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Determination of the oxidative stability by DSC of vegetable oils from the Amazonian area

Juliana J.R. Pardauil [a], Luiz K.C. Souza [a], Fábio A. Molfetta [b], José R. Zamian [a], Geraldo N. Rocha Filho [a], C.E.F. da Costa [a,*]

[a] Laboratório de Catálise e Oleoquímica (LCO), ICEN, Universidade Federal do Pará (UFPA), Belém – Pará, Brazil
[b] Laboratório de Modelagem Molecular, ICEN, Universidade Federal do Pará (UFPA), Belém – Pará, Brazil

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ABSTRACT

Differential scanning calorimetry (DSC) and a Rancimat method apparatus were applied to evaluate the oxidative stability of buriti pulp oil (*Mauritia flexuosa Mart*), rubber seed oil (*Hevea brasiliensis*), and passion fruit oil (*Passiflora edulis*). The Rancimat measurements taken for the oxidative induction times were performed under isothermal conditions at 100 °C and in an air atmosphere. The DSC technique involved the oxidation of oil samples in an oxygen-flow DSC cell. The DSC cell temperature was set at five different isothermal temperatures: 100, 110, 120, 130 and 140 °C. During the oxidation reaction, an increase in heat was observed as a sharp exothermic curve. The value T_0 represents the oxidative induction time, which is determined from the downward extrapolated DSC oxidative curve verses the time axis. These curves indicate a good correlation between the DSC T_0 and oxidative stability index (OSI) values. The DSC method is useful because it consumes less time and less sample.

1. Introduction

Vegetable oils and fats are triesters derived from glycerol, originating from the condensation of a glycerol molecule with three molecules of fatty acid, where the fatty acids contain long chains of carbon (8–24 units long) (Conceição et al., 2007; Vecchio et al., 2008). These triesters are widely used as raw materials in the food, medical and cosmetic industries. They are also essential in the production of industrialized foods because, from a nutritional standpoint, vegetable oils and fat have important functional properties capable of producing metabolically or physiologically useful effects that help maintain good health. These effects, in turn, aid in the reduction of chronic-degenerative diseases. Apart from their basic nutritional function of supplying calories, these triesters contribute to the palatability of foods, act as vehicles for fat-soluble vitamins, such as A, D, E and K, and are sources of essential fatty acids, such as linoleic, linolenic, and arachidonic acid (Castro et al., 2004; Fuentes et al., 2010; Rodrigues et al., 2003).

It is known that fats and fat-based foods deteriorate during processing and storage in an oxidizing atmosphere; this process is referred to as autoxidation. Autoxidation of lipids (LH) proceeds through a radical mechanism involving: initiation ($LH \rightarrow L.$; $L. + O_2 \rightarrow LOO.$), propagation ($LO._2 + LH \rightarrow LOOH + L.$; $L. + O_2 \rightarrow LOO.$), branching ($LOOH \rightarrow LO. + OH.$; $LO + LH + O_2 \rightarrow LOH + LOO.$; $OH. + LH + O_2 \rightarrow H_2O + LOO.$) and termination. These reactions involve an end of the chain reaction, wherein peroxide decomposes to inert products commonly known as secondary oxidation products and the formation of nonradical products or the disproportionation of radicals occur. In highly oxidized fats and oils, aldehydes, ketones, furanones, lactones, hydrocarbons, organic acids and polymeric compounds are present (Ostrowska-Ligeza et al., 2010). Therefore, this reaction can be characterized by the emergence of sweet and unpleasant odors that worsen progressively until the oil or fat reaches the smell and characteristic of rancid fat (Souza et al., 2004).

Resistance to oxidation of an oil or fat is known as oxidative stability and can be expressed as the period of time necessary for the secondary products of the reaction to be formed and detected under different conditions. This period is known as the induction time, and it leads to a quick increase in the lipid oxidation rate (Arain et al., 2009).

Because the oxidation and thermal-oxidative decomposition of oils and fats are exothermal reactions, enthalpic changes by calorimetry or by thermal analysis can be applied to determine the oxidative stability or the thermal-oxidative resistance of greasy materials. The most promising techniques for this application are Differential scanning calorimetry (DSC) and Pressurized differential scanning calorimetry (Kowalski et al., 1997). Compared to conventional methods, these methods are more advantageous because they are more precise and sensible, require less sample and rapidly

* Corresponding author. Tel.: +55 9181111883.
E-mail address: emmerson@ufpa.br (C.E.F. da Costa).

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produce results (Garcia et al., 2007; Kowalski et al., 1997; Santos et al., 2002; Souza et al., 2004).

Accelerated methods, most commonly used for oxidative stability assessments of edible oils and fats, include the Rancimat method developed by Hadorn and Zurcher (1974). The Rancimat method determines the amount of time it takes for the maximum alteration to the lipid oxidation rate. This time is determined by the airflow that passes through a sample of heated oil and transfers the volatile compounds of the oxidation reaction to a separate container of deionized water. This shift in the specimens causes an increase in conductibility (Farhoosh, 2007). This time, known as the oxidative stability index (OSI), has a direct correlation to the stability measured by different conditions for lipid oxidation (Velasco et al., 2004).

The Amazon region, with its richness of vegetable species, is known to produce vegetable oils with unique aromas and flavors. The properties of these vegetable oils have been intensely researched, mainly by international companies, due to their various applications in food, pharmaceutical, cosmetic and other industries. In light of this knowledge, the objective of the present work was to evaluate and compare the oxidative stability of buriti pulp oil (*Mauritia flexuosa Mart*), rubber seed oil (*Hevea brasiliensis*), and passion fruit oil (*Passiflora edulis*) by DSC and Rancimat measurements.

2. Methods

Oil was extracted from the buriti pulp oil and the rubber seeds using hexane and a Soxhlet apparatus. The passion fruit oil samples were obtained from a local oil provider, Beraca Sabará Químicos Ingredientes LTDA. All chemicals and reagents used were of the highest purity.

2.1. Fatty acid determination by gas chromatography (GC)

The fatty acid compositions of the oils were determined by gas chromatography (GC) using an AOCS Ce 1-62 method (AOCS, 1995b). The fatty acid methyl esters were prepared by the AOCS Ce 2-66 method (AOCS, 1995a). Chromatographic analysis was performed with a Varian CP 3800 gas chromatograph equipped with a hydrogen flame ionization detector and a capillary column (30 m × 0.32 mm CP WAX 52 CB; 1 μm DF) (California/USA). The column temperature was programmed to ramp from 80 °C to 250 °C at 10 °C/min; the injector temperature was set to 200 °C, and the detector temperature was set to 250 °C. Helium was used as the carrier gas.

2.2. Rancimat measurements

The oxidative stability index (OSI) was evaluated by a Metrohm Rancimat model 743 (Herisau/Switzerland) following the AOCS Official Method Cd 12b-92, AOCS 1992. Increasing water conductivities were continually measured while air (20 L/h) was bubbled into each oil (5 g) heated to 100 °C and their volatile compounds were collected in water. The time taken to reach the conductivity inflection time was recorded.

2.3. Differential scanning calorimetry analysis

The oxidative stability of vegetable oils was determined by a Shimadzu DSC – 60 Differential scanning calorimeter (Kyoto/Japan). The equipment was calibrated with pure indium, and the baseline was obtained with an empty open aluminum pan sample. Oil samples of 5.0 ± 0.5 mg were weighed into open aluminum pans and were placed in the equipment's sample chamber. The isothermal temperature was programmed for five different temperatures (100, 110, 120, 130, and 140 °C), and purified oxygen (99.8%) passed through the sample enclosure at 50 ml/min. The induction point (T_0) of the oxidative reaction corresponded closely to the intersection of the extrapolated baseline and the tangent line (leading edge) of the isotherm. To verify changes in samples weight, thermogravimetric (TG) curves were obtained using a Shimadzu DTG-60H simultaneous DTA/TG apparatus (Kyoto/Japan) under the same conditions of isothermal DSC curves.

2.4. Statistical analysis

Each sample experiment was performed three times, and the statistical data were analyzed with MiniTab 14 software (Wild, 2004). Pearson correlations compared the values obtained for the DSC induction times (DSC T_0) and the OSI. These correlations were applied because they measure the strength and direction of their linear relationship, describing the direction and degree to which one variable is linearly related to the other.

3. Results and discussion

3.1. Fatty acid determination by gas chromatography (GC)

The values obtained by gas chromatography for the chemical composition of fatty acids in the vegetable oils are presented in Table 1. It was observed that the vegetable oils had a high content of unsaturated fatty acids (61% of oleic acid for buriti, 33% of linoleic acid and 23% of linolenic acid for rubber seeds, and 68% of linoleic acid for passion fruit). The high concentration of oleic acid found in buriti oil makes it useful for the food industry as a frying or salad oil. It also shows a high concentration of palmitic acid, which offers the appropriate amount of plasticity for soap manufacturing (Garcia et al., 2007).

Rubber seed oil displayed a fatty acid composition similar to linseed oil, while passion fruit oil was found to be a good source of linoleic acid, widely found in vegetable oils, and linolenic acid, present in soybean and rapeseed oils, its isomer γ-linolenic acid can be found in evening primrose oil. Linoleic and linolenic acids are essential in human nutrition because they represent a group of essential fatty acids, omega six and three, respectively. Others representatives of the essential fatty acids are eicospentaenoic acid and docosahexaenoic acid, both belonging to the group Ω-3, and are found in fish oils. A deficient intake of these essential fatty acids causes dry, rough skin, a tendency for eczema and rash, weak hair, eventual alopecia and weak nails (Regitano-d'Arce et al., 2006).

3.2. Oxidative stability by DSC

The assessment of oxidative stability by DSC was measured by the induction period through exothermal curves of oxidation. T_0

Table 1
Fatty acid compositions of oils.

	Fatty acid composition (%)		
	Buriti oil	Rubber seeds oil	Passion fruit oil
14:0 (Miristic acid)	0.1	–	0.1
16:0 (Palmitic acid)	23	8.5	11
18:0 (Stearic acid)	5.2	5	3
16:1 (Palmitoleic acid)	0.05	–	0.05
18:1 (Oleic acid)	61	27	17
18:2 (Linoleic acid)	6	33	68
18:3 (Linolenic acid)	0.5	23	3.5
20:0 (Araquidic acid)	0.7	0.3	–
22:0 (Behenic acid)	0.2	0.1	–