

# A THERMOANALYTIC AND KINETIC STUDY OF SUNFLOWER OIL

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**Abstract** - Recently, thermoanalytic methods have frequently been used in the characterization of oils and fats. In this work, thermoanalytic and kinetic parameters of sunflower oils, with and without antioxidants, were evaluated using thermogravimetry / derivative thermogravimetry and differential scanning calorimetry. The thermogravimetric profiles for the sunflower oils had similar characteristics, showing a level stretch indicative of stability up to about 200°C. Thermal decomposition of these oils occurred in three stages, related to the decomposition of polyunsaturated, monounsaturated and saturated fatty acids, respectively. DSC curves show two events that characterize the polymerization and decomposition of triglycerides. The heat capacities of the sunflower oils, obtained by DSC, showed a good correlation and were dependent on the composition of fatty acids. The kinetic parameters, obtained by non isothermal thermogravimetry by the Coats and Redfern, Madhusudanan, Horowitz and Metzger and Van Krevelen methods, were dependent on the antioxidant used. Increasing the frying time produced a decrease in the onset of thermal decomposition temperature in the sunflower oils analyzed.

**Keywords:** sunflower oil, thermogravimetry, kinetics.

## INTRODUCTION

Edible vegetable oils are highly appreciated for culinary uses because of the properties they impart on food, and technicians and experts have been called on to develop new analytical methods capable of evaluating processing and storage conditions (Felsner and Matos, 1998). These products deteriorate when processed inadequately, with the principal decomposition reaction being oxidation. Oxidation of the oils occurs through a free radical mechanism, initially characterized by the emergence of a sweetish and unpleasant odor, which becomes progressive worse until attaining the characteristic

smell of rancid fat, i.e., the decomposition of hydroxides and peroxides in low molecular weight acids and aldehydes occurs (Gennaro et al., 1998).

Frying is one of the most commonly used methods of food preparation in the home and in industry, and the prolonged use of oil for this purpose causes changes in its physical and/or chemical properties (Moretto and Fett, 1998).

Several methods have been proposed to evaluate the quality of edible oils (Felsner and Matos, 1998). Most of these methods submit a sample to conditions that accelerate the normal oxidation process. The older methods used to estimate the quality of vegetable oils cause deterioration by maintaining the

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sample at elevated temperatures in contact with air and then periodically weighing to verify the gain in mass or examining organoleptically for rancidity. The peroxides or other oxidation products formed can be determined by spectral or chemical analysis (Kowalski, 1989). Some of the frequently used tests employed to predict the quality of vegetable oils are the periodic determination of peroxide index, the active oxygen method (AOM), the automated AOM method and the oxygen pump method (Lee and Min, 1990). Currently, thermoanalytic methods such as differential scanning calorimetry (DSC) and thermogravimetry / derivative thermogravimetry (TG/DTG) are receiving considerable attention. TG/DTG curves can be used to estimate the quality of edible oil by determining the kinetic parameters (Santos et al., 2001; Santos et al., 2002) and the oxidative induction period. On the other hand, as the oxidative thermal decomposition involves exothermic and endothermic reactions, it is possible to estimate the energy involved in the determination process by thermal techniques such as DTA and DSC. Therefore, these methods are more advantageous than the conventional methods, because they are more precise and sensitive and require a smaller sample mass and results are obtained more rapidly (Souza et al., 1998).

In view of these advantages, it becomes indispensable to analyze the stability of these oils during thermal treatment (frying) and storage. The thermoanalytic (specific heat, stability, decomposition enthalpy) and the kinetic (activation energy, frequency factor, order of reaction) parameters were determined in this study; deterioration of sunflower oil under frying conditions was also studied with the use of differential scanning calorimetry and non isothermal thermogravimetry, in an atmosphere of nitrogen and air, respectively.

## EXPERIMENTAL

### Materials

Samples of edible sunflower oils with and

without artificial antioxidants, acquired at a local market and produced by Brazilian industry, and having the composition listed in Table 1, were used in the study.

### Thermal Analysis

The non isothermal TG/DTG curves were obtained in a Shimadzu TGA-50 thermobalance in air (20 mLmin<sup>-1</sup>), using an alumina crucible with heating rates of 2, 5, 10 and 20°Cmin<sup>-1</sup> and a sample mass of 8.0±0.5mg in a temperature range of 25 to 800°C.

The DSC curves were obtained in a Shimadzu DSC-50 differential scanning calorimeter, in nitrogen (50 mLmin<sup>-1</sup>) using an alumina crucible with heating rates of 5, 10 and 20°Cmin<sup>-1</sup> and a sample mass of 8.0±0.5mg in a temperature range of 25 to 500°C.

### Specific Heat Measurement

The heat capacities of the sunflower oils were determined from the data obtained by DSC. The calculations were based on implementation of the temperature program. The oil samples were heated at a rate of 5°Cmin<sup>-1</sup> up to 30°C during five minutes. Then, they were heated at a rate of 10°Cmin<sup>-1</sup> up to 200°C during five minutes.

The following ratio was used to calculate the heat capacities:

$$c = \frac{m_0 c_0}{m} \cdot \frac{S_3 - S_1}{S_2 - S_1} \quad (1)$$

where  $c_0$  and  $c$  are the specific heat of the reference material and of the sunflower oil, respectively;  $m_0$  and  $m$  refer to the mass of samples and of the reference material, respectively, and  $S_1$ ,  $S_2$  and  $S_3$  are the thermal displacements of the DSC in relation to the blank, reference and sample, respectively (Kasprzycka-Guttman et al., 1995).

**Table 1: Compositions of the sunflower oils analyzed.**

Composition	Sunflower Oil A	Sunflower Oil B
Monounsaturated (%)	22.8	23.0
Polyunsaturated (%)	65.2	65.0
Saturated (%)	12.0	12.0
Artificial antioxidant	Citric acid	—

## Kinetic Study

The theoretical basis for the kinetic calculations by non isothermal thermogravimetry is expressed in the following equation:

$$g(\alpha) = \frac{A}{\phi} \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (2)$$

where  $A$  is the frequency factor,  $T$  is the temperature,  $R$  is the universal gas constant,  $\phi$  is the heating rate and  $E_a$  is the activation energy. This mathematical equation describes the thermogravimetric curve, where  $g(\alpha)$  represents the reaction mechanism and the second term in the equation can not be solved analytically; it can only be solved by approximation numerical methods. Various approximations for calculation of this integral have been proposed, giving rise to the different methods for determining kinetic parameters from thermogravimetric curves (Guo and Lua, 2000).

The integral methods proposed by Coats and Redfern and Madhusudanan and the approximation methods proposed by Horowitz and Meltzger and Van Krevelen were used in this study (Coats and Redfern, 1964; Horowitz and Meltzger, 1963; Madhusudanan et al., 1993; Van Krevelen et al., 1951).

## Thermal Degradation

The study of thermal degradation of sunflower oils was carried out by thermogravimetric measurement. For this purpose the oils were heated

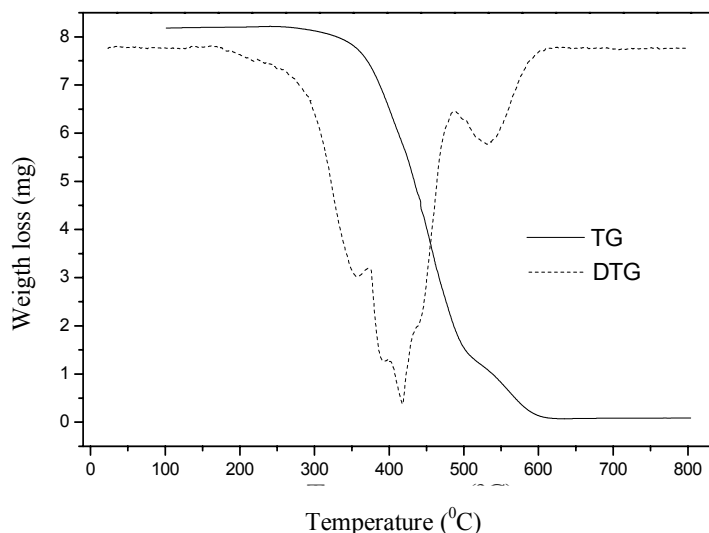
to 190°C for periods of 0.5, 4.0 and 8.0 h. The sunflower oils were heated in a 500 mL flask with a surface diameter of about 4 cm that was exposed to air. Afterwards, TG/DTG curves were obtained in a Shimadzu TGA-50 thermobalance in air (20 mLmin<sup>-1</sup>) at a heating rate of 5°Cmin<sup>-1</sup> with the objective of verifying of influence the frying time and temperature on the thermal stability of sunflower oils.

## RESULTS AND DISCUSSION

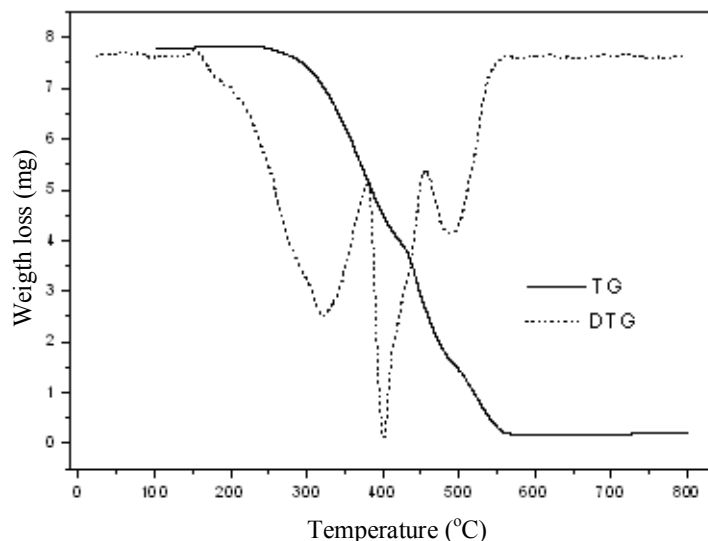
### Thermal Behavior

The thermal decomposition profiles for the sunflower oils have similar characteristics, as can be observed in Figs. 1 and 2, where all the non isothermal TG/DTG curves have three thermal decomposition steps in the range of 230 to 550°C, with no residue remaining at 800°C. Thermal decomposition of these oils occurred in three stages, related to the decomposition of polyunsaturated, monounsaturated and saturated fatty acids, respectively.

In relation to the thermal decomposition steps, it was observed that the first step (230 to 380°C) corresponds to the decomposition of the polyunsaturated fatty acids. During heating, the triglycerides, which form 96 to 98% of the edible oils, produce volatile compounds, which are constantly removed by vapor generated during heating. These products (dimers, trimers, polymers) are formed principally by thermal reactions of unsaturated fatty acids, such as linoleic acid.



**Figure 1:** TG/DTG curves for sunflower oil with artificial antioxidants.



**Figure 2:** TG/DTG curves for sunflower oil without artificial antioxidants

The first step is the most important for the thermal stability of edible oils, because this is the step where decomposition of the unsaturated fatty acids begins. On the basis of the temperature at the beginning of thermal decomposition, it can be established that sunflower oil A, containing the antioxidants citric acid and vitamin E, had a higher thermal stability than that observed for sunflower oil B. Thus, it can be verified that the thermal stability of sunflower oils is dependent on the composition of the fatty acids, as it is influenced by artificial antioxidants.

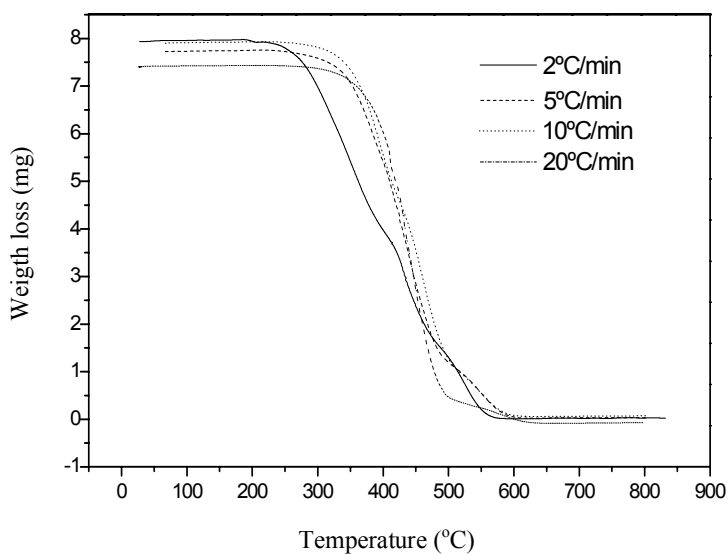
The beginning of oxidation in edible vegetable oils is characterized by absorption of oxygen through the fatty acid chain, subsequently forming the oxidation product as peroxides. This behavior is generally identified by an increase in the initial mass of the sample. For the sunflower oil samples analyzed in air, a small gain in mass in the DTG curve for oil B was observed (Fig. 2), indicating that the process of thermal decomposition involved the absorption of oxygen as well as the liberation of volatiles. This was not observed for sunflower oil A (Fig. 2), where the reaction resulted only the liberation of volatiles.

The second step in the thermal decomposition of sunflower oils (380 to 480°C) corresponds to the decomposition of monounsaturated fatty acids, such as oleic acid. During this reaction, the double bonds are broken, causing the triglyceride molecules in the edible vegetable oils to become saturated. The third step in the thermal decomposition, which occurs in a temperature range of around 480 to 550°C, corresponds to the thermal decomposition of saturated fatty acids, such as palmitic acid.

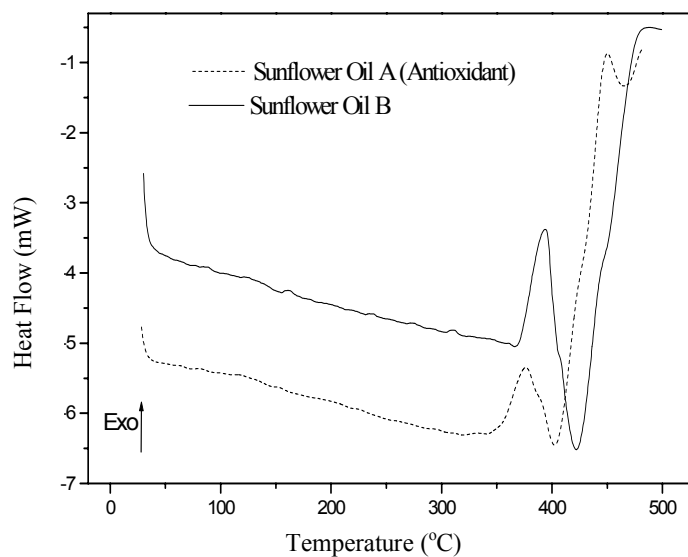
To verify the dependence of the thermogravimetric profile for sunflower oils on experimental factors, the heating rate was varied from 2 to 5, 10 and 20°Cmin<sup>-1</sup>, as shown in Fig. 3. It can be observed (Fig. 3) that there is a displacement in the initial decomposition temperature with the increase in heating rate. The thermal decomposition occurred in three steps at the heating rates 2, 5 and 10°Cmin<sup>-1</sup>, whereas at 20°Cmin<sup>-1</sup> only two events corresponding to thermal decomposition were observed. This was probably due to the superposition of the steps.

DSC curves (see Fig. 4) for sunflower oils have similar profiles, verifying the endothermic and exothermic transitions. The exothermic transitions probably correspond to polymerization of a fatty acids component of the sunflower oils, occurring at around 340°C, whereas the endothermic transitions refer to thermal decomposition of saturated and unsaturated fatty acids, component of the vegetable oils, in agreement with the thermogravimetric results. The increase in heating rate produces a broadening and, consequently, an increase in the area of the peaks corresponding to the thermal decomposition of these oils. As the events observed refer to chemical processes, the increase in heating rate results in the decomposition of a larger quantity of fatty acids.

The enthalpies involved in the thermal decomposition process, observed in the DSC curves correspond to the molar enthalpies of polymerization and decomposition and have differentiated values, as shown in Table 2. These results indicate that the polymerization and decomposition enthalpies are directly related to the fatty acids composition of sunflower oils.



**Figure 3:** TG curves for sunflower oils at different heating rates.



**Figure 4:** DSC curves for sunflower oils with and without artificial antioxidants.

**Table 2:** Polymerization and decomposition enthalpies ( $\text{J.g}^{-1}$ ) of sunflower oils.

Sunflower oils	Heating rate ( $^{\circ}\text{Cmin}^{-1}$ )	$\Delta H_{\text{pol}}$	$-\Delta H_{\text{dec}}$
A	5	11.30	32.84
	10	7.93	28.93
	20	1.74	26.90
B	5	18.76	55.26
	10	8.13	42.50
	20	2.61	18.13

## Heat Capacity

The standard molar heat capacities in the liquid phase were determined by the method described earlier. The curves related to the standard heat capacities in the liquid phase of sunflower oils are shown in Fig. 5.

The specific heat values for the sunflower oils analyzed do not vary substantially. The calculated  $C_p$  values are in agreement with those found in the literature for other vegetable oils (Kasprzycka-Guttman et al., 1995).

## Kinetic Parameters

Kinetic parameters for the three steps of thermal decomposition of sunflower oils were determined by using an interval of decomposed fraction ( $\alpha$ ) of 0.10 to 0.90 and applying the thermogravimetric data in the Program for Determination of Kinetic Parameters developed in Turbo Basic language.

The program for determination of kinetic parameters calculates the reaction order ( $n$ ), activation energy ( $E_a$ ) and frequency factor ( $A$ ) by the approximation and integral methods, using kinetic equations proposed by Coats and Redfern (CR), Horowitz and Meltzger (HM), Madhusudanan (MD) and Van Krevelen (VK) (Coats and Redfern, 1964; Horowitz and Meltzger, 1963; Madhusudanan et al., 1993; Van Krevelen et al., 1951). The calculated kinetic parameters and linear correlation

coefficient ( $r$ ) found for all the steps in thermal decomposition of sunflower oils are summarized in Tables 3 and 4.

The different heating rates used resulted the same mechanism, only varying the values of the kinetic parameters. Nevertheless, there was a good correlation between the kinetic parameters obtained by the integration and approximation methods, but the values obtained by the approximation methods were higher than the values obtained by the integration methods, which can be ascribed to the different mathematical treatments of the methods.

The results presented in Tables 3 and 4 indicate that the first step in the thermal decomposition of sunflower oils corresponds to the first-order reaction, whereas, the second and the third steps behave as second-order reactions.

The medium activation energy from sunflower oil with artificial antioxidants was higher than that from sunflower oil without artificial antioxidants, indicating that the artificial antioxidant citric acid produced an increase in thermal stability of the oils analyzed.

The increase in activation energy in relation to the steps in thermal decomposition of samples occurred due to the possible break in the molecular bonds of unsaturated fatty acid, which than the molecular bonds of is are less stable saturated fatty acids, requiring higher activation energy for degradation.

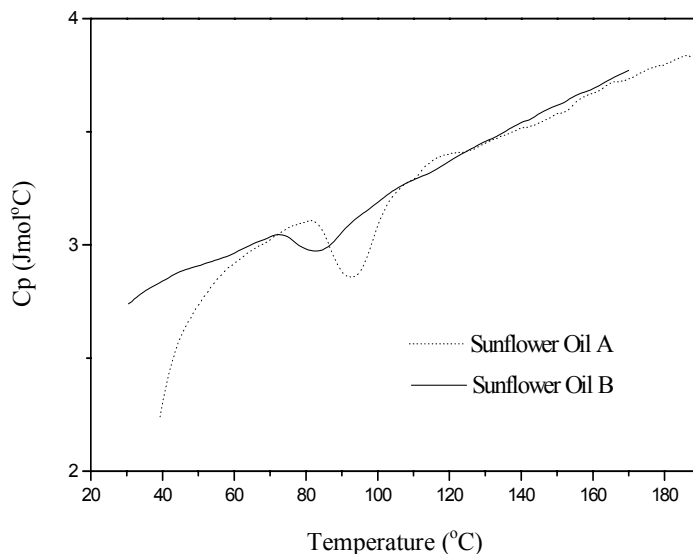


Figure 5:  $C_p$  curves for sunflower oils.

**Table 3: Kinetic parameters obtained by thermogravimetry for the steps in thermal decomposition of sunflower oil A.**

Kinetic method	Kinetic parameters	Steps		
		1	2	3
CR	n	0.94	2.11	2.07
	$E_a$ [kJmol <sup>-1</sup> ]	92.76	288.39	355.95
	A [s <sup>-1</sup> ]	1.7E+04	1.5E+19	2.9E+21
	r	1.0000	0.9994	0.9991
MD	n	0.92	2.12	2.11
	$E_a$ [kJmol <sup>-1</sup> ]	92.45	289.48	352.14
	A [s <sup>-1</sup> ]	1.8E+04	1.7E+19	1.5E+22
	r	1.0000	0.9994	0.9990
HM	n	1.06	2.13	2.15
	$E_a$ [kJmol <sup>-1</sup> ]	107.16	299.45	382.19
	A [s <sup>-1</sup> ]	2.4E+06	9.9E+20	3.2E+23
	r	0.9999	0.9993	0.9994
VK	n	0.94	2.06	2.10
	$E_a$ [kJmol <sup>-1</sup> ]	94.48	298.37	398.96
	A [s <sup>-1</sup> ]	7.7E+10	4.4E+23	3.3E+28
	r	1.0000	0.9980	1.0000

**Table 4: Kinetic parameters obtained by thermogravimetry for the steps in thermal decomposition of sunflower oil B**

Kinetic method	Kinetic parameters	Steps		
		1	2	3
CR	n	0.96	2.08	1.98
	$E_a$ [kJmol <sup>-1</sup> ]	86.88	208.81	307.43
	A [s <sup>-1</sup> ]	1.7E+07	2.7E+13	4.5E+17
	r	0.9998	0.9990	0.9992
MD	n	0.95	2.03	1.88
	$E_a$ [kJmol <sup>-1</sup> ]	87.61	205.28	296.88
	A [s <sup>-1</sup> ]	1.7E+07	1.5E+13	8.9E+16
	r	0.9998	0.9990	0.9991
HM	n	0.99	2.12	2.05
	$E_a$ [kJmol <sup>-1</sup> ]	108.93	215.67	327.73
	A [s <sup>-1</sup> ]	8.5E+09	2.7E+14	1.0E+19
	r	0.9995	0.9960	0.9991
VK	n	0.97	2.06	1.96
	$E_a$ [kJmol <sup>-1</sup> ]	90.28	208.88	311.74
	A [s <sup>-1</sup> ]	1.0E+14	1.2E+18	5.4E+23
	r	0.9948	1.0000	0.9993

## Thermal Degradation

The study of oils before their use in food permits data to be obtained on the influence of variables (time, temperature) on their thermal decomposition. Comparison with data obtained in earlier tests increases the amount of data available, thereby allowing better conclusions to be drawn in this study.

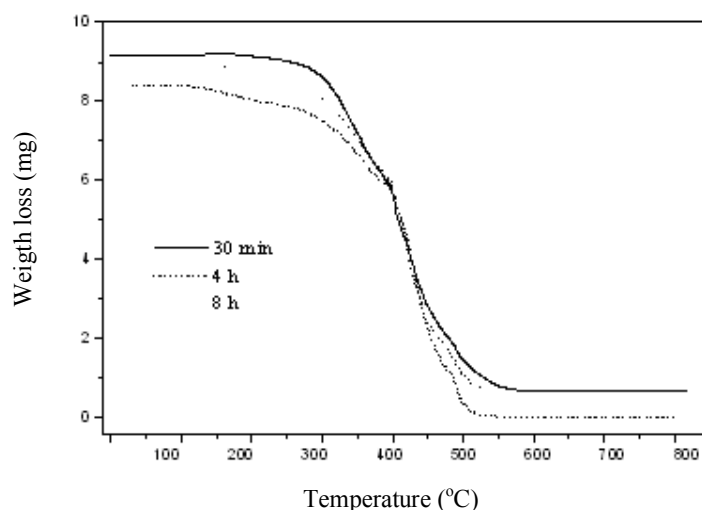
To verify the dependence of the thermogravimetric profiles for the commercial edible oils on frying time and temperature, the oils were heated to 190°C and the TG curves were obtained after 0.5, 4.0 and 8.0 h of heating and are shown in Fig. 6.

According to the thermogravimetric curves for sunflower oil with and without antioxidants as a function of frying time, it can be verified that the

onset temperature of thermal decomposition of the oils analyzed decreased with the increase in frying time, i.e., an increase in frying time led to an increase in the degradation of these oils. This is caused by the decrease in unsaturation due to prior heat treatment, resulting in degradation of the samples of edible oil under analysis.

The auto-oxidation of unsaturated fatty acids produces a decrease in the thermal stability of the vegetable oils, causing a decrease in the oxidative induction time. Factors such as change in color, increase in viscosity and unpleasant odor are observed in the process of degradation of these oils.

The data obtained from TG/DTG curves for the process of degradation of sunflower oils are summarized in Table 5.



**Figure 6:** TG curves for sunflower oil A under frying conditions.

**Table 5:** Decomposition onset temperature ( $T_{\text{onset}}$ ) of sunflower oils after different frying times.

Time (h)	$T_{\text{onset}}$ (°C)	
	Sunflower Oil A	Sunflower Oil B
0	246.67	218.78
0.5	192.80	207.78
4	186.51	177.95
8	184.66	169.60

During the heating of the vegetable oils in the process of frying, a complex series of reactions produces numerous degradation compounds. With the occurrence of the thermal reactions, the functional, sensorial and nutritional qualities are modified. The oils repeatedly used in frying without

immersion undergo degradation by oxidative reactions. In this case, as shown in Table 5, the loss of stability is accelerated by the increase in process time, which is responsible for changes in the physicochemical and organoleptic characteristics of the sunflower oils.



During prolonged heating, edible vegetable oils, including sunflower oils with and without artificial antioxidants, undergo the process of thermal degradation resulting in oxidative rancidity, resulting in the formation of hydroperoxides and other products of degradation that can liberate volatile compounds such as hydrocarbons, aldehydes, ketones, furans and carboxylic acids, lower the temperature of onset of thermal decomposition ( $T_{\text{onset}}$ ) of the samples analyzed.

## CONCLUSIONS

Thermoanalytic and kinetic properties of sunflower oils are dependent on the composition of fatty acids and are influenced by artificial antioxidants.

The thermoanalytic methods were considered to be versatile techniques for this work, because in addition to the study of thermal stability and of the deterioration occurring in frying, they require only a small sample mass, making it possible to obtain results more rapidly and enabling verification of presence of the artificial antioxidants.

## ACKNOWLEDGEMENT

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