H NMR spectra data of sesame oils under thermal oxidation.



**Figure 3** Half-life period of allylic (E), vinylic (V) and bis-allylic (G) hydrogen as determined from <sup>1</sup>H NMR spectra data of sesame oils under thermal oxidation.

As regards commercial sesame oil, the rate constant values were similar from when thermal oxidation began, being used to determine average constant rate (*k*) and half-life periods (Figures 3 and 4). Because the commercial sesame oil was extracted from roasted seeds (previously heated at 240°C for 20 minutes), these procedures suggest partial degradation of natural antioxidants and the formation of secondary oxidation compounds. The sesame oil obtained from unroasted seeds contained more antioxidant to protect it. Analysis of Figures 3 and 4 indicates that sesame oil (obtained from unroasted seeds) is more resistant to thermal oxidation conditions [*k* > *k*<sub>1,2</sub>] than commercial sesame oil (obtained from roasted seeds) [*k* < *k*<sub>1,2</sub>]. The data also reveal that bis-allylic, vinylic and allylic hydrogen concentration is a good oil quality indicator and that its concentration can be easily monitored by <sup>1</sup>H NMR spectroscopy.

From Table 1 data, Figure 4 was performed to show bis-allylic hydrogen (G) concentration reduction as a function of oxidation time for both sesame oils.



**Figure 4** Tendency lines for sesame oil [—] and commercial sesame oil [---], showing bis-allylic hydrogen concentration [G] and thermal oxidation time (t) as obtained from <sup>1</sup>H NMR spectra data in Table 1.

Tendency lines analysis in Figure 4, demonstrated that for both sesame oils, bis-allylic hydrogen concentration and oxidation times obey the correlation as described by Equations 3 and 4.

$$G_{SO} = -7.10 \cdot 10^{-5} t^2 - 8.10 \cdot 10^{-3} t + 2.622 \quad (3)$$

[R<sup>2</sup> = 0.991; R = 0.995; n=8]

$$G_{CSO} = -0.040t + 2.704 \quad (4)$$

[R<sup>2</sup> = 0.998; R = 0.999; n = 7]

Where: G<sub>SO</sub> is bis-allylic hydrogen concentration for sesame oil obtained from unroasted seeds; G<sub>CSO</sub> is bis-allylic hydrogen concentration for commercial sesame oil obtained from roasted seeds; t the time period (h).

Both equations show excellent correlations (R > 0.99) that explain more than 99% of the variance data.

These equations could be applied in human health studies to indicate the time by which sesame oils cannot be used after heating. Official norms (that have not yet been regulated in this respect) define that after heating, bis-allylic hydrogen concentration must be at least 95%. Equations 3 and 4 foresee that sesame oil cannot be used after 14.3 h of heating and commercial sesame oil cannot be used after 3.6 h of heating at 180°C.

Commercial sesame oil is extracted from roasted sesame seeds and, the obtained data indicate significant differences between the studied oils. The

procedure for obtaining the commercial sesame oil making it usable by 3.6 hours of heating at 180 °C.

## CONCLUSION

The kinetic parameters values of rate constants and half-life periods indicated that sesame oil (obtained from unroasted seeds) has higher thermal stability than commercial sesame oil (obtained from roasted seeds). H NMR spectra revealed that bis-allylic, vinylic and allylic hydrogen were, respectively, the most consumed in the thermoxidation process. Monitoring bis-allylic hydrogen, to a level at least 95% of initial concentration, sesame oil and commercial sesame oil cannot be used after 14.3 and 3.6 h of heating at 180°C, respectively.

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