

## Physicochemical evaluation of oil blends of *Glycine max* L., *Helianthus annus* L. and *Cocos nucifera* L. under thermoxidation

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### Abstract

The predominance of mono and polyunsaturated fatty acid of *Glycine max* L. (soybean) and *Helianthus annus* L. (sunflower) oils make them more unstable under high temperatures and susceptible to oxidation. On the other hand, the composition of the *Cocos nucifera* L. (coconut) oil is predominantly saturated and has high oxidative stability. The formulation of oil blends allows some improvements in their nutritional and physicochemical characteristics. Thus, the aim of this work is to evaluate the *G. max* oil (SB), *H. annus* oil (SF), *C. nucifera* oil (C) and the blends *G. max*:*C. nucifera* (SB:C, 75:25 v/v) and *H. annus*:*C. nucifera* (SF:C, 75:25 v/v) as to their physicochemical properties when under thermoxidation (180 °C/15 h). Before the thermoxidation, the C presented less degradation in relation to the others, while the SF:C was the most efficient in inhibiting oxidation due to the presence of low levels of peroxide values, however, it presented less degradation to  $\rho$ -anisidine and conjugated dieneic acids. The SF:C presented higher oxidative stability and less degradation in relation to SB:C. Consequently, the application of these oil blends is recommendable in processes that involve high temperatures, such as frying.

**Keywords:** Fatty acids, high temperatures, oxidation, vegetable oils.

## Avaliação físico-química de misturas de óleos de *Glycine max* L., *Helianthus annus* L. e *Cocos nucifera* L. sob termoxidação

### Resumo

O predomínio de ácidos graxos mono e poli-insaturados nos óleos de *Glycine max* L. (soja) e *Helianthus annus* L. (girassol) os tornam mais instáveis sob elevadas temperaturas e suscetíveis à oxidação. Por outro lado, a composição do óleo de *Cocos nucifera* L. (coco) é predominantemente saturada e possui alta estabilidade oxidativa. A formulação de misturas de óleos permite algumas melhorias em suas características físico-químicas e nutricionais. Assim, o objetivo deste trabalho é avaliar os óleos de *G. max* (SB), *H. annus* (SF), *C. nucifera* (C) e as misturas *G. max*: *C. nucifera* (SB:C, 75:25 v/v) e *H. annus*: *C. nucifera* (SF:C, 75:25 v/v) quanto às suas propriedades físico-químicas quando submetidos à termoxidação (180 °C/15 h). Antes da termoxidação, o C apresentava menor degradação em relação aos demais, enquanto o SF:C foi o mais eficiente em inibir a oxidação devido à presença de baixos teores de peróxidos, porém apresentou menor degradação para  $\rho$ -anisidina e ácidos dienóicos conjugados. O SF:C apresentou maior estabilidade oxidativa e menor degradação em relação ao SB:C. Consequentemente, a aplicação dessas misturas de óleos é recomendável em processos que envolvam altas temperaturas, como fritura.

**Palavras-chave:** Ácidos graxos, altas temperaturas, óleos vegetais, oxidação.

### Introduction

The lipidic oxidation causes the deterioration of the physiological mechanisms of raw materials, which can appear during its heating or long-term storage. The main mechanism of oil and fat oxidation is the self-oxidation. This reaction is spontaneous and it happens between atmospheric oxygen and lipids causing the oxidative deterioration (Weng & Wang, 2000).

The minority components of food, such as the vitamins and the essential fatty acids, can decompose developing flavors and

unpleasant odors, besides forming compounds that are toxic to health (Silva, Borges, & Ferreira, 1999). Vegetable oils with high content of polyunsaturated fatty acids have high potential for self-oxidation. The relation between oleic fatty acids and linoleic is important to determine the shelf life of the oil.

The higher amount of polyunsaturated in relation to monounsaturated, the shorter its lifespan will be and the higher its oxidation (Nyam, Tan, Lai, Long, & Che Man, 2009).

Vegetable oils are fundamental for a good functioning of the human body (Savva & Kafatos, 2016). The fatty acid composition differs each kind of oil. Under the nutritional point of view, the best proportion to be daily consumed for the maintenance of a balanced diet is of approximately 1:1:1 of saturated, monounsaturated and polyunsaturated fatty acids (ICMR, 1989; LaRosa *et al.*, 1990). The *G. max*, *H. annuus* and *C. nucifera* oils are produced in large scale worldwide. The *G. max* is mostly polyunsaturated and its main constituent is the linoleic ( $\omega 6$ ). This fatty acid is capable of having an anti-inflammatory effect, besides preventing cancer (Miles & Calder, 2012; Sawada, 2012). On the other side, it has low oxidative stability in high temperature processes.

The mid-oleic *H. annuus* oil, mostly monounsaturated, mainly oleic fatty acid (*Codex Alimentarius*, 2009). The reduction of occurrences of heart diseases are related to the consumption of oleic, however, in high temperatures, it is not very stable (Mahan & Escott-Stump, 2010).

The *C. nucifera* oil contains medium chain fatty acids, mainly lauric acid (Patil & Benjakul, 2019) and when ingested it is transported to the liver and converted in energy, being easily digested (Dayrit, 2015; Ribeiro, 2017). The composition of more than 90% of saturated fatty acids is responsible for granting the oil oxidative stability. In reason of several health benefits and high stability, gained interest in the consumer and industry (Patil & Benjakul, 2018).

Each oil has its physical-chemical singularity, the combination of two or more kinds of oils is necessary to allow improvements. Some of the changes are new nutritional characteristics, fatty acids diversity, physical-chemical property modification and oxidative stability increase.

Oils and fats change easily when stored, degrade and can form toxic compounds, therefore, it is necessary to analyze them and check if they are suitable for use. The most used parameters for measuring lipid oxidation are: analysis of free fatty acids, peroxides,  $\rho$ -anisidine, total oxidation value (Totox), conjugated dienoic acids, polar compounds and oxidative stability, among others.

Therefore, the study aims at characterizing the physicochemical properties and the profile of the fatty acids of the *G. max*, *H. annuus*, *C. nucifera* and their blends, *G. max*: *C. nucifera* and *H. annuus*: *C. nucifera*. Moreover, analyzing the behavior of these oils under thermoxidation conditions at  $180 \pm 5$  °C during periods of 0, 5, 10, 15 h.

## Materials e Methods

### Raw materials

The extra virgin, cold pressed refined oils of *G. max* (SB), mid-oleic *H. annuus* (SF) and *C. nucifera* (C) were bought in a local store (São José do Rio Preto, São Paulo, Brazil).

The formulation of the oil blends, *G. max*:*C. nucifera* (SB:C) and *H. annuus*:*C. nucifera* (SF:C), was defined after a preliminary test whose objective was to obtain the approximated proportion of 1:1:1 of saturated, monounsaturated and polyunsaturated fatty acids, respectively. The oils SB, SF and C were use in the proportion of 100, however SB:C and SF:C 75:25, v/v.

### Thermoxidation

The thermoxidation of the oils was made under a discontinuous way, that is, 10 h of heating on the first day and 5 h on the following day. The oils were *thermoxidized* on a heated plate at  $180 \pm 5$  °C with surface/volume ratio of 0.4/cm. Samples were collected at 0, 5, 10 and 15 h of heating and afterwards, cooled down in room temperature, stored in amber glass pots and inertized with gaseous nitrogen. The samples were stowed at a temperature of -18 °C until the moment of the analyses.

### Physicochemical analysis

Free fatty acids (FFAs), expressed in % of oleic, were determined according to the norm Ca 5a-40 of AOCS (2009). The acidity value (AV), in mg NaOH/g, was calculated by multiplying FFAs by 1.99. The peroxide values (PV) and  $\rho$ -anisidine ( $\rho$ AV) were measured according to the methods Cd 8-53, expressed in meq O<sub>2</sub>/kg and Cd 18-90 of AOCS (2009), respectively. The total oxidation value (Totox) was calculated according to Huimin *et al.* (2014) by the following formula:  $Totox = 2 PV + \rho AV$ .

The conjugated dienoic acids (CDA), expressed in %, were measured by the method Ti 1a-64 of AOCS (2009). To determine the total polar compounds, expressed in %, the chromatographic method was used in columns according to Dobarganes, Velasco and Dieffenbacher (2000). The refractive index, iodine and saponification values were evaluated according to the Cc 7-25, Cd 1c-85 e Cd 3a-94 methods of AOCS (2009) and expressed in 40 °C, g I/100 g and mg KOH/g, respectively.

The oxidative stability index (OSI) was determined following the Cd 12b-92 of AOCS (2009) method, using the Rancimat equipment (743 model, Metrohm Ltd, Herisau, Switzerland). For this determination, 3 g of oil and airflow at 20 L/h at temperature of 110 °C were used. The induction period was expressed in h.

The fatty acid methyl esters composition was determined according to the Ce 1-62 method of AOCS (2009) by capillary gas chromatography-CGC, using an Agilent 6850 Series GC System equipped with a 60 m Agilent DB-23 capillary column (50% cyanopropyl-methylpolysiloxane), internal diameter of 0.25 mm and 0.25  $\mu$ m film. The conditions for the chromatographic operations were as follows: column flow = 1.0 mL/min; linear velocity 24 cm/s; detector temperature 280 °C; injector temperature 250 °C; oven temperature at 110 °C for 5 min, then rising from 110 to 215 °C at 5 °C/min, followed by 215 °C for 34 min; carrier gas of helium; volume injected 1.0  $\mu$ L; 1:50 split. The fatty acid methyl esters were prepared by adapting the method described by Hartman and Lago (1973) to a micro-scale.

### Reagents

The reagents used in this study were obtained by commercial source: ethylic alcohol 95%, sodium hydroxide 0,1 M, phenolphthalein, acetic acid, chloroform, potassium iodide, sodium thiosulfate 0.01 M, starch,  $\rho$ -anisidine, iso-octane, hexane, ethyl ether, silica gel (granulometry 0.063-0.200 mm, n. 7734, Sigma-Aldrich, Merck, Bellefonte, PA),

sea sand, iodine, potassium hydroxide, cyanopropyl methylpolysiloxane, gaseous nitrogen.

#### Statistical analysis

The results obtained from the analytical determinations, in triplicate, were subjected to variance analysis and the differences between means were tested at 5% probability by the Tukey test. The software used was the ESTAT 2.0 version (UNESP, Jaboticabal, São Paulo, Brasil).

## Results and Discussion

The physicochemical analyses for the characterization of the oils are presented on Table 1. The free fatty acids content and acidity index of oils and fats are related to the occurrence of hydrolysis in the oil and, consequently, its final quality (Farhoosh *et al.*, 2009). According to *Codex Alimentarium* (2009), the recommended acidity index for refined and crude oils cold pressed is of 0.6 and 4 mg KOH/g, respectively.

**Table 1.** Characterization of the *G. max*, *H. annus*, *C. nucifera* oils and their blends.

Analyses	SB	SF	C	SB:C	SF:C
FFAs (%)	0.13 ± 0.01 <sup>b</sup>	0.13 ± 0.01 <sup>b</sup>	0.19 ± 0.01 <sup>a</sup>	0.14 ± 0.00 <sup>b</sup>	0.14 ± 0.00 <sup>b</sup>
AV (mg KOH/g)	0.26 ± 0.01 <sup>b</sup>	0.26 ± 0.01 <sup>b</sup>	0.38 ± 0.01 <sup>a</sup>	0.28 ± 0.00 <sup>b</sup>	0.28 ± 0.00 <sup>b</sup>
RI (40°C)	.468 ± 0.001 <sup>a</sup>	1.467 ± 0.001 <sup>a</sup>	1.446 ± 0.000 <sup>b</sup>	1.463 ± 0.001 <sup>a</sup>	1.462 ± 0.000 <sup>a</sup>
IV (g I <sub>2</sub> /100 g)	23.81 ± 0.00 <sup>a</sup>	111.87 ± 0.00 <sup>b</sup>	8.68 ± 0.00 <sup>c</sup>	97.66 ± 0.00 <sup>c</sup>	86.79 ± 0.00 <sup>d</sup>
SV (mg KOH/g)	00.86 ± 0.00 <sup>d</sup>	197.01 ± 0.00 <sup>e</sup>	264.84 ± 0.04 <sup>a</sup>	217.99 ± 0.05 <sup>b</sup>	213.05 ± 0.03 <sup>c</sup>

SB: *G. max*; SF: *H. annus*; C: *C. nucifera*; SB:C: *G. max*:*C. nucifera*; SF:C: *H. annus*:*C. nucifera*. FFAs: free fatty acids; AV: acidity value; RI: refractive index; IV: iodine value; SV: saponification value. Averages ± standard deviation of the analyses performed in triplicate followed by the same letter on the lines do not differ by Tukey test ( $p > 0.05$ ).

The oils analyzed agree with the stipulated limits and the highest result found for the free fatty acids content and acidity index is the *C. nucifera* oil since it is a crude oil which did not go through refining processes. The oils SB, SF, SB:C and SF:C did not differ statistically, showing the lowest averages.

Khan, Asha, Bhat and Khatoon (2011) found the values of 0.9; 1.6 and 0.5% of free fatty acids, in oleic, for oil blends of virgin *C. nucifera*:*S. indicum* (1:1, v/v), refined *C. nucifera*:*S. indicum* (1:1, v/v) and refined *C. nucifera*:*E. guineensis* oil (1:1, v/v), respectively. On the other hand, Marina, Che-Man, Nazimah and Amin (2009) found for the virgin *C. nucifera* oil of different brands from 0.15 to 0.25% in oleic.

Refractive index and iodine value are measures that analyze the level of instauration of the oils. According to Gunstone (2011), the lower the refractive index, the lower the amount of unsaturation and, consequently, the more stable the oil will be. As reported by The *Codex Alimentarius* (2009), the established levels for the refractive index of the oils SB, SF, and C are 1.466-1.467; 1.461-1.468 and 1.448-1.450, respectively. The SB, SF and C studied oils agree with the established limits for the refractive index and the SB:C and SF:C blends present intermediary levels compared to the pure oils.

In relation to the iodine value, the *G. max* oil presented the highest amount of unsaturation due to its composition of linoleic acid predominantly. Meanwhile, the *C. nucifera* oil presented the lowest index because it is mostly saturated.

The *C. nucifera* oil presented the highest saponification value, approximately 265 mg KOH/g, since it is mostly constituted by fatty acids of low molecular weight. On the other side, the SB:C and SF:C presented approximated values of 215 mg KOH/g, because the highest amounts of fatty acids are monounsaturated and polyunsaturated. According to Toscano, Riva, Foppa-Pedretti and Duca (2012), the refined *G. max* and *H. annus* oils present saponification values of 190.1 and 193.5 mg KOH/g, respectively.

The Table 2 refers to the profile of the fatty acids of the studied oils. The *G. max*, the *H. annus* and the *C. nucifera* oils are mostly constituted by polyunsaturated fatty acids (linoleic), monounsaturated (oleic) and saturated (lauric), respectively.

The *G. max* and *H. annus* oils are rich in  $\omega 6$ , essential fatty acid, which is efficient in fighting diseases, such as cancer (Sawada, 2012), anti-inflammatory processes and migraine (Santos & Weaver, 2018). The *G. max* oil has approximately 50% of  $\omega 6$ , while the *H. annus* oil has 47% of oleic. On the other hand, the *C. nucifera* oil has 47% of lauric.

The varied fatty acid composition, monounsaturated and polyunsaturated, of the *G. max* and *H. annus* oils contribute aggregating more diversity to the *C. nucifera* oil profile. Therefore, the oil blends are more complete, have more variety and more balanced amount of fatty acids when compared to their pure oils (Boukandoul *et al.*, 2019).

The SB:C oil is mostly constituted by polyunsaturated fatty acids (45%). The balance in the composition of these acids is showed in the relation saturated:monounsaturated:polyunsaturated (sat:mono:poly) in which the studied oil presented the proportion 1:1.6:2.2. Another important relation is the one related to the oleic and linoleic (ole/lin) composition which found value is 1/1.19.

According to Nyam *et al.* (2009), the relation between the content of ole/lin fatty acid determines the oil shelf life. Thus, the higher the amount of polyunsaturated in relation to monounsaturated, the higher the oxidation.

The SF:C oil, rich in monounsaturated fatty acids (37%) is the second more thermally stable when compared to the others. The relation oleic and linoleic is 1/0.83 and the proportion sat:mono:poly is 1:1.2:1.1. The SF:C is the only oil that approximated the established proportions (ICMR, 1989; LaRosa *et al.*, 1990).

According to Table 3, initially in relation to the peroxide value, the analyzed oils agreed with the maximum stipulated limit – refined and virgin oils or cold pressed is 10 and 15 meq/kg, respectively. The lowest levels refer to the SB and C oils which did not differ statistically.

During thermoxidation, the *C. nucifera* oil presented variations as to the peroxide value, possibly as a consequence of its production process, since it does not go through the traditional refinement steps (neutralization, clarification and deodorization). The formation of

hydrocarbons, hydroperoxides, free radicals and volatile compounds also contribute to the increase of the oil oxidation.

At the end of the 15 h, the SB and SF oils increased their peroxide values without oscillation. On the other hand, SB:C and SF:C presented the lowest values, although during thermoxidation they presented oscillation due to the significative presence of C.

Khan *et al.* (2011) obtained 6.2; 5.4 and 0.6 meq/kg for the peroxide values on the three kinds of oil blends: virgin *C. nucifera*:*S. indicum* (1:1, v/v), refined *C. nucifera*:*S. indicum* (1:1, v/v) and refined *C. nucifera*:*E. guineensis* oil (1:1, v/v), respectively, in 15 h of frying at 175 °C and S/V of 0.3/cm.

**Table 2.** Profile of the fatty acids of the *G. max*, *H. annus*, *C. nucifera* oils and their blends.

Fatty acids (%)	SB	SF	C	SB:C	SF:C
Saturated					
Caproic	nd	nd	0.24	nd	nd
Caprylic	nd	nd	7.73 ± 0.01 <sup>a</sup>	1.80 ± 0.02 <sup>b</sup>	1.84 ± 0.02 <sup>b</sup>
Capric	nd	nd	6.31 ± 0.02 <sup>a</sup>	1.49 ± 0.02 <sup>b</sup>	1.53 ± 0.01 <sup>b</sup>
Lauric	0.21 ± 0.02 <sup>d</sup>	0.10 ± 0.01 <sup>d</sup>	47.63 ± 0.07 <sup>a</sup>	11.38 ± 0.02 <sup>c</sup>	11.53 ± 0.03 <sup>b</sup>
Myristic	0.21 ± 0.01 <sup>c</sup>	0.13 ± 0.02 <sup>c</sup>	17.60 ± 0.03 <sup>a</sup>	4.33 ± 0.06 <sup>b</sup>	4.33 ± 0.10 <sup>b</sup>
Pentadecanoic	0.02 ± 0.01 <sup>a</sup>	0.03 ± 0.01 <sup>a</sup>	0.02 ± 0.01 <sup>a</sup>	0.03 ± 0.01 <sup>a</sup>	0.02 ± 0.01 <sup>a</sup>
Palmitic	11.21 ± 0.01 <sup>a</sup>	5.47 ± 0.16 <sup>e</sup>	8.60 ± 0.04 <sup>c</sup>	10.37 ± 0.05 <sup>b</sup>	6.52 ± 0.02 <sup>d</sup>
Margaric	0.10 ± 0.01 <sup>a</sup>	0.06 ± 0.01 <sup>a</sup>	0.02 ± 0.01 <sup>a</sup>	0.08 ± 0.02 <sup>a</sup>	0.04 ± 0.01 <sup>a</sup>
Stearic	3.81 ± 0.03 <sup>a</sup>	3.31 ± 0.04 <sup>d</sup>	3.41 ± 0.03 <sup>cd</sup>	3.59 ± 0.09 <sup>b</sup>	3.44 ± 0.02 <sup>c</sup>
Arachidic	0.37 ± 0.02 <sup>a</sup>	0.28 ± 0.03 <sup>ab</sup>	0.12 ± 0.02 <sup>c</sup>	0.31 ± 0.01 <sup>ab</sup>	0.24 ± 0.02 <sup>bc</sup>
Behenic	0.49 ± 0.02 <sup>bc</sup>	0.79 ± 0.02 <sup>a</sup>	0.04 ± 0.02 <sup>d</sup>	0.38 ± 0.02 <sup>c</sup>	0.60 ± 0.02 <sup>b</sup>
Lignoceric	0.18 ± 0.01 <sup>ab</sup>	0.27 ± 0.02 <sup>a</sup>	0.04 ± 0.01 <sup>c</sup>	0.15 ± 0.02 <sup>bc</sup>	0.21 ± 0.01 <sup>ab</sup>
Total	16.60 ± 0.10 <sup>d</sup>	10.44 ± 0.03 <sup>e</sup>	91.76 ± 0.20 <sup>a</sup>	33.91 ± 0.08 <sup>b</sup>	30.31 ± 0.05 <sup>c</sup>
Monounsaturated					
Palmitoleic	0.13 ± 0.01 <sup>a</sup>	0.11 ± 0.01 <sup>a</sup>	0.05 ± 0.01 <sup>a</sup>	0.09 ± 0.02 <sup>a</sup>	0.11 ± 0.01 <sup>a</sup>
Cis-10-heptadecenoic	0.06 ± 0.01 <sup>a</sup>	0.05 ± 0.01 <sup>a</sup>	nd	0.04 ± 0.01 <sup>a</sup>	0.04 ± 0.01 <sup>a</sup>
Oleic	24.96 ± 0.05 <sup>c</sup>	47.55 ± 0.17 <sup>a</sup>	6.29 ± 0.03 <sup>c</sup>	20.33 ± 0.03 <sup>d</sup>	37.36 ± 0.02 <sup>b</sup>
Eicosanoic	0.27 ± 0.01 <sup>a</sup>	0.23 ± 0.01 <sup>a</sup>	0.05 ± 0.01 <sup>b</sup>	0.18 ± 0.01 <sup>a</sup>	0.19 ± 0.01 <sup>a</sup>
Total	25.42 ± 0.02 <sup>c</sup>	47.94 ± 0.02 <sup>a</sup>	6.39 ± 0.07 <sup>e</sup>	20.64 ± 0.05 <sup>d</sup>	37.70 ± 0.03 <sup>b</sup>
Polyunsaturated					
t-Linoleic	0.57 ± 0.01 <sup>a</sup>	0.55 ± 0.03 <sup>a</sup>	0.08 ± 0.02 <sup>c</sup>	0.46 ± 0.02 <sup>ab</sup>	0.43 ± 0.01 <sup>b</sup>
Linoleic	50.50 ± 0.10 <sup>a</sup>	40.36 ± 0.04 <sup>b</sup>	1.67 ± 0.03 <sup>e</sup>	39.62 ± 0.12 <sup>c</sup>	30.93 ± 0.03 <sup>d</sup>
t-Linolenic	1.36 ± 0.01 <sup>a</sup>	0.41 ± 0.01 <sup>c</sup>	nd	1.04 ± 0.01 <sup>b</sup>	0.31 ± 0.01 <sup>c</sup>
α-Linolenic	5.56 ± 0.02 <sup>a</sup>	0.30 ± 0.02 <sup>c</sup>	0.11 ± 0.01 <sup>d</sup>	4.33 ± 0.03 <sup>b</sup>	0.32 ± 0.01 <sup>c</sup>
Total	57.99 ± 0.02 <sup>a</sup>	41.62 ± 0.22 <sup>c</sup>	1.86 ± 0.02 <sup>e</sup>	45.45 ± 0.07 <sup>b</sup>	31.99 ± 0.04 <sup>d</sup>
Sat:Mono:Poly	1:1.5:3.5	1:4.6:4.0	1:4.6:4.0	1:1.6:2.2	1:1.2:1.1
Ole/Lin	1/2.02	1/0.85	1/0.27	1/1.95	1/0.83

SB: *G. max*; SF: *H. annus*; C: *C. nucifera*; SB:C: *G. max*: *C. nucifera*; SF:C: *H. annus*: *C. nucifera*. nd: not detected. Ole/Lin: oleic e linoleic. Averages ± standard deviation of the analyses performed in triplicate followed by the same letter on the lines do not differ by Tukey test ( $p > 0,05$ ).

The formation of secondary compounds of the oils was analyzed by the  $\rho$ -anisidine value, which, according to Guillén and Cabo (2002), an oil of good quality presents the maximum value of 10. Initially the oils agreed with the maximum stipulated value. Among the SB, SF and C oils, during the period of thermoxidation, the C presented the lowest  $\rho$ -anisidine values, meanwhile, among the blends, the SF:C was the least oxidated.

Dias, Menis and Jorge (2015) in a accelerated storage test at 60 °C/10 days with S/V of 0.3/cm obtained  $\rho$ -anisidine values under 4.3. On the other hand, Yu, Cho and Hwang (2018) fried potato chips at 180 °C using refined *C. nucifera* oil and obtained in the times 0, 2, and 4 h the values of 1; 4.7 and 7.3.

In the beginning of the thermoxidation, in relation to Totox, the oils obtained values inside the limits stipulated by Berset and Cuvelier (1996) in which 10 means a good quality oil.

Initially, the *G. max* presented a value of 4.06, the same as the one presented by Dias *et al.* (2015), who obtained 4.3. Meanwhile, the *H. annus* oil and the blends, SC and GC, presented the highest levels of oxidation.

With an increase of the oxidation time, it is possible to observe the Totox variation for the C and SF:C oils due to their higher levels of peroxide. On the other side, the SB:C oil presented a linear increase of the value and could inhibit the formation of oxidation compounds in 5% when compared to the *G. max*.

The thermoxidized oils were analyzed in relation to the conjugated dienoic acids and, initially, the *G. max* at zero time presented 0.34%, a result similar to Silva and Jorge (2012) with 0.35%. On the period of 0 h to 15 h, the oils differed statistically, being the C and GC the ones which reached the lowest values.

**Table 3.** Thermoxidation of the *G. max*, *H. annuus* and *C. nucifera* oils and their blends during heating at 180 °C.

Treat.	Heating times (hour)			
	0	5	10	15
	Peroxide value (meq/kg)			
SB	1.04±0.01 <sup>CB</sup>	6.39±0.00 <sup>BE</sup>	6.53±0.01 <sup>BD</sup>	7.03±0.00 <sup>AE</sup>
SF	1.40±0.00 <sup>DA</sup>	9.91±0.02 <sup>CC</sup>	10.51±0.01 <sup>BC</sup>	11.98±0.01 <sup>AB</sup>
C	0.82±0.00 <sup>DB</sup>	37.05±0.51 <sup>CA</sup>	29.73±0.15 <sup>BA</sup>	39.00±0.00 <sup>AA</sup>
SB:C	1.71±0.01 <sup>DA</sup>	8.64±0.01 <sup>CD</sup>	10.31±0.01 <sup>AC</sup>	9.31±0.01 <sup>BC</sup>
SF:C	1.51±0.01 <sup>DA</sup>	12.61±0.01 <sup>BB</sup>	13.37±0.01 <sup>AB</sup>	7.72±0.01 <sup>CD</sup>
	$\rho$ -anisidine value			
SB	1.98±0.00 <sup>DA</sup>	33.60±0.00 <sup>CB</sup>	34.35±0.00 <sup>BA</sup>	36.75±0.00 <sup>AA</sup>
SF	1.93±0.01 <sup>DA</sup>	33.80±0.00 <sup>CA</sup>	34.27±0.01 <sup>BB</sup>	34.45±0.01 <sup>AB</sup>
C	1.49±0.01 <sup>DD</sup>	9.88±0.00 <sup>CE</sup>	10.27±0.01 <sup>BE</sup>	14.28±0.01 <sup>AE</sup>
SB:C	1.75±0.01 <sup>DB</sup>	20.01±0.01 <sup>CC</sup>	25.19±0.01 <sup>BC</sup>	29.36±0.01 <sup>AC</sup>
SF:C	1.67±0.00 <sup>DC</sup>	17.59±0.01 <sup>CD</sup>	24.95±0.01 <sup>BD</sup>	29.26±0.01 <sup>AD</sup>
	Totox: total oxidation value			
SB	4.06±0.16 <sup>DB</sup>	46.38±0.01 <sup>CC</sup>	47.41±0.01 <sup>BD</sup>	50.80±0.01 <sup>AC</sup>
SF	4.72±0.00 <sup>DA</sup>	53.62±0.08 <sup>CB</sup>	55.29±0.01 <sup>BB</sup>	58.41±0.01 <sup>AB</sup>
C	3.13±0.01 <sup>DC</sup>	83.99±0.21 <sup>BA</sup>	69.72±0.60 <sup>CA</sup>	92.28±0.02 <sup>AA</sup>
SB:C	5.17±0.01 <sup>DA</sup>	37.28±0.01 <sup>CE</sup>	45.82±0.01 <sup>BE</sup>	47.98±0.01 <sup>AD</sup>
SF:C	4.68±0.01 <sup>DA</sup>	42.80±0.00 <sup>CD</sup>	51.70±0.01 <sup>AC</sup>	44.70±0.01 <sup>BE</sup>
	Conjugated dienoic acid (%)			
SB	0.34±0.01 <sup>DA</sup>	0.89±0.01 <sup>CA</sup>	2.56±0.01 <sup>BA</sup>	3.00±0.00 <sup>AA</sup>
SF	0.23±0.01 <sup>DB</sup>	0.78±0.00 <sup>CB</sup>	2.13±0.00 <sup>BC</sup>	2.51±0.00 <sup>AB</sup>
C	0.14±0.00 <sup>DE</sup>	0.17±0.01 <sup>BE</sup>	0.18±0.01 <sup>BE</sup>	0.23±0.01 <sup>AE</sup>
SF:C	0.19±0.01 <sup>DC</sup>	0.52±0.02 <sup>CC</sup>	2.21±0.02 <sup>BB</sup>	2.46±0.02 <sup>AC</sup>
SB:	0.17±0.01 <sup>DD</sup>	0.49±0.00 <sup>CD</sup>	1.76±0.02 <sup>BD</sup>	2.39±0.02 <sup>AD</sup>
	Total polar compounds (%)			
SB	5.67±0.06 <sup>DA</sup>	23.25±0.13 <sup>CA</sup>	35.20±0.08 <sup>BA</sup>	42.50±0.50 <sup>AA</sup>
SF	3.15±0.05 <sup>DB</sup>	22.23±0.13 <sup>CA</sup>	32.15±0.05 <sup>BB</sup>	43.15±0.50 <sup>AA</sup>
C	2.25±0.13 <sup>DB</sup>	13.25±0.13 <sup>CB</sup>	22.25±0.50 <sup>BC</sup>	24.50±0.50 <sup>AB</sup>
SB:C	2.35±0.25 <sup>DB</sup>	14.25±0.13 <sup>CB</sup>	22.50±0.50 <sup>BC</sup>	24.50±0.50 <sup>AB</sup>
SF:C	2.30±0.18 <sup>DB</sup>	14.15±0.05 <sup>CB</sup>	22.50±0.50 <sup>BC</sup>	25.50±0.50 <sup>AB</sup>
	Oxidative stability index (hour)			
SB	5.58±0.01 <sup>AD</sup>	0.94±0.10 <sup>BC</sup>	1.06±0.20 <sup>BB</sup>	0.90±0.08 <sup>BB</sup>
SF	5.80±0.01 <sup>AD</sup>	1.07±0.00 <sup>BC</sup>	0.50±0.05 <sup>BBC</sup>	0.66±0.01 <sup>BBC</sup>
C	100.50±0.50 <sup>AA</sup>	71.01±0.01 <sup>BA</sup>	25.31±0.01 <sup>CA</sup>	25.35±0.01 <sup>CA</sup>
SB:C	7.49±0.25 <sup>AC</sup>	3.16±0.01 <sup>BB</sup>	0.79±0.00 <sup>CB</sup>	0.31±0.00 <sup>CB</sup>
SF:C	8.32±0.03 <sup>AB</sup>	0.55±0.01 <sup>BC</sup>	0.13±0.00 <sup>BC</sup>	0.15±0.03 <sup>BC</sup>

SB: *G. max*; SF: *H. annuus*; C: *C. nucifera*; SB:C: *G. max*: *C. nucifera*; SF:C: *H. annuus*: *C. nucifera*. Averages±standard deviation of the analyses performed in triplicate followed by the same lowercases on the lines and uppercases on the columns do not differ by Tukey test ( $p > 0,05$ ).

Yu *et al.* (2018) fried potato chips in refined *C. nucifera* oil at 180 °C and obtained at times 0, 2 and 4 h the values 4.5; 5.6 and 6.8% respectively for conjugated dienoic acids. Differently, Jorge, Veronezi and Del Ré (2015) thermoxidatized the *G. max* oil at 180 °C/15 h with S/V of 0.4/cm and they obtained the results from 0.51 to 2.35% of conjugated dienoic acids.

According to Paul and Mittal (1997), good quality oils cannot exceed 25% of total polar compounds after processed in high temperatures. Observing Table 3, it is possible to see that initially the oils agreed with the established pattern, but as time passed at 10 h of heating, S and G could not be used anymore. However, the C, SB:C and SF:C oils reached the maximum value of 24.5% and did not differ statistically at the end of the 15 h and did not need to be disposed.

Luzia and Jorge (2013) thermoxidized *G. max* oil at 180 °C/15 h with S/V of 0.4/cm and obtained 4.43% to 35.5%, meanwhile Jorge, Veronezi and Pereira (2016) under the same conditions obtained from 4.12 to 23.52%. Casarotti and Jorge

(2012) by the thermoxidation of the *G. max* oil at 180 °C/20 h and S/V of 0.4/cm obtained results from 1.38% to 33.16% of polar compounds.

Veronezi and Jorge (2018) formulated mixtures of *G. max*, *C. papaya* and *C. melo* oils in different proportions and subjected them to thermoxidation. The oil blends showed lower percentages of total polar compounds, greater oxidative stability, in addition to retaining tocopherols better than pure oils, in 20 h of heating.

The *C. nucifera* oil presented the highest oxidative stability during the period of thermoxidation. The major composition of this oil in saturated fatty acids made its stability more possible under high temperatures, providing it at the end of the 15 h approximately 24 more than the other oils. *G. max* and *H. annuus* oils began with the lowest values of oxidative stability and at the end they reached the values of the SB:C and SF:C blends. The composition of natural antioxidants in the SB and SF oils allowed a better stability for these oils at the end of the 15 h compared to the *C. nucifera* when allowing stability to the SB:C and SF:C blends.

In a study carried out with mixtures of *L. usitatissimum*, *G. hirsutum* and *C. nucifera* oils under accelerated storage conditions, Pazzoti *et al.* (2018) observed that although the oils have degraded over time, it was possible to verify that *G. hirsutum* and *C. nucifera* oils contributed to increase the stability of the *L. usitatissimum* oil, which in turn increased the levels of bioactive compounds in *C. nucifera* oil.

## Conclusion

The mostly saturated composition of the *C. nucifera* oil contributed for the formation of the oil blends with balanced fatty acids profile. The SF:C oil reached approximately the desired composition of 1:1:1 in saturated, monounsaturated and polyunsaturated fatty acids. The thermoxidation proved the efficiency of the oil blends with the lowest values of oxidation and highest oxidative stability. Therefore, the SB:C and SF:C oils can be used as substitutes of the SB and SF oils in processes that require high temperatures, as they provide greater oxidative stability and nutritional quality.

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