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Evaluation Of The Thermal Stability Of Vegetable Oils From Activation Energy

Corresponding Author

J.C.O.Santos
Unidade Academica de Educacao, CES,
Universidade Federal de Campina Grande,
UFCG, 58175-000, Cuite, Paraiba, (BRAZIL)
Phone-Fax: 55-83-33722299
E-mail: josecos@ufcg.edu.br

Co-Author

A.G.Souza
Laboratorio de Termoquimica e Materiais, Departamento de Quimica,
CCEN, Universidade Federal da Paraiba, UFPB, 58059-900,
Joao Pessoa, Paraiba, (BRAZIL)

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ABSTRACT

Thermal stability of vegetable oils was evaluated from activation energy determined by non-isothermal thermogravimetric analysis. Kinetic parameters were calculated by integral and approximation methods. 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 activation energy the following thermal stability sequence was suggested: sunflower > corn > soybean > rice > soybean + olive > rapeseed > sunflower + olive > olive.

KEYWORDS

Vegetable oils;
Kinetic;
Thermal stability;
Activation energy.

INTRODUCTION

Vegetable 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[4,8,11,12,17,20,]. The oil quality depends on its fatty acid composition and consequently on its oxidation resistance. A higher stability of vegetable oils may be attained by addition of antioxidants, hydrogenation, blending, fragmentation and genetic modification of fatty acid composition[3,13]. A more detailed knowledge of vegetable oil thermal decomposition may lead to a technological development in order to improve their stability[13,21]. Moreover this knowledge is really important for a rigorous process control and establishment of standards for each specific use.

Recently the use of thermal analytical methods, thermogravimetry / derivative thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC), for oil and fat characterization have greatly interested food industries. These methods provide stability data which are important for proposals of fast application[4,13,14,21].

Thermal analysis is defined 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. When a substance is heated, decomposition is one of changes it may undergo. Even when stoichiometric equations describing these changes are simple, many intermediate steps may occur, requiring great care in kinetic studies. The main steps in thermal decomposition kinetic study of foods are: separation and identification of final and intermediate reaction products; determination of velocity constants; determination of kinetic parameters that characterize thermal decomposition reactions. Procedure often used in this kind study consists in determining decomposed fraction (α) as a function of reaction time, not only in processes occurring at constant temperature, but also in process in which temperature varies linearly with time. The α determination can be done using many techniques, as UV-visible spectroscopy. These methods require a considerable sample handling, leading to mistakes and increasing time required for analysis. Actually, these values are frequently obtained by thermal analysis, being thermogravimetry the most used one. The use of these techniques represents a great simplification in obtainment of experimental results[1,16,].

In recent years, two kinds of methods have been developed for kinetic analysis using TG/DTG and DSC data. Isothermal methods for determining reaction kinetic are still used, but dynamic methods have many advantages as less time required for each analysis and availability of a number of methods for data evaluation. Mathematical accuracy of the methods using thermogravimetric data has been shown to be satisfactory for determination of kinetic data[7].

The present work seeks to evaluate the thermal stability of vegetable oils by using activation energy determined using non-isothermal thermogravimetric analysis.

EXPERIMENTAL

Vegetable oils

Samples of vegetable oils (olive, soybean, sunflower, corn, rapeseed, rice, soybean + olive and sunflower + olive) were used. The olive, the rice, the rapeseed and the soybean + olive oils do not present artificial antioxidant. The soybean and the corn ones contain citric acid and tertiarybutyl hydroquinone (THBQ), used as artificial antioxidants. The sunflower oil contains citric acid and E vitamin, while the sunflower + olive oil only contains citric acid. A 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.

Thermogravimetric measurements

Thermogravimetric analysis investigated the thermal stability of vegetable oil samples under air atmosphere (50 $\mathrm{mLmin^{-1}}$). This study was accomplished using Shimadzu TGA-50 thermal balance, using alumina crucibles, and sample masses of 8.0 ± 0.5 mg. The analyses were carried out using heating rate of $10^{\circ}\mathrm{Cmin^{-1}}$ up to 800°C.

Kinetic analysis

The calculation of kinetic data by using thermogravimetry is based on the equation:

$$\frac{d\alpha}{dt} = k\alpha^n \quad (1)$$

where α is the decomposed fraction of sample undergoing reaction, n is the reaction order and k is the specific rate constant. The Arrhenius equation expresses the temperature dependence of k:

$$k = A\exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where A is the Arrhenius constant, E_a is the activation energy and R is the gas constant.

TABLE 1: Fatty acid composition (%) of some vegetable oils

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

From Eq. (1) and (2):

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \tag{3}$$

where: $f(\alpha) = \alpha^n$. The linear equation is:

$$\frac{dT}{dt} = \phi \tag{4}$$

Combining Eq. (3) with Eq. (4):

$$\frac{d\alpha}{dT} = \left(\frac{A}{\phi}\right)\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \tag{5}$$

Integrating the equation above, the theoretical basis for kinetic calculations by non-isothermal methods (integral and approximations) is obtained.

$$g(\alpha) = \frac{A}{\phi}\int_0^T \exp\left(-\frac{E_a}{RT}\right)dT \tag{6}$$

where: A is the frequency factor, T is the temperature, R is the gas constant, ϕ is the heating rate and E_a is the activation energy.

Among dynamic methods, differential, integral and approximation ones can be cited, whose studies were carried out in previous works[18]. In this work we have selected the following methods, representative of different categories, and applied several equations to the thermal data: Coats-Redfern, Madhusudanan, Horowitz-Metzger and Van Krevelen methods[15,20]. The kinetic parameters calculated were: reaction order (n), activation energy (E_a) and frequency factor (A).

Coats and Redfern[2] 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 ¹ 1, the equation used for analysis is:

$$\log\left[\frac{1-\ln(1-\alpha)^{1-n}}{T^2}\right] = \log\frac{AR}{\phi} - \frac{E_a}{2.303(RT)} \tag{7}$$

An other integral method to evaluate a kinetic model was developed by Madhusudanan and others[9], 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 $n \neq 1$, the activation energy can be calculated from the following expression:

$$\ln\left[\frac{1-\ln(1-\alpha)}{T^{1.9206}(1-n)}\right] = \ln\frac{AR}{\phi R} + 0.02 - 1.9206\ln\frac{E_a}{R} - 0.12040\frac{E_a}{RT} \tag{8}$$

An alternative method for calculating activation energies according to best linear plot is also proposed by Horowitz and Metzger[5] that used an approximate integration of the rate equation. In this method, -ln(1-α) is plotted versus ϕ, resulting in a straight line whose slope is E_a/RT_s. For $n \neq 1$, the activation energy is calculated from the slope as follows:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right] = \frac{E_a\phi}{RTs} \tag{9}$$

As in the previous derivations, the Van Krevelen method[19] is based on approximate integration of the rate equation, resulting in a linear plot of data, from which activation energy and pre-exponential factor can be easily calculated using the following expression, for $n \neq 1$:

$$\log\left[\frac{-\ln(1-\alpha)^{1-n}}{1-n}\right] = \log\left[\frac{A}{\phi}\left(\frac{0.368}{T_s}\right)^{\frac{E_a}{RT_s}} \cdot \frac{1}{\left(\frac{E_a}{RT_s}+1\right)}\right] + (E_aRT_s+1)\log T \tag{10}$$

where: T = absolute temperature, R = gas constant, ϕ = heating rate, T_s = peak temperature of DTG curve.

Thermal data were processed in several steps. The values of α and $d\alpha/dT$ were calculated from each datum point using a computer program. Using the least squares method, an straight line, with the best fitting, was obtained and E_a and A were determined. The linear correlation coefficient (r) was considered as a quantitative value for determination of the most appropriate model.

RESULTS AND DISCUSSION

Thermogravimetric study

The thermogravimetric curves (Figure 1) show the thermal behavior of all samples analyzed, indicating that the thermal decomposition profile of the vegetable oils are similar. A plateau may be observed, indicating a thermal stability of the materials up to

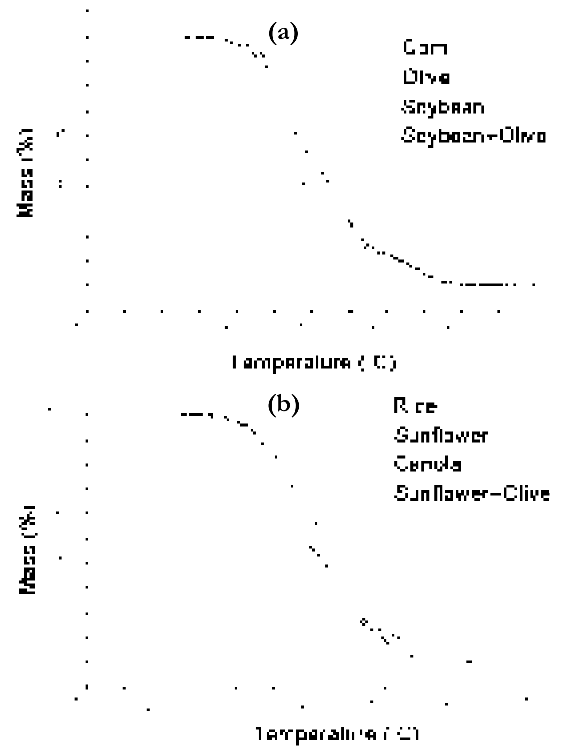

Figure 1: TG curves of the vegetable oils in air atmosphere

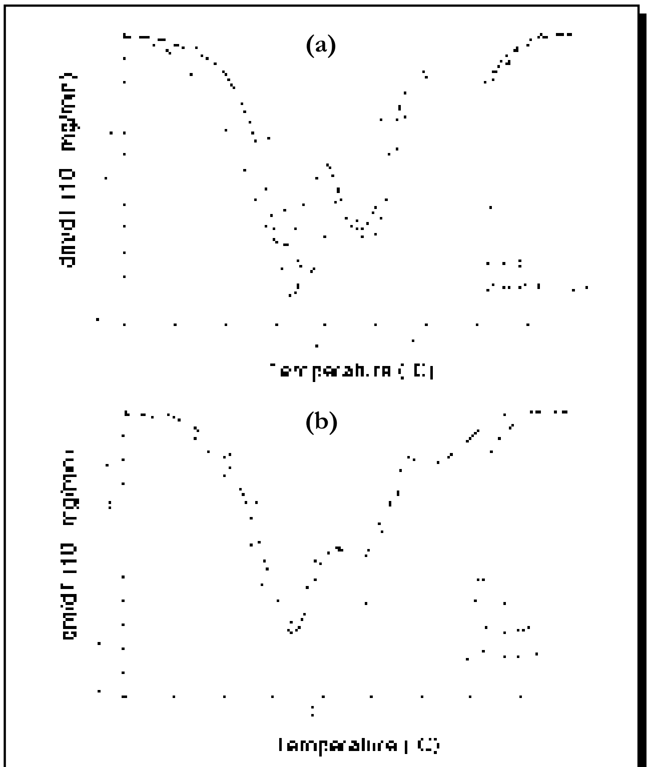

Figure 2: DTG curves of the vegetable oils

about 200°C and the end of the decomposition is at about 600°C.

A derivative thermogravimetric curve of the vegetable oils is showed in figure 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[15]. 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 (TABLE 2), indicating that the method is reliable. The parameters obtained from TG/DTG curves are listed in TABLE 2.

The beginning of oxidation in vegetable oils is characterized by oxygen absorption by fatty acid chain, leading to later formation of oxidation products known as peroxides. This behavior is usually identified by an increase in the initial sample mass. For vegetable commercial oils analyzed under air atmosphere, no mass gain was observed in TG/DTG curves, indicating that thermal decomposition was not related to oxygen absorption. On the other hand, release of volatile products was observed. This may be better shown when synthetic air atmosphere enriched with oxygen is used[3,16].

The first step of thermal decomposition of vegetable 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 + olive > sunflower + olive > rapeseed > olive. This ranking suggests that the corn oil is less susceptible to thermal deterioration that the other vegetable oils.

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 vegetable 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.

TABLE 2: Thermal decomposition data of vegetable oils obtained from TG/DTG curves

Vegetable oils	1st step			2nd step			3rd step		
	Temperature range (ºC)	Δm (%)	Ts (ºC)	Temperature range (ºC)	Δm (%)	Ts (ºC)	Temperature range (ºC)	Δm (%)	Ts (ºC)
Rice	221.5 - 391.6	52.3	342.5	391.6 - 482.9	34.1	425.4	482.9 - 584.1	13.3	520.9
Soybean	222.7 - 441.2	55.0	366.9	411.2 - 501.3	32.2	436.0	501.3 - 597.4	12.7	539.4
Corn	227.2 - 400.3	49.7	362.9	400.3 - 496.5	36.9	430.5	496.5 - 599.2	12.9	531.4
Sunflower	223.4 - 402.8	43.4	364.4	402.8 - 506.8	45.8	436.8	506.8 - 596.8	10.5	530.1
Rapeseed	209.6 - 409.7	56.9	356.8	409.7 - 497.9	30.3	436.8	497.9 - 595.5	12.5	534.1
Olive	196.0 - 420.7	70.2	352.7	420.7 - 495.7	17.8	428.7	495.7 - 606.0	11.8	525.4
Soybean+Olive	221.2 - 392.6	52.7	351.8	392.6 - 485.2	33.1	426.9	485.2 - 589.8	14.1	521.6
Sunflower+Olive	214.0 - 398.9	53.0	350.7	398.9 - 491.6	32.0	428.0	491.6 - 595.8	14.6	523.5

***Δm is the weight loss under heating and Ts is the peak temperature**

TABLE 3:Kinetic parameters obtained for the first step of thermal decomposition of vegetable oils

Kinetic model	Kinetic parameters	Vegetable Oils							
		Soybean	Corn	Rice	Olive	Rapeseed	Sunflower	Soybean+Olive	Sunflower+Olive
CR	n	1.06	1.08	0.96	0.92	1.02	0.96	1.05	0.96
	E_a [kJ mol^{-1}]	92.84	99.20	94.42	78.52	87.32	106.88	94.21	80.16
	A [s^{-1}]	$1.31x10^{5}$	$6.78x10^{5}$	$1.87x10^{5}$	$2.89x10^{2}$	$5.42x10^{7}$	$1.69x10^{7}$	$1.99x10^{5}$	$8.42x10^{3}$
	r	1	1	0.999	0.999	1	0.999	0.999	0.999
	sd	0.023	0.125	0.001	0.003	0.025	0.001	0.234	0.001
MD	n	1.07	1.11	0.97	0.99	1.06	0.94	1.02	0.95
	E_a [kJ mol^{-1}]	94.12	94.42	91.82	78.88	88.88	106.61	93.52	87.37
	A [s^{-1}]	$1.89x10^{5}$	$1.85x10^{6}$	$1.45x10^{5}$	$6.29x10^{2}$	$8.38x10^{4}$	$1.72x10^{7}$	$1.86x10^{5}$	$4.62x10^{4}$
	r	0.999	1	0.999	0.999	1	0.999	0.999	1
	sd	0.006	0.0023	0.234	0.005	0.456	0.001	0.001	0.002
HM	n	1.03	1.07	1.08	0.90	1.08	0.99	1.03	1.02
	E_a [kJ mol^{-1}]	104.80	93.32	107.38	88.97	80.71	108.93	92.79	92.72
	A [s^{-1}]	$1.75x10^{7}$	$1.16x10^{8}$	$2.46x10^{6}$	$5.59x10^{4}$	$8.06x10^{6}$	$8.49x10^{9}$	$3.02x10^{7}$	$7.85x10^{6}$
	r	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999
	sd	0.004	0.123	0.023	0.0033	0.025	0.123	0.001	0.089
VK	n	1.09	1.08	0.99	0.93	1.04	0.96	1.04	1.01
	E_a [kJ mol^{-1}]	102.66	98.85	101.71	88.64	93.53	90.28	92.78	97.63
	A [s^{-1}]	$3.89x10^{11}$	$3.69x10^{12}$	$3.16x10^{11}$	$1.84x10^{9}$	$6.49x10^{11}$	$1.02x10^{14}$	$4.46x10^{11}$	$1.36x10^{12}$
	r	0.996	0.997	0.994	1	1	0.994	0.996	1
	sd	0.001	0.789	0.456	0.123	0.453	0.001	0.001	0.032

Kinetic study

The non-isothermal kinetic study of weight loss during a thermal decomposition process of vegetable oil samples is extremely complex, because of the presence of many components and their consecutive reactions. Four different methods, all based on Arrhenius kinetic theory, were used for the kinetic analysis of the TG/DTG data: two based on integral methods and the other based on approximation methods. In all these methods, calculations were performed to estimate the kinetic parameters as activation energy, Arrhenius constant and reaction order. Computational programs were used and kinetic parameters were determined by regression analysis, from the slope and intercept of a straight line calculated by curve fitting.

The thermal decomposition kinetic study of the vegetable oils was realized using the best experimental conditions, according to the relation between thermogravimetric profile and heating rate, using decomposed fraction (α) from 0.10 to 0.90.

Evaluation of the kinetic parameters (n, E_a, A) in the three steps of the vegetable oil thermal decomposition was done using the integral methods proposed by Coats-Redfern (CR) and Madhusudanan (MD) and the approximation methods proposed by Horowitz-Metzger (HM) and Van Krevelen (VK). The results obtained using the four methods are listed in TABLES 3, 4 and 5 and indicate that the reaction of the first step was of 1st order, while the 2nd and 3rd steps presented a 2nd order reaction. The linear correlation coefficients of the eight samples were approximately the same for the CR, MD, HM and VK methods ($r \approx 1$), and the standard deviations (sd) were satisfactory (0.01-1), indicating a good precision and agreement among kinetic parameters. Frequency factor did not present this uniformity, being difficult to interpret A values qualitatively, as for most solid state reactions. In reaction kinetics, the frequency factor (A) indicates the collision fraction between fatty acid molecules that presents enough energy to lead to a decomposition reaction.

As mentioned before, the first step of thermal decomposition of the vegetable oils is the most important one in the study of thermal stability, due to the beginning of fatty acid decomposition and to the highest weight loss. The activation energies of the first step of thermal decomposition, calculated by the integral methods proposed by CR and MD, are in the range of 78-107 kJmol^{-1}, suggesting the following stability order: sunflower > corn > soybean > rice > soybean + olive > rapeseed > sunflower + olive > olive. For the HM and VK methods, these activation energies are in the range of 80-103 kJmol^{-1} respectively, not being too different from integral method results (TABLE 3). The result obtained is similar to the TG data, indicating that the thermal stability of the samples showed dependence on fatty acid composition, also being influenced by presence of natural and artificial antioxidants. Apparently, the

TABLE 4: Kinetic parameters obtained for the second step of thermal decomposition of vegetable oils

Kinetic model	Kinetic parameters	Vegetable Oils							
		Soybean	Corn	Rice	Olive	Rapeseed	Sunflower	Soybean+Olive	Sunflower+Olive
CR	n	2.07	2.04	1.86	1.89	2.11	2.08	2.11	2.06
	E_a [kJ mol^{-1}]	290.13	349.39	264.88	270.05	271.09	208.81	280.48	311.08
	A [s^{-1}]	6.71×10^{26}	7.24×10^{23}	2.50×10^{17}	5.53×10^{7}	5.84×10^{17}	2.69×10^{13}	3.34×10^{18}	6.46×10^{20}
	r	0.999	0.999	0.999	0.999	0.999	0.999	0.999	1
	sd	0.002	0.029	0.439	0.126	0.008	0.003	0.001	0.235
MD	n	2.04	2.10	1.87	1.91	2.05	2.03	2.04	2.08
	E_a [kJ mol^{-1}]	273.63	333.07	265.97	272.16	279.81	205.28	283.53	302.85
	A [s^{-1}]	3.76×10^{25}	4.09×10^{22}	3.19×10^{17}	8.45×10^{17}	2.90×10^{18}	1.47×10^{13}	6.03×10^{18}	1.55×10^{20}
	r	0.999	0.999	0.999	0.999	0.999	0.998	0.999	0.999
	sd	0.002	0.023	0.123	0.001	0.003	0.345	0.123	0.001
HM	n	2.03	2.05	2.14	2.11	2.07	2.12	2.03	2.12
	E_a [kJ mol^{-1}]	281.11	369.44	302.52	302.47	295.75	215.67	296.34	342.11
	A [s^{-1}]	5.54×10^{27}	2.56×10^{25}	2.25×10^{20}	1.69×10^{20}	6.23×10^{19}	2.66×10^{14}	3.78×10^{20}	1.77×10^{23}
	r	0.999	0.996	0.999	0.999	0.999	0.998	0.999	0.999
	sd	0.129	0.236	0.120	0.009	0.004	0.018	0.029	0.001
VK	n	2.06	2.12	1.95	1.97	2.10	2.06	2.01	2.07
	E_a [kJ mol^{-1}]	288.06	353.22	271.62	290.58	279.89	208.88	286.75	322.79
	A [s^{-1}]	2.32×10^{32}	7.13×10^{29}	4.11×10^{23}	1.00×10^{25}	1.43×10^{24}	1.21×10^{19}	5.09×10^{24}	2.52×10^{27}
	r	0.990	0.997	0.987	1	0.982	1	0.987	0.997
	sd	0.567	0.003	0.124	0.001	0.234	0.001	0.002	0.003

TABLE 5: Kinetic parameters obtained for the third step of thermal decomposition of vegetable oils

Kinetic model	Kinetic parameters	Vegetable Oils							
		Soybean	Corn	Rice	Olive	Rapeseed	Sunflower	Soybean+Olive	Sunflower+Olive
CR	N	1.91	1.93	1.87	1.96	2.13	1.98	1.95	1.98
	E_a [kJ mol^{-1}]	337.72	274.21	329.08	277.71	370.33	307.43	316.71	342.18
	A [s^{-1}]	1.31x10^{20}	3.80x10^{17}	1.58x10^{19}	1.02x10^{29}	2.19x10^{22}	4.50x10^{17}	3.59x10^{18}	7.26x10^{33}
	r	0.998	0.999	0.999	1	0.998	0.999	0.998	0.994
	sd	0.128	0.932	0.001	1	0.234	0.120	0.008	0.004
MD	n	1.90	1.98	1.96	1.87	2.12	1.88	1.97	1.98
	E_a [kJ/mol]	324.99	279.24	328.08	293.24	374.24	296.88	319.13	342.14
	A [s^{-1}]	1.78x10^{19}	8.91x10^{15}	1.41x10^{22}	1.12x10^{29}	4.25x10^{22}	8.92x10^{16}	5.51x10^{18}	7.47x10^{33}
	r	0.998	0.999	0.999	1	0.998	0.999	0.998	0.995
	sd	0.002	0.120	0.001	0.564	0.003	0.003	0.234	0.231
HM	n	1.97	1.92	1.91	2.02	2.03	2.05	1.95	1.99
	E_a [kJ mol^{-1}]	359.41	321.06	349.17	299.89	380.21	327.73	348.22	328.88
	A [s^{-1}]	3.35x10^{21}	5.37x10^{18}	2.03x10^{21}	3.22x10^{30}	1.99x10^{23}	1.00x10^{19}	3.62x10^{20}	8.16x10^{32}
	r	0.998	0.999	0.999	0.999	0.998	0.999	0.998	0.992
	sd	0.002	0.125	0.765	0.001	0.002	0.034	0.356	0.125
VK	n	1.91	1.94	1.94	1.92	2.03	1.96	1.91	1.99
	E_a [kJ mol^{-1}]	367.97	308.38	337.24	287.12	384.79	311.74	343.68	337.84
	A [s^{-1}]	8.77x10^{27}	5.22x10^{23}	3.58x10^{25}	2.64x10^{35}	1.31x10^{29}	5.44x10^{23}	1.51x10^{26}	7.87x10^{32}
	r	1	1	0.990	1	0.998	0.999	1	0.995
	sd	0.019	0.002	0.001	0.234	0.006	0.001	0.003	0.456

variation in the activation energies is related to an increase in monounsaturated fatty acids and a decrease in polyunsaturated fatty acids.

The second step of thermal decomposition of the vegetable oils (temperature between 380-480°C) corresponds to the thermal decomposition of the monounsaturated fatty acids, mainly the oleic acid. During this step, the double bindings are broken, leading to a saturation of the triglyceride molecules. The activation energy of the second step is slightly higher than the first step one. The values obtained, are 205-350 kJmol^{-1} for CR and MD methods and 208-370 kJmol^{-1} for HM and VK methods (TABLE 4).

The third step is at the temperature around 480 and 600°C. The high activation energy is related to the saturated fatty acid decomposition, which requires higher energy than the unsaturated fatty acids. Values obtained are in the range of 274-374 kJmol^{-1} for CR and MD methods and 287-385 kJmol^{-1} for HM and VK methods (TABLE 5). This result is in agreement with the research developed for peanut oil[6].

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 presences of the some artificial antioxidants justify the stability of soybean oil. The low concentration of linolenic acid and steroids besides the high content of tocopherols and oryzanol 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 vegetable oils was investigated by thermogravimetric curves and activation energy obtained from thermogravimetric data. 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 > rapeseed > olive. The activation energy indicated the following stability order: sunflower > corn > soybean > rice > soybean + olive > rapeseed > sunflower + olive > olive.

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