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Kinetic Parameters on Thermal Degradation of Edible Vegetable Oils by Thermogravimetric Data

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Abstract: Kinetic parameters of commercial edible oils were evaluated. The thermal decomposition process of the oils occurred in three steps, due to polyunsaturated, monounsaturated and saturated fatty acids decomposition, respectively. Kinetic parameters were obtained using Coats-Redfern and Madhusudanan methods and presented good correlation. According to activation energy of the first thermal decomposition step, the following stability order is proposed: corn (A) > rice > corn > soybean > sunflower (A) > canola (A) > sunflower > olive.

Key words: Edible oils,thermal decomposition, kinetic

INTRODUCTION

Edible oils, very appreciated on cooking, have required the development of new analytical methods to evaluate its processing and storing conditions. When manipulated in a non adequate way, this products get deteriorated, oxidation being the main decomposition reaction. Oil oxidation occur through a free radical mechanism, due to hydroperoxides and peroxides decomposition in low molecular weight aldehydes and acids (Felsner and Matos, 1998).

Actually, thermoanalytical methods as differential scanning calorimetry and thermogravimetry have received considerable attention (Kowalsk, 1989; Santos *et al.*, 2001). These methods are advantageous in relation to the conventional ones because present a higher precision and sensitivity as well as use smaller amount of sample and results are obtained faster.

In this research, kinetic parameters (activation energy, frequency factor and reaction order) on thermal degradation of commercial edible oils were determined using non-isothermal thermogravimetry.

MATERIALS AND METHODS

The edible oils used in this research, were: soybean, sunflower, olive, canola, corn and rice. All oils are produced by brazilian industries. The compositions are presented in Table 1.

Table 1: Fatty acids composition (%) of the edible vegetable oils

	Fatty acids			
Vegetable oils	Monounsaturated	Polyunsaturated	Saturated	Artificial antioxidants
Olive	71.3	12.7	16.0	-
Canola (A)	65.2	29.3	5.5	Citric acid/E vitamin
Canola	65.0	29.0	5.0	-
Sunflower (A)	22.8	65.2	12.0	Citric acid/E vitamin
Sunflower	23.0	65.0	12.0	-
Corn (A)	33.5	51.0	15.5	Citric acid/ TBHQ
Corn	34.0	50.0	16.0	-
Soybean	24.3	60.0	15.7	Citric acid/ TBHQ
Rice	40.8	40.1	19.1	-

Non-isothermal TG/DTG curves were obtained in a thermobalance (TGA-50, Shimadzu), in air atmosphere (20 mL min^{-1}), using alumina crucibles, heating rates: 2, 5, 10 and 20°C min^{-1}, sample mass of 8.0±0.5 mg, in a temperature range of 25-800°C. From this data, a kinetic study was done, using equations described in literature (Santos *et al.*, 2004) solved using integral methods proposed by Coats Redfern and Madhusudanan.

Coats and Redfern (Santos *et al.*, 2006) developed an integral method that can be applied to TG/DTG data, assuming the different reaction orders. The order related to the most appropriate mechanism is presumed to lead to the best linear plot, from which the activation energy is determined. For $n \neq 1$, the equation used for analysis is:

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Table 2: Kinetic parameters of the thermal decomposition events of edible vegetable oils, calculated by thermogravimetry, using Coats-Redfern equation

Events	Kinetic Parameters	Edible oils: Soybean	Corn	Rice	Olive	Canola	Sunflower
	n	1.06	1.08	0.96	0.92	1.02	0.96
	E_a [kJ mol^{-1}]	92.84	99.20	94.42	78.52	87.32	106.88
1	A [s^{-1}]	1.3×10^5	6.8×10^5	1.8×10^5	2.9×10^2	5.4×10^7	1.7×10^7
	r	1	1	0.999	0.999	1	0.999
	sd	0.023	0.125	0.001	0.003	0.025	0.001
	n	2.07	2.04	1.86	1.89	2.11	2.08
	E_a [kJmol^{-1}]	290.13	349.39	264.88	270.05	271.09	208.81
2	A [s^{-1}]	6.7×10^{26}	7.2×10^{23}	2.5×10^{17}	5.5×10^7	5.8×10^{17}	2.7×10^{13}
	r	0.999	0.999	0.999	0.999	0.999	0.999
	sd	0.002	0.029	0.439	0.126	0.008	0.003
	n	1.91	1.93	1.87	1.96	2.13	1.98
	E_a [kJmol^{-1}]	337.72	274.21	329.08	277.71	370.33	307.43
3	A [s^{-1}]	1.3×10^{20}	3.8×10^{17}	1.6×10^{19}	1.0×10^{29}	2.2×10^{22}	4.5×10^{17}
	r	0.998	0.999	0.999	1	0.998	0.999
	sd	0.128	0.932	0.001	1	0.234	0.120

Table 3: Kinetic parameters of the thermal decomposition events of edible vegetable oils, calculated by Thermogravimetry, using Madhusudanan equation

Events	Kinetic Parameters	Edible oils: Soybean	Corn	Rice	Olive	Canola	Sunflower
	n	1.07	1.11	0.97	0.99	1.06	0.94
	E_a [kJmol^{-1}]	94.12	94.42	91.82	78.88	88.88	106.61
1	A [s^{-1}]	1.9×10^5	1.9×10^6	1.5×10^5	6.29×10^2	8.4×10^4	1.7×10^7
	r	0.999	1	0.999	0.999	1	0.999
	sd	0.006	0.0023	0.234	0.005	0.456	0.001
	n	2.04	2.10	1.87	1.91	2.05	2.03
	E_a [kJmol^{-1}]	273.63	333.07	265.97	272.16	279.81	205.28
2	A [s^{-1}]	3.7×10^{25}	4.1×10^{22}	3.2×10^{17}	8.45×10^{17}	2.9×10^{18}	1.5×10^{13}
	r	0.999	0.999	0.999	0.999	0.999	0.998
	sd	0.002	0.023	0.123	0.001	0.003	0.345
	n	1.90	1.98	1.96	1.87	2.12	1.88
	E_a [kJmol^{-1}]	324.99	279.24	328.08	293.24	374.24	296.88
3	A [s^{-1}]	1.8×10^{19}	8.9×10^{15}	1.4×10^{22}	1.12×10^{29}	4.3×10^{22}	8.9×10^{16}
	r	0.998	0.999	0.999	1	0.998	0.999
	sd	0.002	0.120	0.001	0.564	0.003	0.003

$$\log\left[\frac{1-\ln(1-\alpha)^{1-n}}{T^2}\right]=\log\frac{AR}{\phi}-\frac{E_a}{2.303(RT)} \quad (1)$$

An other integral method to evaluate a kinetic model was developed by Madhusudanan and others (Santos *et al*., 2004) for estimates the kinetic parameters from TG/DTG curves. The plot of the left side of equations versus the reciprocal of the absolute temperature gives linear curves. E_a and A can be calculated from the slope and intercept, respectively. For $n\neq1$, the activation energy can be calculated from the following expression:

$$\ln\left[\frac{1-\ln(1-\alpha)}{T^{1.9206}(1-n)}\right]=\ln\frac{AR}{\phi R}+0.02-1.9206 \ln\frac{E_a}{R}-0.12040\frac{E_a}{RT} \quad (2)$$

RESULTS AND DISCUSSION

Thermal decomposition profile of the different edible vegetable oils presented similar characteristics, as it may be observed in Fig 1. All TG/DTG dynamic curves presented three events of thermal decomposition, between 200 and 600°C, with no residues after thermal treatment up to 800°C. In relation to thermal decomposition events, it was observed that the first event (200-380°C) is due to polyunsaturated fatty acid decomposition-this is the most important step to determine the edible oils thermal stability order. The second thermal decomposition event (380-480°C) is due to monounsaturated fatty acids decomposition. The third thermal decomposition event, in the temperature range of 480-600°C, is due to saturated fatty acids thermal decomposition.

The determination of the kinetic parameters-reaction order (n), activation Energy (E_a) and frequency factor (A)-of the thermal decomposition events of the edible vegetable oils was done using integral methods and the equations proposed by Coats-Redfern and Madhusudanan, in a decomposed fraction range of 0.10 to 0.90. The kinetic parameters calculated to the thermal decomposition events of the edible vegetable oils, besides the standard deviation (sd) and linear regression coefficient (r), are listed in Table 2 and 3.

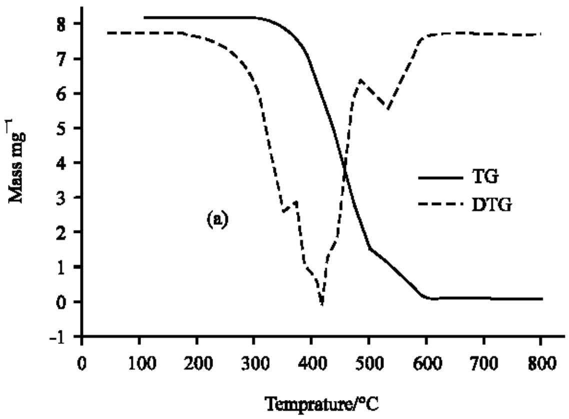

Fig. 1: TG/DTG curves of sunflower oil

According to the activation energy of the first thermal decomposition event, the following stability order is proposed: corn (A) > rice > corn > soybean > sunflower (A) > canola (A) > sunflower > olive.

CONCLUSION

Thermoanalytical and kinetic properties of edible vegetable oils depend on composition and are changed by the presence of artificial antioxidants. Thermoanalytical methods are interesting techniques, which permit the study of thermal stability and degradation caused by frying, with a small amount of material.

Results are obtained faster than conventional techniques and the presence of artificial antioxidant may also be detected. Rheological properties of vegetable edible oils are similar in the temperature range 10-80°C, during heating and cooling, indicating that no thermal degradation occurred in this temperature range.

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