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Thermal Stability of Edible Oils by Thermal Analysis

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Abstract: Thermal stability of commercial edible oils were investigated by non-isothermal Thermogravimetry/ Derivative Thermogravimetry (TG/DTG). Results obtained indicated that these parameters were dependent on composition of fatty acids, being influenced by the presence of natural and artificial antioxidants. According to the thermogravimetric curves, the following thermal stability sequence was suggested: corn>sunflower>soybean>rice>soybean+olive>sunflowe+olive>canola>olive.

Key words: Thermogravimetry, edible oils, thermal stability

INTRODUCTION

Commercial edible oils are appreciated on cooking due to the taste they give to food. In the last years, new analytical methods have been required to evaluate their processing and storage conditions (Gennaro *et al.*, 1998; (Vianni and Braz-filno, 1996). The oil quality depends on its fatty acid composition and consequently on its oxidation resistance. A higher stability of edible oils may be attained by addition of antioxidants, hydrogenation, blending, fragmentation and genetic modification of fatty acid composition (Moretto and Fett, 1998).

A more detailed knowledge of edible oil thermal decomposition may lead to a technological development in order to improve their stability. Moreover this knowledge is really important for a rigorous process control and establishment of standards for each specific use.

Thermal analysis is defined by the International Confederation of Thermal Analysis as all techniques that measure a change in a physical property of a substance as a function of temperature, while this substance is subjected to a controlled temperature program. Recently the use of thermal analytical methods, Thermogravimetry/ Derivative Thermogravimetry (TG/DTG), for oil and fat characterization have greatly interested food industries. These methods provide stability data which are important for proposals of fast application (Gennaro *et al.*, 1998; Wesolowki, 1998).

The present research seeks to evaluate the thermal stability of commercial edible oils using non-isothermal Thermogravimetry/Derivative Thermogravimetry (TG/DTG).

MATERIALS AND METHODS

Eight samples of commercial edible oils (olive, soybean, sunflower, corn, canola, rice, soybean+olive and sunflower+olive) were used. The olive, the rice, the canola and the soybean+olive oils do not present artificial antioxidant. The soybean and the corn ones contain citric acid and THBQ, used as artificial antioxidants. The sunflower oil contains citric acid and vitamin E, while the sunflower+olive oil only contains citric acid.

An usual characteristic in most vegetable oils is the high amount of unsaturated fatty acids present in the triglyceride molecules (Table 1). In the triglyceride, the main route of deterioration and possible loss of stability is the oxidative rancidity.

The thermal stability of commercial edible oil samples was investigated by TG/DTG under air atmosphere (30 mL min^{-1}). This study was accomplished using Shimadzu TGA-50 thermobalance, using alumina crucibles, and sample masses of 8.0±0.5 mg. The analysis were carried out using heating rates of 10 °C min up to 800 °C. The thermal stability of edible oil samples was measured as a function of initial decomposition temperature (T_{onset}).

RESULTS AND DISCUSSION

The thermogravimetric curves (Fig. 1) show the thermal behavior of all samples analyzed, indicating that

Table 1: Fatty acid composition (%) of some commercial edible oils

Fatty acids	Sunflower	Soybean	Rice	Corn	Canola	Olive
Saturated	11	15	17	13	6	14
Monounsaturated	20	23	42	25	58	77
Polyunsaturated	69	62	41	62	36	9

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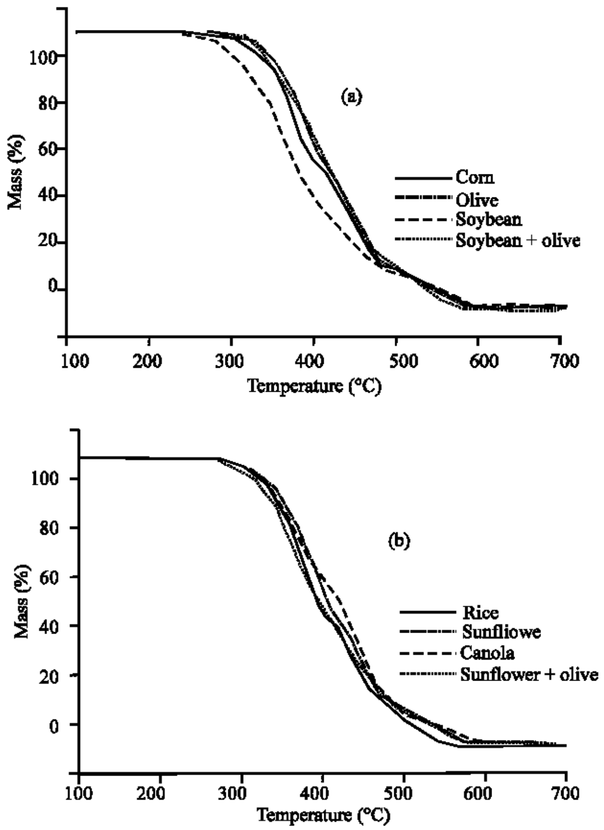

Fig. 1: TG curves of the commercial edible oils in air atmosphere

the thermal decomposition profile of the commercial edible oils are similar. A plateau may be observed, indicating a thermal stability of the materials up to ~200°C. The end of the decomposition is at about 600°C.

A derivative thermogravimetric curve of the commercial edible oils is showed in Fig. 2. The thermal decomposition process occurs in three steps, probably corresponding to polyunsaturated (200-380°C), monounsaturated (380-480°C) and saturated (480-600°C) fatty acids decomposition, respectively. It may be observed that the olive oil, containing about 86% of unsaturated fatty acids, presents a weight loss around 88% in the first two steps, indicating that the method is reliable. The parameters obtained from TG/DTG curves are listed in Table 2.

The first step of thermal decomposition of commercial edible oils is the most important one in the thermal stability study, as decomposition of unsaturated fatty acid starts in this step. According to the initial decomposition temperature (T_{onset}) referring the first step of thermal decomposition, obtained from thermogravimetric curves, the stability order proposed is: corn>sunflower>soybean>rice>soybean+oliv >sunflower +olive>canola>olive. This ranking suggests that the corn

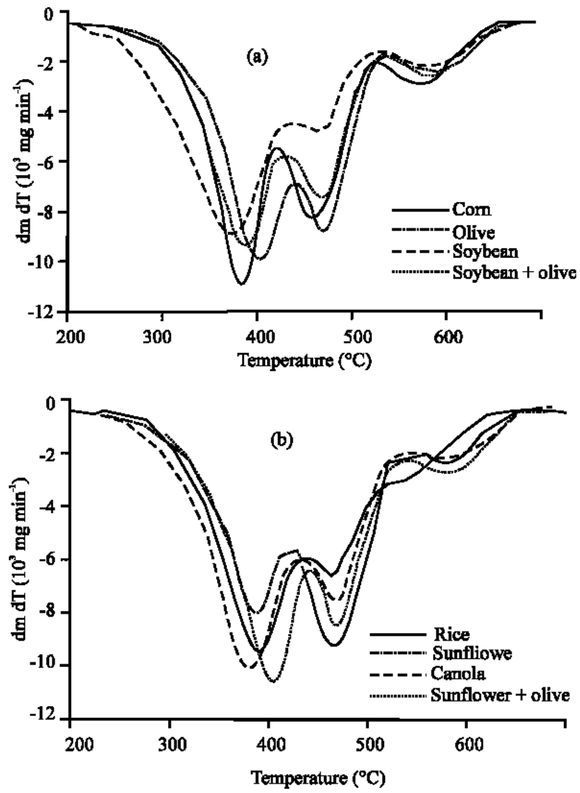

Fig. 2: DTG curves of the commercial edible oils

Table 2: Thermal decomposition data of commercial edible oils obtained from TG/DTG curves

	1st step		2nd step		3rd step	
Commercial Edible Oils	Temperature range (°C)	Δm (%)	Temperature range (°C)	Δm (%)	Temperature range (°C)	Δm (%)
Rice	221.5-391.6	52.3	391.6482.9	34.1	482.9584.1	133
Soybean	222.7-441.2	55.0	411.2501.3	32.2	501.3597.4	12.7
Corn	227.2-400.3	49.7	400.3496.5	36.9	496.5599.2	12.9
Sunflower	223.4-402.8	43.4	402.8506.8	45.8	506.8596.8	10.5
Canola	209.6-409.7	56.9	409.7497.9	30.3	497.9595.5	12.5
Olive	196.0-420.7	70.2	420.7495.7	17.8	495.7606.0	11.8
Soybean+olive	221.2392.6	52.7	392.6485.2	33.1	485.2589.8	14.1
Sunflower+olive	214.0398.9	53.0	398.9491.6	32.0	491.6595.8	14.6

oil is less susceptible to thermal deterioration that the other edible vegetable oils.

The thermal stability of the commercial edible oils showed dependence on fatty acid composition, also being influenced by presence of natural and artificial antioxidants. In spite of being highly unsaturated (Table 1), the high stability of corn oil is attributed to the presence of natural antioxidants, such as tocopherols and ferulic acid, besides the artificial antioxidants (tertiary butylhydroquinone and citric acid) specified on the packet (Kowalski, 1989).

The sunflower oil showed a slightly higher stability than the oils of soybean, rice and the mixture of soybean + olive. This may be due to the presence of natural antioxidants, besides the presence of small amounts of oleic acid. The presence of the same artificial antioxidants justify the stability of soybean oil. The low concentration of linolenic acid and steroids besides the high content of tocopherols and orizanol assure great stability to the rice oil. Another point is that oils used as spices (olive oil and mixtures of oils of soybean + olive and sunflower + olive) present lower stability.

CONCLUSION

The thermal stability of commercial edible oils was evaluated by thermogravimetric curves. The results obtained indicated that it depended on composition of fatty acids, being influenced by presence of natural and artificial antioxidants. according to the thermogravimetric curves, the stability order observed was: corn>sunflower >soybean>rice>soybean+olive>sunflower+olive>canola >olive.

In general, the higher the unsaturation degree of the fatty acids of the vegetable oils, more those oils will be susceptible to thermal deterioration. In spite of this, it was observed that several commercial edible oils, with a smaller unsaturation, presented an equivalent or smaller thermal stability than other ones with a higher unsaturation degree, indicating that other factors are involved in the thermal stability of the vegetable oils, mainly when exposed to inadequate storage conditions.

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