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THERMAL STABILITY STUDIES OF SOME CERRADO PLANT OILS

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Thermogravimetry technique is useful to determine the thermal stability of vegetable oils. In this paper some vegetable oils obtained from brazilian Cerrado native plants were studied based on their high oleic acid content. Amburana, baru and pequi pulp oils presented higher yield of extraction compared to soybean oil. The thermal stability of oils in nitrogen was very close hence their fatty acid composition was very similar. Amburana and baru oils have major amount of unsaturated fatty acids, especially linoleic acid and pequi pulp oil has the highest short chain fatty acid content which can explain its lowest thermal stability in synthetic air.

Keywords: *thermal stability, thermogravimetry, vegetable oils*

Introduction

In the nature fatty acids exist as free or esterified substances. Oils and fats are formed by triglycerides, the most frequent lipids in nature. Glycerol and three fatty acids constitute the triacylglicerides. Many medicine and foods contain fatty acids and often are submitted to thermal treatment during processing or storage. Thus, knowing the thermal stability profile of the oils is very important in industries [1–3].

Brazilian Cerrado is a unique biome of the midwest center of the country and shows an enormous variety of oil-rich vegetable species. These vegetables can offer new perspectives for sustainable development of this region. They have high oleic acid content making them useful for human consumption [1, 4, 5].

Thermal stability of oils depends on their chemical structures. Oils with a high content of unsaturated fatty acids are less stable than the saturated ones [1, 6].

In the recent years, thermal analysis was successfully used for the determination of some physical properties, study of chemical reaction and in the investigation of thermal stability of oils. Thermoanalytical methods (among them thermogravimetry) present many advantages since they are precise, sensitive, fast and use small sample amount [2, 3, 6–9].

In this work thermal stability of oils taken from brazilian Cerrado plants (amburana (*Amburana cearensis* (Fr. Allem) A. C. Smith), baru (*Dypterix alata* Vog.) and pequi (*Caryocar brasiliense* Camb.) pulp) were studied in nitrogen and synthetic air using TG/DTG techniques.

Experimental

Three oils were selected for this study based on their high oleic acid content and potential for human consumption: amburana (*Amburana cearensis* (Fr. Allem) A. C. Smith) almond, baru (*Dypterix alata* Vog.) almond and pequi (*Caryocar brasiliense* Camb.) pulp oils. Brazilian Cerrado plant seeds/pulp were macerated and dryed at 110°C for 2 h. Oil extraction was done in a Sohxlet equipment for 6 h using hexane as solvent.

Oils composition was obtained by gas chromatography as described in [5].

TG/DTG curves were obtained using Mettler Toledo TG/SDTA 851^e TG/SDTA equipment in synthetic air and nitrogen (100 mL min^{-1}) using alumina crucibles, at heating rate of 10°C min^{-1} in the 25–650°C temperature range. The initial sample masses were between 12–17 mg.

Results and discussion

Composition of oils

Table 1 presents the composition of fatty acids of amburana, baru and pequi pulp oils.

The high oleic acid content of the studied oils (Table 1) makes them useful in food industry as frying or salad oils. Pequi pulp oil showed high palmitic acid content, which offers appropriate plasticity in soap production [5].

Fatty acid composition of amburana and baru oils have similarities with the industrially used oils: amburana oil is similar to cottonseed oil and baru oil has

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Table 1 Fatty acid composition of vegetable oils

	Fatty acid composition/%		
	amburana oil	baru oil	pequi pulp oil
Miristic acid	–	–	0.2
Palmitic acid	15.6	7.8	41.1
Palmitoleic acid	0.3	0.1	0.5
Margaric acid	0.1	0.1	–
Stearic acid	4.5	6.2	1.9
Oleic acid	46.9	46.8	54.0
Vacenic acid	0.1	0.1	0.3
*cis*6, *cis*9 – octadecadienoic acid	1.0	–	–
Linoleic acid	11.9	24.3	0.9
Linolenic acid	4.8	0.1	–
Araquidic acid	2.6	1.6	0.2
Gadoleic acid	3.0	3.1	0.7
*cis*11 – eicosenoic acid	–	–	0.2
Behenic acid	5.1	4.5	–
Erucic acid	0.2	0.4	–
Lignoceric acid	3.9	4.8	–

similarities with peanut oil [5]. Besides, amburana and baru oils can be considered as sources of linoleic and linolenic acids, which are essential for the human body.

Linoleic and linolenic acids were the essential fatty acids found in the studied samples. Amburana and baru oils presented enough amounts of essential fatty acids: 16.7 and 24.4%, respectively, assuring its possible use in human feeding (Table 1). However, pequi pulp oil has less amount of these fatty acids (Table 1).

Yield of extraction

The yield of extraction of soybean oil in food industry is around 20%. On the contrary, in our experiments higher yields were obtained (Table 2). In other words, the oils investigated in this present study can have great importance in industrial scale.

The high oleic acid content (Table 1) in Cerrado oils make them interesting for food industry as frying or salad oils. Table 2 summarizes the yield of extraction obtained for the studied species.

Table 2 Yields of extraction of amburana and baru plant seeds and of pequi pulp oils

Vegetable species	Yields of extraction/%
Amburana	21.5
Baru	37.6
Pequi pulp	51.9

Thermogravimetric analysis

Thermal stabilities of the three studied oils are shown in Table 3. It could be seen that the stabilities in nitrogen are similar. However pequi pulp oil has the highest stability followed by baru oil, while amburana oil is the least stable. Thermal stability results can be related to the degree of unsaturation of the fatty acids that constitute the oils. Normally, the higher the unsaturation level is the lower of the thermal stability. This could be explained by the lower boiling point of the unsaturated fatty acids compared to their saturated equivalents [1].

In synthetic air amburana and baru oils showed the same, while pequi pulp oil showed lower thermal stability compared to the others, which can be attributed to its higher content of volatile short-chain fatty acids present in the acylglyceride molecules (Table 1) [6]. It is supposed that the higher amounts of unsaturated fatty acids in amburana and baru oils (Table 1) can increase the thermal stability of these oils and shift the process of mass loss towards higher temperatures. When oxygen reacts with the double bonds and incorporates, it causes a mass gain. However, this increase is compensated by the mass loss of the samples due to their decomposition. So the samples are gaining and loosing mass at the same time. Consequently, the mass loss measured by TG somewhat shifted to higher temperatures.

Figures 1 and 2 show the TG curves of amburana, baru and pequi pulp oil in synthetic air and in nitrogen, and Figs 3–5 present TG/DTG curves for amburana, baru and pequi pulp oils in both atmospheres, respectively.

Table 3 Amounts of unsaturated (UFA) and saturated fatty acids (SFA) and the starting temperatures of the mass losses in nitrogen (TSN) and synthetic air (TSA)

Vegetable oils	UFA/%	SFA/%	TSN/°C	TSA/°C
Amburana	78.2	31.8	340	290
Baru	74.9	25.1	342	290
Pequi pulp	56.6	43.4	345	260

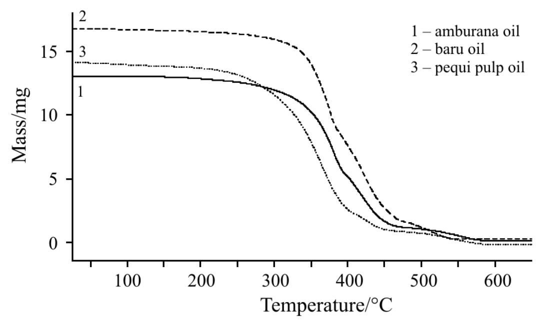

Fig. 1 TG curves of amburana, baru and pequi pulp oils in synthetic air

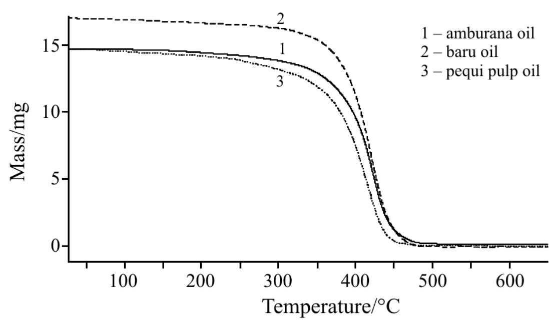

Fig. 2 TG curves for amburana, baru and pequi pulp oils in nitrogen

Thermal decomposition profiles of the three different oils are similar in both atmospheres. Between 280–500°C in nitrogen, TG/DTG curves show only one mass loss, which can be attributed to the thermal decomposition of the oils (Figs 3–5).

Between 250–600°C in synthetic air three mass loss steps can be seen because of the oxidation [10, 11] of the samples (Figs 3–5).

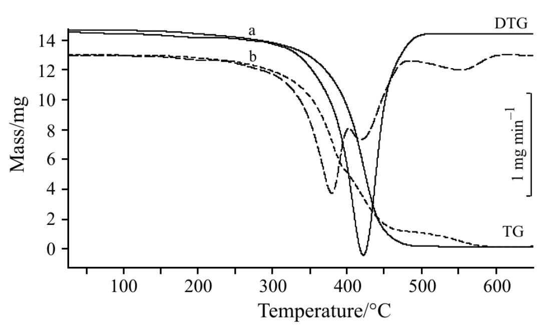

Fig. 3 TG/DTG curves of amburana oil: a – in nitrogen and b – under synthetic air

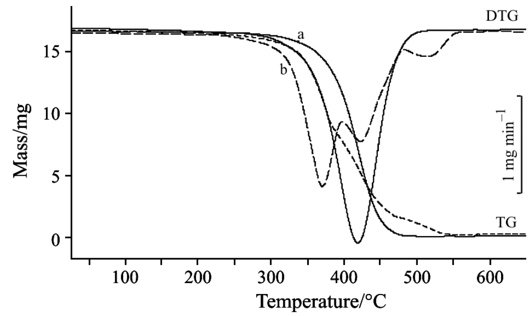

Fig. 4 TG/DTG curves of baru oil: a – in nitrogen and b – under synthetic air

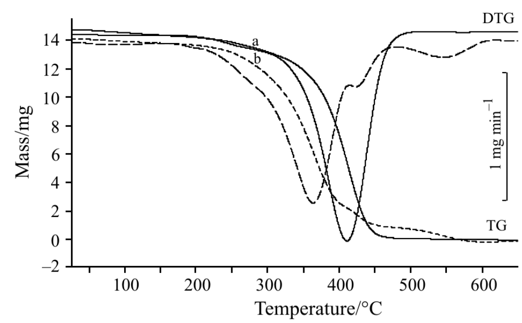

Fig. 5 TG/DTG curves of pequi pulp oil: a – in nitrogen and b – under synthetic air

The TG curves of the oils recorded in air showed three mass loss steps. The first one (from 250 to 410°C) was probably due to the oxidation of unsaturated fatty acids. The second event (between 410–480°C) can be attributed to the oxidation of the saturated fatty, while the last one (in the range of 480–600°C) is representative to the decomposition of the polymers formed during the oxidation process [8, 9]. At the beginning of the oils decomposition, slight mass gain was noticed (Figs 3–5), which can be the result of the oxygen uptake at he first part of the oxidative decomposition of oils [8–10].

Conclusions

The present work showed that some Cerrado plant species have a great importance for oil production. The studied oils (amburana, baru and pequi pulp) presented higher yields of extraction compared to soybean oil. They seemed to be available for oil production in food industry once they are also rich in unsaturated fatty acids, especially on oleic acid.

It could be observed that the thermal stability of the oils in nitrogen atmosphere were very similar to each other, probably due to their similar fatty acids composition. Due to the larger amount of short chain fatty acids in pequi pulp oil, it has the lowest thermal stability in synthetic air.

References

1 E. A. Farias, M. I. G. Leles, M. Ionashiro, T. O. Zuppa and N. R. Antoniosi Filho, Ecl. Quím., 27 (2002) 111.
2 J. Dweck and M. S. Sampaio, J. Therm. Anal. Cal., 75 (2004) 385.
3 N. Jorge and L. A. G. Gonçalves, Ciênc. Tecnol. Aliment., 18 (1998) 3.
4 R. Vianni and R. Braz-Filho, Quím. Nova, 19 (1996) 400.
5 T. O. Zuppa, Avaliação das Potencialidades de Plantas Nativas e Introduzidas no Cerrado na obtenção de Óleos e Gorduras, Dissertação mestrado, Instituto de Química, Universidade Federal de Goiás, Goiânia 2001, pp. 1–5, 34, 35, 58–63, 107.
6 J. U. Garcia, H. I. dos Santos, A. P. Fialho, F. L. T. Garro, N. R. Antoniosi Filho and M. I. G. Leles, Ecl. Quím., 29 (2004) 41.
7 G. Litwinienko and T. Kasprzycka-Guttman, Thermochim. Acta, 319 (1998) 185.
8 J. C. O. Santos, M. G. O. Santos, J. P. Dantas, M. M. Conceição, P. F. Athaide-Filho and A. G. Souza, J. Therm. Anal. Cal., 79 (2005) 283.
9 J. C. O. Santos, I. M. G. Santos, M. M. Conceição, S. L. Porto, M. F. S. Trindade, A. G. Souza, S. Prasad, V. J. Fernandes Jr. and A. S. Araújo, J. Therm. Anal. Cal., 75 (2004) 419.
10 E. Rudnik, A. Szczucinska, H. Gwardiak, A. Szulc and A. Winiarska, Thermochim. Acta, 370 (2001) 135.
11 E. Coni, E. Podestà and T. Catone, Thermochim. Acta, 418 (2004) 11.

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