Functional and technological potential of arabica coffee oils Potencial funcional e tecnológico de óleos do café arábica Potencial funcional y tecnológico de los aceites de café arábica

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Abstract

The purpose of the study was to evaluate the antioxidant activity, rheological behaviour, oxidative stability, and antibacterial potential of coffee oils (*Coffea arabica* L.). The extraction process took place from green and roasted beans, by cold pressing, and filtration via filtering card. The experimental design consisted of five treatments: R100 (100% roasted oil); R75G25 (75% roasted oil and 25% green oil); R50G50 (50% roasted oil and 50% green oil); R25G75 (25% roasted oil and 75% green oil), and G100 (100% green oil). The treatment R75G25 showed a higher content of total phenolic compounds and higher DPPH[•] and ABTS^{•+}

anti-radical efficiency. Regarding rheological behaviour, all coffee oils can be characterized as Newtonian fluids because the shear stress and strain rate varied linearly, with the line intersecting at zero. The treatments R75G25 and R25G75 showed a longer oxidation induction time, in the oxidative stability analysis, in addition to antibacterial activity having been verified for all oil samples. Besides that, the investigated green and roasted coffee oils are sources of fatty acids, including from the omega 3, 6, and 9 classes. Therefore, the use of arabica coffee oil mixtures as natural preservatives in food can be considered a promising alternative for the partial replacement of chemical additives in food matrices and in cosmetic formulations allowing the development of innovative products.

Keywords: Arabica coffee; Fluids; Industry; Healthiness; Fatty acid profile.

Resumo

A proposta do estudo foi avaliar a atividade antioxidante, o comportamento reológico, a estabilidade oxidativa e o potencial antibacteriano de óleos de café (Coffea arabica L.). O processo de extração ocorreu a partir de grãos crus e torrados, por prensagem a frio e filtração por cartão filtrante. O delineamento experimental constou de cinco tratamentos: R100 (100% de óleo torrado); R75G25 (75% de óleo torrado e 25% de óleo cru); R50G50 (50% de óleo torrado e 50% de óleo cru); R25G75 (25% de óleo torrado e 75% de óleo cru); e G100 (100% de óleo cru). O tratamento R75G25 apresentou maior teor de compostos fenólicos totais e maior eficiência anti-radical DPPH' e ABTS'⁺. Em relação ao comportamento reológico, todos os óleos de café podem ser caracterizados como fluidos newtonianos, pois a tensão de cisalhamento e a taxa de deformação variaram linearmente, com a reta interceptando no zero. Os tratamentos R75G25 e R25G75 apresentaram maior tempo de indução à oxidação, na análise da estabilidade oxidativa, além de atividade antibacteriana ter sido verificada para todas as amostras de óleo. Além disso, os óleos de café cru e torrado investigados são fontes de ácidos graxos, inclusive das classes ômega 3, 6 e 9. Portanto, a utilização de misturas de óleos de café arábica como conservantes naturais em alimentos pode ser considerada uma alternativa promissora para a substituição parcial de aditivos químicos em matrizes alimentares e em formulações de cosméticos permitindo o desenvolvimento de produtos inovadores.

Palavras-chave: Café arábica; Fluidos; Indústria; Saudabilidade; Perfil de ácidos graxos.

Resumen

El propósito del estudio fue evaluar la actividad antioxidante, comportamiento reológico, estabilidad oxidativa y potencial antibacteriano de aceites de café (Coffea arabica L.). El proceso de extracción se realizó a partir de granos crudos y tostados, mediante prensado en frío y filtración por tarjeta filtrante. El diseño experimental consistió en cinco tratamientos: R100 (100% aceite tostado); R75G25 (75% de aceite tostado y 25% de aceite crudo); R50G50 (50% de aceite tostado y 50% de aceite crudo); R25G75 (25% aceite tostado y 75% aceite crudo) y G100 (100% aceite crudo). El tratamiento R75G25 tuvo un mayor contenido de compuestos fenólicos totales y una mayor eficacia anti-radicales DPPH[•] y ABTS^{•+}. En cuanto al comportamiento reológico, todos los aceites de café se pueden caracterizar como fluidos newtonianos, ya que el esfuerzo cortante y la velocidad de deformación variaron linealmente, con la línea interceptada en cero. Los tratamientos R75G25 y R25G75 mostraron un mayor tiempo de inducción de oxidación, en el análisis de estabilidad oxidativa, además de que se haya verificado la actividad antibacteriana de todas las muestras de aceite. Además, los aceites de café crudo y tostado investigados son fuentes de ácidos grasos, incluidas las clases omega 3, 6 y 9. Por lo tanto, el uso de mezclas de aceite de café arábica como conservantes naturales en los alimentos puede considerarse una alternativa prometedora para la sustitución parcial de aditivos químicos en matrices alimentarias y em formulaciones cosméticas que permitan el desarrollo de productos innovadores.

Palabras clave: Café arábica; Fluidos; Indústria; Salubridad; Perfil de ácidos grasos.

1. Introduction

The increase in the world population has driven the demand for improving the quality, quantity, and diversity of oil sources (Prates-Valério, Celayeta & Cren, 2019). This led to the popularization of the consumption of vegetable oils associated with the search and development of new sources (Senger et al., 2017) aiming its beneficial effects on human health and high consumer acceptance (Vieira, Souza, Rodrigues & Sousa, 2019). In this context, studies with bioactive lipids from easily available plant sources have been conducted in order to analyse their quality, stability, and nutritional characteristics (Hashempour-baltork, Torbati, Azadmard-damirchi & Savage, 2016; Ramadan & Wahdan, 2012).

The lipid fraction of coffee beans is mainly composed of free and esterified fatty acids, diterpenes, sterols, and volatile compounds (Pokrovskiy et al., 2018). The functional properties of coffee and its co-products have been extensively evaluated as they constitute

potential ingredients in several industrial segments (Heck et al., 2019; Wang et al., 2019). The main components of arabica coffee oil are triacylglycerols (75.2%), diterpene esters and fatty acids (18.5%), free diterpenes (0.4%), steroid esters and fatty acids (3.2%), free sterols (2.2%), tocopherol (0.04–0.06%), phosphatides (0.1–0.5%), and caffeine (\pm 0.3%) (Chu, 2012). The lipid content present in green arabica coffee is around 12-18% while in roasted arabica coffee is at levels of 14.5-20%. Lipids are important in the quality of food, contributing to attributes such as texture, flavour, nutrition, and caloric density. It is essential to understand the physical properties and chemical stability of the group of compounds in order to produce functional foods with bioactive lipids (Chew, 2020).

The use of mixtures of vegetable oils can be suggested as a simple way to improve nutritional properties and oxidative stability (Hashempour-baltork et al., 2016). Combinations of canola and palm oils showed that tocopherols and tocotrienols were comparatively more stable in the mixture when compared to pure oils, besides, different antioxidant compounds can synergize and enhance the nutritional and technological effects (Mba, Dumont & Ngadi, 2017). The study of Ramadan and Wahdan (2012) presented the functional, stability, and anti-radical DPPH⁻ activity effects in mixtures of corn oils with black cumin and coriander and predicted the commercial exploitation of mixtures of corn and coriander oils. In this sense, it is proposed that the mixture of coffee oils from green and roasted beans is a promising alternative to meet the demands of some industrial segments.

Also, sterols, tocopherols, and diterpenes received broader attention due to their anticarcinogenic properties (Lee & Jeong, 2007) and protection against aflatoxin B1-induced genotoxicity (Huber, Scharf, Peter & Schulte-hermann, 2002). Considering the presence of pentacyclic diterpenes, caveol, and cafestol in green and roasted coffee beans as fatty acid esters, these bioactivities can also be expected in this food (Kurzrock & Speer, 2001).

For robusta coffee, the lipids levels are in the range of 9.0-13.0% and 11.0-16.0% in green and roasted beans, respectively (Lago, 2001). On the other hand, arabica coffee has better quality when compared to robusta coffee. In this sense, the objective of this study was to evaluate, in an unprecedented way, the antioxidant activity, the rheological behaviour, the oxidative stability, and the antibacterial potential of coffee oils (*Coffea arabica* L.) from green and roasted beans.

2. Materials and Methods

2.1 Coffee oils preparation and experimental design

The oils of green and roasted coffee were provided by Cooperativa Regional de Cafeicultores em Guaxupé – COOXUPÉ, located in Minas Gerais, Brazil. The process of preparation of the oil samples occurred from the green and roasted *Coffea arabica* L. grains by cold pressing and subsequent filtration through the filter cart. The samples were stored in commercial oil packaging until the moment of analysis. The experiment was conducted in a completely randomized design - CRD, as shown in Table 1.

Treatment	Content of oils in percentage (%)		
	Roasted coffee oil	Green coffee oil	
R100	100	-	
R75G25	75	25	
R50G50	50	50	
R25G75	25	75	
G100	-	100	

Table 1. Experimental design of coffee (Coffea arabica L.) oils.

Source: Authors

2.2 Determination of the fatty acid profile

The esterification of fatty acids was carried out according to the methodology described by Hartman and Lago (1973). Subsequently, the fatty acid profile was determined by gas chromatography on a Shimatzu CG 2010 chromatograph (Agilent Technologies Inc., Palo Alto, CA, USA), equipped with flame ionization detector, Split injection with a 1:100 ratio and SPTM-2560 Supelco capillary column, 100 m \times 0.25 mm \times 0.20 µm (Supelco Inc., Bellefonte, PA, USA). The initial temperature of the column was 140 °C, maintained for 5 min, changing to 240 °C, maintained for 30 min, for a total of 60 min. The injector and detector were kept at a temperature of 260 °C and helium was used as the carrier gas. After the analysis was completed, the peaks obtained were integrated.

The identification of fatty acids occurred by comparing the retention times presented by the SupelcoTM37 chromatographic standard FAME Mix standard (Supelco Inc., Bellefonte, PA, EUA) and were expressed as a percentage (%) of the total fatty acids.

2.3 Total phenolic content and antioxidant activity analyses

The coffee oils extraction was realized according to the methodology described by Larrauri, Rupérez, and Saura-Calixto (1997) with adaptations. About 1 g of the sample from each treatment was homogenized with 80 mL of methanol 50%. After an hour, in a dark environment, the tubes were centrifuged for 15 minutes at 21,952 g. Then, after a filtration step was performed, the volume was completed to 100 mL and the extracts were stored in a freezer (-18 °C) until analyses.

The total phenolic content of each treatment was evaluated using the Folin Ciocalteau methodology, according to Waterhouse (2003). Aliquots of 0.5 mL of the sample extracts were added in test tubes, in combination with 2.5 mL of the Folin Ciocalteau reagent 10% and 2 mL of sodium carbonate 4%, with readings taken at 750 nm after two hours incubation. The standard used was gallic acid and the results were expressed in mg gallic acid equivalent (GAE) 100 g⁻¹ sample.

For the determination of antioxidant activity by the DPPH method, the methodology described by Rufino et al. (2007a) was employed. The results were expressed as EC_{50} in g of sample per g of DPPH. Meanwhile, the determination of antioxidant activity by the ABTS⁺ method was carried out according to the methodology described by Rufino et al. (2007b), and the results were expressed in μ M Trolox equivalent (TE) g⁻¹ sample.

2.4 Rheological behavior

The determination of the viscosity of the treatments containing different proportions of green and roasted coffee oil (Table 1) was performed on a rotational rheometer HAAKE MARS (Modular Advanced Reometer System, Thermo Electron Corp., Germany), equipped with thermostatic bath (Phoenix 2C30P, Thermo Electron Corp., Germany), using a double gap sensor (DG41 Ti), at temperatures of 20 °C, 30 °C, and 40 °C.

Flow curves were applied to the fluids through three continuous ramps (increasing, decreasing, and increasing ramp), with the shear rate varying between 0.1 to 300 s⁻¹, for 2 min

for each curve (Mitschka, 1982). Newtonian model (Equation A) was adjusted to the rheological data obtained from the second rising ramp, which represents steady-state flow.

$$\tau = \mu \dot{\gamma}$$
 (Equation A)

where τ is the shear stress (Pa); $\dot{\gamma}$ is the shear rate (s⁻¹); μ is the Newtonian viscosity (Pa s).

The model was adjusted using the software *Statistical Analysis System* - SAS[®] University Edition.

2.5 Oxidative stability

The oxidative stability of each treatment was estimated by measuring the time of oxidative induction in Metrohm equipment (model 873, Biodisel Rancimat, Switzerland). The temperature of 110 °C was used, 50 mL in the conductivity cell, samples of 3 g of each treatment, and airflow of 20 Lh⁻¹ according to AOCS Official Method Cd 12b-92 (AOCS, 2009).

2.6 Antibacterial activity by disc-diffusion method

The strains *Staphylococcus aureus* ATCC 25923, *Escherichia coli* CDC 055, *Salmonella enteritidis* S64, *Cronobacter sakazakii* ATCC 29004, and *Listeria monocytogenes* ATCC 19117 were kindly provided by the Enterobacteria Laboratory - LABENT of the Osvaldo Cruz Foundation - FIOCRUZ, Rio de Janeiro, Brazil. The stock cultures were stored in freezing medium (15 mL of glycerol; 0.5 g of bacteriological peptone; 0.3 g of yeast extract; 0.5 g of NaCl; 100 mL of distilled water, and pH 7.0).

The cultures were thawed and reactivated by inoculating 50 μ L aliquots in tubes containing 10 mL of BHI broth (Brain Heart Infusion - Himedia, India) and incubated at 37 °C for 24 hours. The inoculum was standardized according to growth curves previously determined for a population of 1.0 x 10⁸ CFU mL⁻¹ using spectrophotometric measurements (600 nm).

One hundred μ L aliquots of each respective strain were spread in BHI agar, separately. Subsequently, a set of three 0.8 mm diameter test disks were placed in the agar medium

previously delimited on the plates. Ten μ L of the antibiotic chloramphenicol, as the negative control, and the oils of green and roasted coffee, diluted in Tween 80 at 0.5%, were added on the top of each test disks. The plates were incubated at 37 °C for 24 hours and then analysed (EUCAST, 2020).

2.7 Statistical analysis

The analysis of variance of the data was performed using the software Statistical Analysis System - SAS[®] University Edition. The differences between the mean values obtained were assessed using the Duncan means test at a level of 5% probability (p < 0.05).

3. Results and Discussion

3.1 Fatty acid profile

Table 2 shows the percentage of fatty acids identified in green coffee oil, in which the values of individual components ranged from 0.05 to 46.77%. Most of the lipids in foods have linear fatty acids with an even number of carbons (Ordóñez et al., 2007). Oliveira et al. (2014) studied the characterization of green arabica coffee oil and found palmitic (32%), linoleic (38.3%), and oleic (12.8%) acids in greater concentration, which corroborates with the results obtained in the present study.

Fatty acid	Content (%)	Chemical structure
Methyl myristate (SFA)	0.05 ± 0.01	C 14:0
Methyl palmitate (SFA)	32.45 ± 1.43	C 16:0
Methyl palmitoleate (MUFA)	0.05 ± 0.00	C 16:1
Methyl heptadecanoate (SFA)	0.09 ± 0.00	C 17:0
Methyl stearate (SFA)	7.03 ± 0.18	C 18:0
Oleic acid (MUFA)	8.17 ± 0.52	C 18:1 Ω9
Linoleic acid (PUFA)	46.77 ± 2.10	C 18:2 Ω6
Methyl arachidate (SFA)	2.67 ± 0.03	C 20:0
Methyl eicosanoate (SFA)	0.19 ± 0.00	C 20:0
Linolenic acid (PUFA)	1.47 ± 0.02	C 18:3 Ω3
Methyl henicosanoate (SFA)	0.05 ± 0.00	C 21:0
Octadecadienoic acid (PUFA)	0.08 ± 0.00	C 20:2 Ω6
Methyl behenate (SFA)	0.65 ± 0.00	C 22:0
Eicosatetraenoic acid (PUFA)	0.07 ± 0.00	C 20:5 Ω6
Methyl lignocerate (SFA)	0.21 ± 0.01	C 24:0
Σ SFA = 43.39 ± 1.66		

Table 2. Fatty acid profile of green coffee (Coffea arabica L.) oil.

 Σ MUFA + PUFA = 56.61 ± 2.64

SFA – Saturated Fatty Acid, MUFA – Monounsaturated Fatty Acid, PUFA – Polyunsaturated Fatty Acid.Source: Authors

The fatty acid content in roasted coffee oil ranged from 0.09 to 49.39% as shown in Table 3, in which palmitic and linoleic acids were the majority compounds. In the study

conducted by Hurtado-Benavides, Dorado, and Sánchez-Camargo (2016) a higher concentration of palmitic and linoleic acids were found in roasted arabica coffee oils obtained by extraction with supercritical fluid. Romano et al. (2014) also detected linoleic, palmitic, oleic, stearic, arachidic, linolenic, and behenic acids in samples of roasted arabica coffee oil, by gas chromatography with flame ionization detector.

The high content of poly and monounsaturated fatty acids found in the present study for both green and roasted arabica coffee oils, in particular $\Omega 3$, $\Omega 6$, and $\Omega 9$, are relevant due to impacts on human health, including anticarcinogenic (Cavin et al., 2002) and antioxidants effects (Lee, Choi & Jeong, 2007). Also, due to the roasting of coffee beans, the content of linoleic acid ($\Omega 6$) is increased (Garrett et al., 2013), a fact that is confirmed by the results obtained in the present study. Therefore, the mixture of both oil types can improve the general functional and technological potential when compared to the pure oils.

Fatty acid	Content (%)	Chemical structure
Methyl palmitate (SFA)	24.43 ± 1.22	C 16:0
Methyl stearate (SFA)	7.53 ± 0.36	C 18:0
Oleic acid (MUFA)	10.25 ± 0.87	C 18:1 Ω9
Linoleic acid (PUFA)	49.39 ± 3.27	C 18:2 Ω6
Methyl arachidate (SFA)	2.52 ± 0.00	C 20:0
Methyl eicosanoate (SFA)	0.31 ± 0.00	C 20:0
Linolenic acid (PUFA)	4.56 ± 0.08	C 18:3 Ω3
Methyl henicosanoate (SFA)	0.09 ± 0.00	C 21:0
Methyl behenate (SFA)	0.72 ± 0.01	C 22:0
Methyl lignocerate (SFA)	0.20 ± 0.00	C 24:0
Σ SFA = 35.80 ± 1.68		

Table 3. Fatty acid profile of roasted coffee (*Coffea arabica* L.) oil.

 Σ MUFA + PUFA = 64.20 ± 4.22

SFA – Saturated Fatty Acid, MUFA – Monounsaturated Fatty Acid, PUFA – Polyunsaturated Fatty Acid. Source: Authors

3.2 Total phenolic content and antioxidant activity

The results of the analyses of total phenolic compounds, total antioxidant activity by DPPH[•] free radical scavenging and total antioxidant activity by ABTS^{•+} free radical scavenging is shown in Table 4.

Total phenolic content	DPPH EC ₅₀	ABTS
(mg GAE 100 g ⁻¹)	(g sample g ⁻¹ DPPH)	$(\mu M TE g^{-1})$
$519.52 \pm 1.34^{\circ}$	2638.18 ± 3.57^{b}	$34.36\pm0.72^{\text{b}}$
809.55 ± 0.90^{a}	$1366.13 \pm 2.31^{\circ}$	$69.90\pm0.94^{\rm a}$
620.78 ± 2.10^{b}	2647.55 ± 1.98^{b}	34.67 ± 0.26^{b}
660.94 ± 0.87^{b}	2661.67 ± 3.74^{b}	32.64 ± 0.35^{b}
447.89 ± 0.74^{d}	3447.54 ± 3.84^{a}	$21.55\pm0.27^{\circ}$
	(mg GAE 100 g ⁻¹) $519.52 \pm 1.34^{\circ}$ 809.55 ± 0.90^{a} 620.78 ± 2.10^{b} 660.94 ± 0.87^{b}	(mg GAE 100 g ⁻¹) (g sample g ⁻¹ DPPH) $519.52 \pm 1.34^{\circ}$ $2638.18 \pm 3.57^{\circ}$ 809.55 ± 0.90^{a} $1366.13 \pm 2.31^{\circ}$ $620.78 \pm 2.10^{\circ}$ $2647.55 \pm 1.98^{\circ}$ $660.94 \pm 0.87^{\circ}$ $2661.67 \pm 3.74^{\circ}$

Table 4. Total	phenolic content and antioxidant a	activity using	the DPPH and ABTS methods.

^{a-d} Means followed by the same letter in the same column do not differ by Duncan test at 5% significance (p < 0.05); GAE – gallic acid equivalent; EC₅₀ – concentration of oil extract required to reduce the initial concentration of DPPH radical by 50%; TE – Trolox equivalent.Source: Authors

For the analysis of total phenolic compounds, it was observed that the values in the mixtures of oils (R50G50, R75G25, and R25G75) were higher than that of roasted coffee oil (R100) and green coffee oil (G100), in which the treatment R75G25 showed the best result. Considering the results found, it is possible to suggest the roasting influence on the phenolic content of the coffee oils, since it is known that this process affects the composition of phenolic compounds through Maillard reactions, for example. The compounds in question are formed by the thermal degradation of carbohydrates, chlorogenic acids, and lignins. In addition, the time and temperature ranges used in the roasting process influence the oil chemical composition (Araújo, 2012).

The results found in the present study occurred due to the presence of bioactive phenolic compounds present in coffee, which are characterized by their antioxidant action. Among these compounds, chlorogenic acids stand out, in which coffee representing the main source of chlorogenic acids in human nutrition (Rodrigues & Bragagnolo, 2013).

The DPPH method is based on the capture of the DPPH[•] radical (2,2-diphenyl-1picryl-hydrazil) by antioxidants, producing a decrease in absorbance at 515 nm. In this study, the final result corresponds to the amount of sample needed to decrease the initial concentration of the DPPH[•] radical by 50%. Thus, the lower the EC_{50} value, the greater the antioxidant activity of the sample. Thus, all treatments demonstrated DPPH[•] radical scavenging ability (Table 4), but the treatment R75G25 differed statistically from the other treatments, with the highest antiradical efficiency value. The antiradical efficiency of a

compound is directly proportional to its activity as an antioxidant (Chen, Bertin & Froldi, 2013).

Another methodology used in this study to measure the antioxidant activity of coffee oils was that based on the capture of the radical ABTS⁺⁺ (3-ethylbenzothiazoline-6-sulfonic acid) which can be generated through a chemical, electrochemical, or enzymatic reaction (Lucas-González, Viuda-Martos, Pérez Álvarez & Fernández-López, 2018). The treatment R75G25 showed the highest antioxidant activity value for this method when compared to the other treatments. The structure of the radicals in question is planar, which makes them react more easily with reducers, such as ABTS⁺⁺ either by transferring an electron or hydrogen. Another important factor is that ABTS⁺⁺ can be dissolved in both aqueous and organic solvents, and its antioxidant activity can be measured considering the hydrophilic and lipophilic nature of the antioxidants in the sample, unlike the DPPH method, which is solubilized only in organic medium (Kuskoski, E. M; Asuero, A. G.; Troncoso, A. M.; Mancini-Filho & J. Feet, 2009). Despite that, the treatment R75G25 showed the highest antioxidant activity, for both methods employed in this study, as well as the highest total phenolic content. In this sense, these findings suggest a correlation between these parameters, in which the phenolic compounds can be indicated as an important bioactive group with antioxidant effect present in the coffee oils.

3.3 Rheological behavior

Information on the rheology of products is essential to design equipment and industrial pipes, control the quality of raw materials and finished products, in addition to contributing to the prediction of the shelf life of products (Rao, 2014).

In this study, the Newton's Law was adequate to describe the behaviour of all treatments since they presented high values of determination coefficient ($0.98 < R^2 < 0.99$). Coffee oils can be characterized as Newtonian fluids, as can be seen in Figure 1, since the shear stress and shear rate varied linearly, with the line intersecting at zero. The rheological properties of these fluids are independent of a previous history of shear and depend only on the composition and temperature (Irgens, 2014).

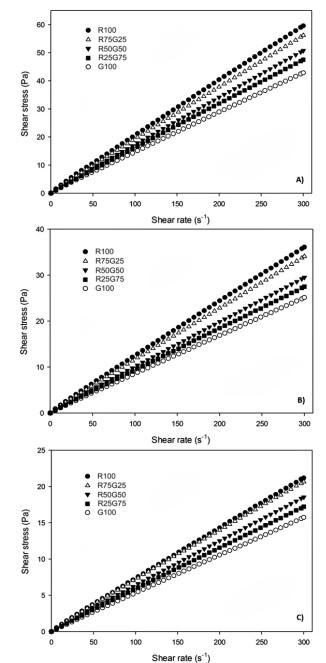


Figure 1. Flow curve of oil samples for temperatures of 20 (A), 30 (B), and 40 °C (C).

Source: Authors.

In Table 5 are present the values of the determined rheological parameter, the Newtonian viscosity. The temperatures of 20, 30, and 40 °C were chosen to be studied in the rheological tests because they are in the temperature range in which food processing containing vegetable oil are carried out as well as the sensory analysis of new products that will be placed on the market. Oliveira et al. (2009) reported that the viscosity of fluid tends to decrease with increasing temperature, a fact that was observed in the resent study.

Table 5. Newtonian viscosity values (μ), coefficient of determination (\mathbb{R}^2), and root-meansquare deviation (RMSE), respectively, for temperatures of 20, 30, and 40 °C.

Temperature (°C)	Treatment	Viscosity µ (Pa•s)	\mathbb{R}^2	RMSE
20	R100	0.20 ± 0.01	0.98	2.22
	R75G25	0.18 ± 0.00	0.99	0.79
	R50G50	0.17 ± 0.00	0.99	0.34
	R25G75	0.15 ± 0.00	0.99	0.46
	G100	0.14 ± 0.00	0.99	0.25
30	R100	0.12 ± 0.00	0.99	0.28
	R75G25	0.11 ± 0.00	0.99	0.72
	R50G50	0.09 ± 0.00	0.99	0.22
	R25G25	0.09 ± 0.00	0.99	0.18
40	G100	0.08 ± 0.00	0.99	0.13
40	R100	0.07 ± 0.00 0.06 ± 0.00	0.99	0.27 0.23
	R75G25 R50G50	0.06 ± 0.00 0.06 ± 0.00	0.99 0.99	0.25
	R25G75	0.00 ± 0.00 0.05 ± 0.00	0.99	0.10
	G100	0.05 ± 0.00 0.05 ± 0.00	0.99	0.28
	0100	0.05 ± 0.00	0.77	0.20

Source: Authors.

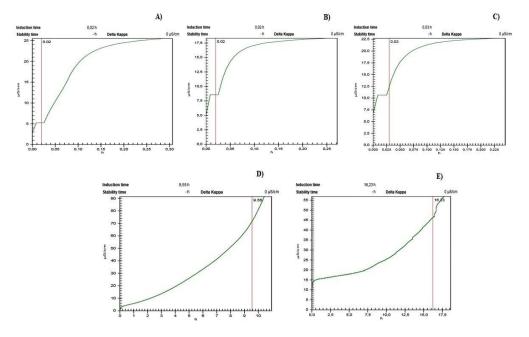
The decrease in viscosity with an increase in temperature is attributed to the increase in intermolecular distances caused during heating, which reduces the forces of attraction between molecules (Ahammed, Asirvatham & Wongwises, 2016). In this sense, the viscosity is directly proportional to the force of attraction between the molecules. As the temperature increases, this attraction force decreases, also decreasing the viscosity (Brunetti, 2008). Thus, the information that coffee oils behave like Newtonian fluids is relevant to the planning and adequate sizing of pumps and pipes, in order to guarantee the correct functioning of an industry that processes this raw material, generating a high-quality final product.

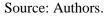
3.4 Oxidative stability

Among the oxidative stability tests, the Rancimat method makes possible to measure the oxidation index of lipids through volatile acids formed during oxidation (Aktar & Adal,

2019). The results obtained in the evaluation of the susceptibility of coffee oils to oxidative degradation are shown in Figure 2.

Figure 2. Oxidative stability of the treatments under study: (A) R100; (B) R75G25; (C) R50G50; (D) R25G75; and (E) G100.





Regarding the total amount of unsaturated fatty acids, green coffee oil showed 56.61% and roasted coffee oil presented 64.2%, a fact that may have contributed to the treatments R100 (A), R50G50 (C), and R75G25 (D) had a shorter oxidation induction time. It is known that vegetable oils that have a high fatty acid index with two or three unsaturations have lower oxidative stability due to the presence of allylic or bile-allylic carbons (Pratt, Mills & Porter, 2003). Probably, the most relevant factor for the rapid oxidation of the aforementioned treatments is the coffee roasting process, since the green and roasted coffee oils were from the same batch. In addition, because coffee oils are crude, it is believed that vacuum drying can provide higher oxidation stability.

3.5 Antibacterial activity

The sensibility test applied for the verification of coffee oils samples antibacterial activity showed that no inhibition halos were present for all five pathogens studied using disc diffusion tests. On the other hand, it was observed that after the removal of the filter paper

with coffee oil samples from the agar, the area where the disc embedded was lying down did not show microbial growth for any species. These evidences imply that all coffee oil treatments exhibit an inhibition of bacterial growth by contact, which is an interesting outcome in the bioactive packing context. As reported by Sanla-Ead, Jangchud, Chonhenchob and Suppakul (2012), the plant-based oils used in *in vitro* tests failed to exhibit a clear inhibitory zone probably because of low water solubility of the oils, however, the application in antimicrobial packaging film or coating could be considered due to the inhibitory effect presented by the oils when in contact with a surface.

The antibacterial activity of coffee can be attributed to chlorogenic, caffeic, protocateic acids (Dogasaki, Shindo, Furuhata & Fukuyama, 2002), nicotinic, 5-caffeoylquin acids (Daglia et al., 1994), trigonelline (Antonio et al., 2010) and caffeine (Almeida, Farah, Silva, Nunan & Glória, 2006). Daglia, Papetti, Dacarro, and Gazzani (1998) concluded that the coffee roasting process induces antimicrobial activity due to the compounds generated by the Maillard reaction, caramelization of carbohydrates, thermal decomposition, and the pyrolysis of organic compounds.

The mechanism of action of antimicrobial agents occurs through one of the following factors: reaction with the cell membrane causing increased permeability and loss of cellular constituents; inactivation of enzyme systems or essential enzymes, including those involved in the energy production process and synthesis of structural components; and/or destruction or functional inactivation of genetic material (Kim, Cornell & Preston, 1995).

4. Final Considerations

The green and roasted arabica coffee oils investigated in this study are sources of fatty acids, mainly the omega 3, 6, and 9 class, which are health promoters. An increase in the functionality of the oils was observed when they were mixed, with a high functional potential of the treatment R75G25, evidenced by the total phenolic content and antioxidant activity values. Also, all the tested oils behaved like Newtonian fluids at all temperatures to which they were subjected to rheological tests. Regarding oxidative stability, treatments G100 and R25G75 showed longer oxidation induction times, and the antimicrobial sensitivity tests demonstrated inhibition of bacterial strains in the area of contact with all the coffee oils samples. Therefore, the use of mixtures of arabica coffee oils as natural preservatives in food can be considered a promising alternative for the partial replacement of chemical additives in

food matrices and the formulation of cosmetic products allowing the development of innovative products.

Referências

Ahammed, N., Asirvatham, L. G., & Wongwises, S. (2016). Effect of volume concentration and temperature on viscosity and surface tension of graphene-water nanofluid for heat transfer applications. *Journal of Thermal Analysis and Calorimetry*, *123*(2), 1399–1409.

Aktar, T., & Adal, E. (2019). Determining the Arrhenius kinetics of avocado oil: Oxidative stability under rancimat test conditions. *Foods*, 8(7), 1–13.

Almeida, A. A. P., Farah, A., Silva, D. A. M., Nunan, E. A., & Glória, M. B. A. (2006). Antibacterial activity of coffee extracts and selected coffee chemical compounds against enterobacteria. *Journal of Agricultural and Food Chemistry*, *54*(23), 8738–8743.

Antonio, A. G., Moraes, R. S., Perrone, D., Maia, L. C., Santos, K. R. N., Iório, N. L. P., & Farah, A. (2010). Species, roasting degree and decaffeination influence the antibacterial activity of coffee against *Streptococcus mutans*. *Food Chemistry*, *118*(3), 782–788.

AOCS. (2009). Official methods and recommended practices of the American Oil Chemists' Society. Champaign, IL, USA: AOCS Press.

Araújo, M. A. (2012). *Química de Alimentos – Teoria e Prática*. Viçosa, MG, Brasil: Editora UFV.

Brunetti, F. (2008). Mecânica dos Fluidos. São Paulo, SP, BR: Pearson Education.

Cavin, C., Holzhaeuser, D., Scharf, G., Constable, A., Huber, W. W., & Schilter, B. (2002). Cafestol and kahweol, two coffee specific diterpenes with anticarcinogenic activity. *Food and Chemical Toxicology*, *40*(8), 1155–1163.

Chen, Z., Bertin, R. & Froldi, G. (2013). EC 50 estimation of antioxidant activity in DPPH Å assay using several statistical programs. *Food Chemistry*, *138*(1), 414–420.

Chew, S. C. (2020). Cold-pressed rapeseed (*Brassica napus*) oil: Chemistry and functionality. *Food Research International*, *131*, 108997.

Chu, Y.-F. (2012). *Coffee: Emerging Health Effects and Disease Prevention*. Oxford, UK: Wiley-Blackwell.

Daglia, M., Cuzzoni, T., Dacarrot, C., Farmaceutica, C., Taramelli, V., Farmacologia, I. & Taramelli, V. (1994). Antibacterial Activity of Coffee : Relationship between Biological Activity and Chemical Markers, *Journal of Agricultural and Food Chemistry*, *18*, 2273–2277.

Daglia, M., Papetti, A., Dacarro, C. & Gazzani, G. (1998). Isolation of an antibacterial component from roasted coffee, *Journal of Pharmaceutical and Biomedical Analysis*, *18*, 219–225.

Dogasaki, C., Shindo, T., Furuhata, K. & Fukuyama, M. (2002). Identification of chemical structure of antibacterial components against *Legionella pneumophila* in a coffee beverage. *Journal of the Pharmaceutical Society of Japan*, *122*(7), 487–494.

EUCAST. (2020). European Committee on Antimicrobial Susceptibility Testing. European Society of Clinical Microbiology and Infectious Diases. Antimicrobial susceptibility testing EUCAST disk diffusion method.

Garrett, R., Schmidt, E. M., Filipe, L., Pereira, P., Kitzberger, C. S. G., Brígida, M., Scholz, S., et al. (2013). Discrimination of arabica coffee cultivars by electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry and chemometrics. *LWT - Food Science and Technology*, *50*(2), 496–502.

Hartman, L. & Lago, R. C. A. (1973). Rapid preparation to fatty acids methyl esters. *Laboratory practice*, 22(6), 475–476.

Hashempour-baltork, F., Torbati, M., Azadmard-damirchi, S. & Savage, G. P. (2016). Vegetable oil blending : A review of physicochemical , nutritional and health effects. *Trends in Food Science & Technology*, 57, 52–58.

Heck, R., Saldaña, E., Manuel, J., Pereira, L., Bittencourt, M., José, A., Ragagnin, C., et al. (2019). Hydrogelled emulsion from chia and linseed oils : A promising strategy to produce low-fat burgers with a healthier lipid pro fi le. *Meat Science*, *156*(June), 174–182.

Huber, W. W., Scharf, E. G., Peter, B. G. E. B. & Schulte-hermann, R. J. T. E. R. (2002). The coffee components kahweol and cafestol induce c -glutamylcysteine synthetase , the rate limiting enzyme of chemoprotective glutathione synthesis , in several organs of the rat, 685–694.

Hurtado-Benavides, A., Dorado, D., Sánchez-Camargo, A. D. P. (2016). Study of the fatty acid profile and the aroma composition of oil obtained from roasted Colombian coffee beans by supercritical fluid extraction. *The Journal of Supercritical Fluids*, *113*, 44–52.

Irgens, F. (2014). *Rheology and non-newtonian fluids*. New York, NY, USA: Springer International Publishing.

Kim, J. M., Cornell, J. A. & Preston, J. F. (1995). Antibacterial Activity of Carvacrol, Citral, and Geraniol against *Salmonella typhimurium* in Culture Medium and on Fish Cubes, *60*(6), 1364–1368.

Kurzrock, T. & Speer, K. (2001). Identification of kahweol fatty acid esters in Arabica coffee by means of LC/MS. *Journal of Separation Science*, *24*(10–11), 843–848.

Kuskoski, E. M., Asuero, A. G., Troncoso, A. M., Mancini-Filho, J. & J. Feet, R. (2009). Aplicación de diversos métodos químicos para determinar actividad antioxidante en pulpa de frutos. *Ciência e Tecnologia de Alimentos*, *25*(4), 726–732.

Lago, R. C. A. (2001). Lipídios Em Grãos De Café. Boletim do Centro de Pesquisa de Processamento de Alimentos, 19(2), 319–340.

Larrauri, J. A., Rupérez, P. & Saura-Calixto, F. (1997). Effect of Drying Temperature on the Stability of Polyphenols and Antioxidant Activity of Red Grape Pomace Peels. *Journal of Agricultural and Food Chemistry*, 45(4), 1390–1393.

Lee, K. J., Choi, J. H. & Jeong, H. G. (2007). Hepatoprotective and antioxidant effects of the coffee diterpenes kahweol and cafestol on carbon tetrachloride-induced liver damage in mice. *Food and Chemical Toxicology*, *45*(11), 2118–2125.

Lee, K. J. & Jeong, H. G. (2007). Protective effects of kahweol and cafestol against hydrogen peroxide-induced oxidative stress and DNA damage. *Toxicology Letters*, *173*(2), 80–87.

Lucas-González, R., Viuda-Martos, M., Pérez Álvarez, J. A. & Fernández-López, J. (2018). Changes in bioaccessibility, polyphenol profile and antioxidant potential of flours obtained from persimmon fruit (*Diospyros kaki*) co-products during in vitro gastrointestinal digestion. *Food Chemistry*, 256, 252–258.

Mba, O. I., Dumont, M. J. & Ngadi, M. (2017). Thermostability and degradation kinetics of tocochromanols and carotenoids in palm oil, canola oil and their blends during deep-fat frying. *LWT - Food Science and Technology*, 82, 131–138.

Mitschka, P. (1982). Simple conversion of Brookfield R.V.T. readings into viscosity functions. *Rheologica Acta*, 21(2), 207–209.

De Oliveira, A. C., Valentim, I. B., Goulart, M. O. F., Silva, C. A., Bechara, E. J. H. & Trevisan, M. T. S. (2009). Fontes vegetais naturals de antioxidantes. *Quimica Nova*, *32*(3), 689–702.

Oliveira, P., Henrique, R., Almeida, D., Albertina, N., Oliveira, D., Bostyn, S. & Gonc, C. B. (2014). Enrichment of diterpenes in green coffee oil using supercritical fluid extraction – Characterization and comparison with green coffee oil from pressing. *The Journal of Supercritical Fluids*, 95, 137–145.

Ordóñez, J. A., Rodíguez, M. I., Álvarez, L. F., Sanz, M. L. G., Miguillón, G. D. G. F., Perales, L. H. & Cortecero, M. D. S. (2007). *Tecnologia de Alimentos*. Porto Alegre, RS, Brasil: Editora Artmed.

Pokrovskiy, O. I., Prokopchuk, D. I., Kostenko, M. O., Ustinovich, K. B., Parenago, O. O. &

Lunin, V. V. (2018). Effect of Pressure on the Efficiency of Supercritical Fluid Extraction of Black Coffee Oil. *Russian Journal of Physical Chemistry B*, *12*(7), 1176–1181.

Prates-Valério, P., Celayeta, J. M. F. & Cren, E. C. (2019). Quality Parameters of Mechanically Extracted Edible Macauba Oils (*Acrocomia aculeata*) for Potential Food and Alternative Industrial Feedstock Application. *European Journal of Lipid Science and Technology*, *121*(5), 1–8.

Pratt, D. A., Mills, J. H. & Porter, N. A. (2003). Theoretical calculations of carbon-oxygen bond dissociation enthalpies of peroxyl radicals formed in the autoxidation of lipids. *Journal of the American Chemical Society*, *125*(19), 5801–5810.

Ramadan, M. F. & Wahdan, K. M. M. (2012). Blending of corn oil with black cumin (*Nigella sativa*) and coriander (*Coriandrum sativum*) seed oils: Impact on functionality, stability and radical scavenging activity. *Food Chemistry*, *132*(2), 873–879.

Rao, M. A. (2014). *Rheology of Fluid, Semisolid, and Solid Foods – Principles and Applications*. New York, NY, USA: Springer International Publishing.

Rodrigues, N. P. & Bragagnolo, N. (2013). Identification and quantification of bioactive compounds in coffee brews by HPLC-DAD-MSn. *Journal of Food Composition and Analysis*, *32*(2), 105–115.

Romano, R., Santini, A., Le Grottaglie, L., Manzo, N., Visconti, A. & Ritieni, A. (2014). Identification markers based on fatty acid composition to differentiate between roasted *Arabica* and *Canephora* (Robusta) coffee varieties in mixtures. *Journal of Food Composition and Analysis*, *35*(1), 1–9.

Rufino, M. D. S. M., Alves, R. E., De Brito, E. S., de Morais, S. M., Sampaio, C. de G., Pérez-Jiménez, J. & Saura-Calisto, F. D. (2007a). Metodologia científica: determinação da atividade antioxidante total em frutas pela captura do radical livre DPPH. Comunicado Técnico, 127. Fortaleza, Brasil: Embrapa Agroindústria Tropical.

Rufino, M. D. S. M., Alves, R. E., De Brito, E. S., de Morais, S. M., Sampaio, C. de G.,

Pérez-Jiménez, J. & Saura-Calisto, F. D. (2007b). Metodologia científica: determinação da atividade antioxidante total em frutas pela captura do radical livre ABTS.+. Comunicado Técnico, 128. Fortaleza, Brasil: Embrapa Agroindústria Tropical.

Sanla-Ead, N., Jangchud, A., Chonhenchob, V. & Suppakul, P. (2012). Antimicrobial Activity of Cinnamaldehyde and Eugenol and Their Activity after Incorporation into Cellulose-based Packaging Films. *Packaging and Technology and Science*, *25*, 7–17.

Senger, E., Bohlinger, B., Esgaib, S., Hernández-Cubero, L. C., Montes, J. M. & Becker, K. (2017). Chuta (edible *Jatropha curcas* L.), the newcomer among underutilized crops: a rich source of vegetable oil and protein for human consumption. *European Food Research and Technology*, *243*(6), 987–997.

Vieira, A. S. P., Souza, X. R., Rodrigues, L. C., & Sousa, D. C. (2019). Replacement of animal fat by canola oil in chicken meatball. *Brazilian Journal of Poultry Science*, 21(3), 1–10.

Wang, S., Xiao, W., Ma, X., Li, J., Chen, L., & Yao, H. (2019). Analysis of the application potential of coffee oil as an ilmenite flotation collector. *Minerals*, *9*(9), 1–10.

Waterhouse, A. L. (2003). Determination of Total Phenolics. *Current Protocols in Food Analytical Chemistry*. Hoboken, NJ, USA: John Wiley & Sons, Inc.

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