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Effect of alpha-tocopherol (vitamin E) on the thermal degradation behavior of edible oils

Multiple-heating rate kinetics

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Abstract Alpha-tocopherol (vitamin E) is the most widely used antioxidant for edible oils. The present investigation presents its effect on the thermal degradation behavior of edible oils (sunflower, soybean, and their blend) through the use of dynamic thermogravimetry. The study is based on the comparison of activation energies of decomposition process which were subsequently calculated using preferred and reliable multiple-heating rate methods viz. Kissinger, Friedman, Ozawa–Flynn–Wall, and Coats–Redfern (modified). It is concluded that the role of alpha-tocopherol as antioxidant at higher temperature is nearly accomplished.

Keywords Thermal degradation · Thermogravimetry (TG) · Kinetic · Activation energy · Edible oils and their blend · Alpha-tocopherol

Nomenclature

SF+	Sunflower oil with antioxidant
SF−	Sunflower oil without antioxidant
SB+	Soybean oil with antioxidant
SB−	Soybean oil without antioxidant
SF+/SB+	Blend oil with antioxidant
SF−/SB−	Blend oil without antioxidant
A	Pre-exponential factor or frequency factor (min^{-1})
E	Activation energy of degradation reaction (kJ mol^{-1})
R	Universal gas constant (J K^{-1} mol^{-1})
t	Time (s^{-1})
T	Absolute temperature (K)
T_m	Temperature value at the maxima of the first derivative mass loss curve

Greek

α	Degree of conversion or degree of decomposition or the fraction reacted
β	Linear heating rate (K min^{-1})

Introduction

India occupies an important place in the world in the production of major oilseeds [1]. About 60% of the oil extracted from these oilseeds contains 40% or more unsaturated fatty acids. Edible oil quality is defined mainly in terms of organoleptic parameters such as flavor, odor, and color. Vegetable oils and fats constitute a major component of human diet ranking third after cereals and animals products.

It is estimated that about 90% of vegetable oils are used for edible purposes, while the remaining part finds industrial applications. Edible oils processing presents challenges due to its high content of polyunsaturated fatty acids and bioactive compounds [2]. These compounds are prone to oxidation and degradation under the conditions used for conventional edible oil extraction and refining methods [3, 4].

Recently, the use of thermal analytical methods, thermogravimetry/derivative thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC), for oil characterization have greatly interested researchers [3–8]. TG has a main advantage in respect of the high reproducibility of results in dynamic mode that assures the calculation of precise kinetic parameters.

Further, the calculation of degradation activation energy using single heating rate methods is facing criticism due to

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problematic procedures and unreliable results [9, 10]. On the other hand, the use of multiple-heating rate methods, e.g., Kissinger [11], Friedman [12], Ozawa–Flynn–Wall (O-F-W) [13, 14], and Coats–Redfern (modified) [15, 16] methods, is preferred. There are many reports in literature regarding the kinetics of oil degradation [3, 4, 6, 7, 17–19], most of them represent kinetic data regarding single heating rate methods [3, 4, 17], very few deal with multiple heating rate kinetics using TG [18].

Alpha-tocopherol (vitamin E) is the most widely used antioxidant for edible oils [2–4]. Within the framework of this study addressing the kinetic treatment to thermal degradation process of edible oils, we initially investigated the breakdown behavior of alpha-tocopherol (vitamin E) contained in them using thermogravimetry. Nowadays, the use of blending of oils has become popular as it contains more nutritious value than sole oil and for the same reason both are produced on commercial scale.

The present work seeks to estimate the thermal stability and to determine the thermal degradation activation energy of edible oils (sole/combination and with/without antioxidant) using non-isothermal TG/DTG.

Experimental

Raw material

Edible oil samples (sunflower and soybean) were extracted from seeds and vitamin E (Sigma Aldrich) was added to them as antioxidant (0.04 g l^{-1}). These oils were stored in small airtight and dark colored plastic sample tubes until they were needed for thermal analysis. Also, the blend of the oils (sunflower and soybean) was prepared by proper mixing of edible oils in the ratio 1:1.

Thermal analysis

The samples were heated from ambient temperature to 923 K under flowing air atmosphere at three different heating rates 5, 10, and 20 K min^{-1} using Perkin Elmer, Diamond Thermogravimetric/Differential Thermal Analyzer. The instrument was calibrated before recording thermograms. Dried alumina powder (Al_2O_3) was employed as reference material using ceramic sample holder for taking thermograms. In order to ensure the uniformity of temperature of the sample and good reproducibility, small amount (2–6 mg) were taken. The apparatus detects the mass loss with a resolution of 0.2 μg as a function of temperature. To verify the reproducibility of obtained mass loss curve, two sample runs were performed under the same experimental conditions for each kind of oil at all selected heating rates. Activation energy with respective error, standard deviation (SD), and correlation coefficient (*R*) were calculated with a specially designed program in MS-Excel and origin 6.1 which takes specific TG and DTG data from the Pyris manager software.

Results and discussion

Thermal studies based on TG data

TG data for all the samples were obtained in the standard form of % mass loss as a function of temperature at three heating rates (5, 10, and 20 K min^{-1}), as shown in Figs. 1, 2, and 3. As expected, the shapes of TG curves are quite similar shifting toward higher temperatures at higher heating rates. All the thermograms showed a slight increase in the mass in the temperature range 423–473 K. This might be due to oxidation of edible vegetable oil on absorbing oxygen from the purge gas (air).The start of the oxidation of edible oils is characterized during oxygen absorption by fatty acids, leading to the formation of oxidation products such as peroxide [20]. Santos and co-authors [3, 4, 17] also reported the similar behavior which tends to prove the validity of our findings as well. Thermal degradation of all oils proceeds via three degradation steps

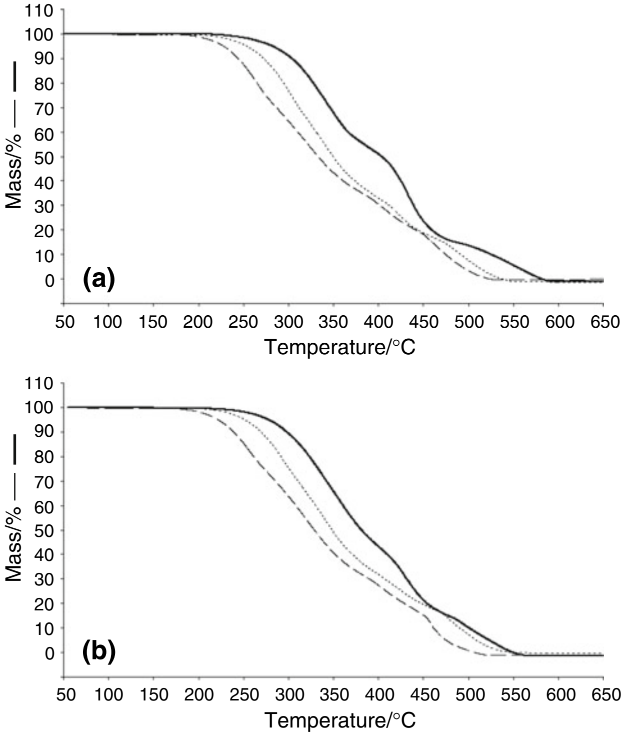

Fig. 1 TG curves of **a** sunflower with antioxidant and **b** sunflower without antioxidant at heating rates of 5 K min^{-1} (_ _ _ _ _), 10 K min^{-1} (…….) and 20 K min^{-1} (_______) in dynamic air atmosphere

in the temperature range of 433–863 K involving polyunsaturated, monounsaturated, and saturated fatty acids decomposition [3, 4], in the respective order, with no residue remaining at 923 K. The initiation temperature, final temperature, and the temperature at which maximum mass loss occurred during the three stages for all the samples are summarized in Table 1.

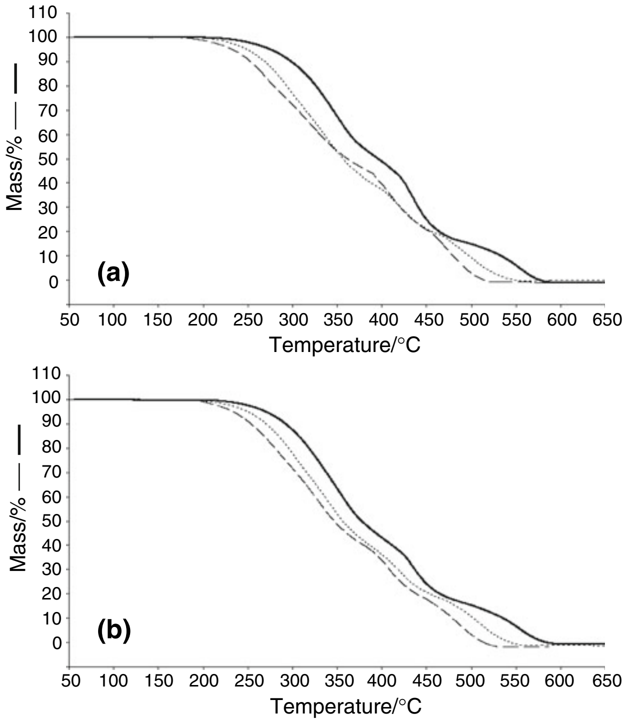

Fig. 2 TG curves of **a** soybean with antioxidant and **b** soybean without antioxidant at heating rates of 5 K min^{-1} (_ _ _ _ _), 10 K min^{-1} (…….) and 20 K min^{-1} (_______) in dynamic air atmosphere

In the TG curves of oil samples, from the thermal stability point of view the first step is the most important, relating to start of unsaturated fatty acid degradation [3, 4]. It can be seen from Fig. 4 and Table 1 that alpha-tocopherol (vitamin E) is stable up to a temperature of about 503 K, thereafter it undergoes a sharp mass loss up to 723 K, losing about 95% of its original mass. As mentioned above, the average initial thermal degradation temperature of edible oil is around 433 K, while on the other hand it is about 503 K for alpha-tocopherol. So, it can be concluded that alpha-tocopherol may act as a thermal stabilizer. Further, alpha-tocopherol decomposes almost completely at about 773 K, suggesting that its role is over after this temperature. This statement is true as TG curves of soybean oil with/without alpha-tocopherol are overlapping each other above the temperature of about 773 K (Fig. 5).

Now, according to the initial degradation temperature obtained from thermograms, the following stability order is proposed: sunflower + soybean (blend) > sunflower > soybean. This order suggests that the blend oil is less susceptible to thermal deterioration than the single edible oils.

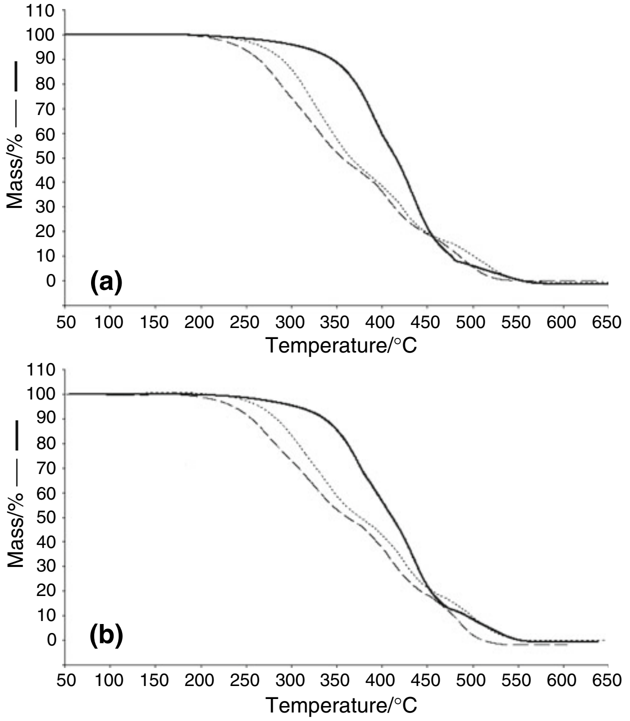

Fig. 3 TG curves of **a** blend with antioxidant and **b** blend without antioxidant at heating rates of 5 K min^{-1} (_ _ _ _ _), 10 K min^{-1} (…….) and 20 K min^{-1} (_______) in dynamic air atmosphere

Kinetic study

The TG curves of oil samples showed three important areas of mass loss. Because of the three-step nature of thermal decomposition reactions, it was necessary to determine and use different kinetic methods to describe the thermal degradation over the entire temperature range. Therefore, the kinetic parameters of oil samples were established for the first, second, and third stages, separately.

The Friedman method is the iso-conversional method, which directly leads to $(-E/R)$ for a given value of α by plotting $\ln(\beta(\mathrm{d}\alpha/\mathrm{d}T))$ against $1/T$. The O-F-W method is also iso-conversional method but has integral equation unlike Friedman which is a differential method, which leads to $-(0.4567\ E/R)$ from the slope of line determined by plotting $\log \beta$ against $1/T$ at any degree of conversion. The modified Coats–Redfern method is a multiple-heating rate application of the Coats–Redfern equation. Plotting the left-hand side for each heating rate versus $1/T$ at that heating rate gives a series of straight lines having slope $(-E/R)$. In the Kissinger method, the activation energy, E, can be obtained from a plot of $\ln(\beta/T_{\mathrm{m}}^2)$ against $1/T_{\mathrm{m}}$ for

Table 1 TG and DTG data of edible oils at heating rate of 10 K min^{-1}

Oil	Thermal degradation stages	Initiation temperature, T_i/K	Maximum mass loss temperature, T_m/K	Final temperature, T_f/K	Mass loss/%
SF+	I	441	573	672	66.5
	II	672	691	734	16.3
	III	734	768	849	18.1
SF−	I	440	561	667	66.5
	II	667	699	731	15.1
	III	731	747	840	18.4
SB+	I	426	618	664	60.5
	II	664	694	735	20.3
	III	735	781	850	19.2
SB−	I	434	616	673	63.5
	II	673	687	735	17.5
	III	735	770	857	19.8
SF+/SB+	I	485	584	655	53.9
	II	655	696	744	29.6
	III	744	783	861	16.6
SF−/SB−	I	453	617	651	51.2
	II	651	697	740	31.8
	III	740	776	846	17.7
Alpha-tocopherol	I	507	648	723	95.2
	II	723	773	818	4.8
	III	–	–	–	–

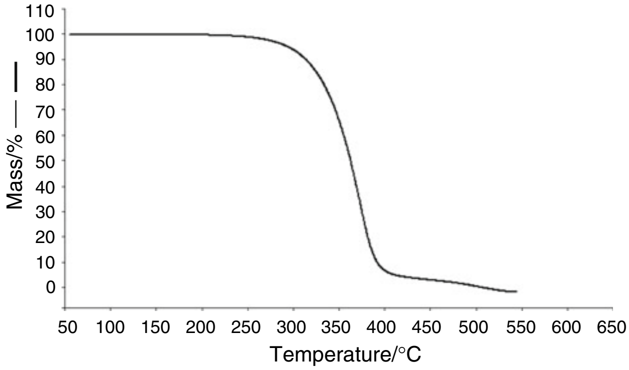

Fig. 4 TG curve of alpha-tocopherol at 10 K min^{-1}

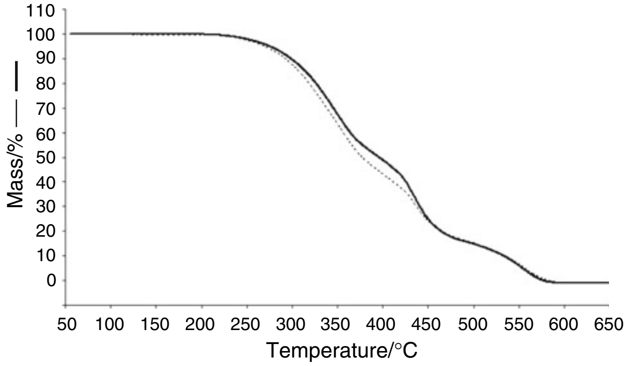

Fig. 5 TG of soybean with antioxidant (______) and soybean without antioxidant (……..) at a heating rate of 20 K min^{-1}

a particular stage of decomposition since the slope of such line is given by ($-E/R$).

The plots of iso-conversional Friedman, O-F-W, and modified Coats–Redfern methods show a general trend of activation energy. As an example, the Friedman plot for without antioxidant is shown in Fig. 6, while Figs. 7 and 8 show the specific results of application of O-F-W and modified Coats–Redfern methods using sunflower and blend of sunflower/soybean as examples, respectively. It can be seen from these figures that the fitted lines are almost parallel, which indicates approximate activation energies at different conversions and consequently, implying the possibility of single reaction mechanism. Figure 9 shows the linear plots of $\ln(\beta/T_{\mathrm{m}}^{2})$ against $1/T_{\mathrm{m}}$ for sunflower oil with antioxidant from Kissinger method.

The evaluated kinetic parameters obtained for all the three steps in thermal degradation of oils are summarized in Table 2.

It can be noticed that the values by Kissinger's method are lower than the ones by iso-conversional methods [21–23]. However, the results calculated by these methods

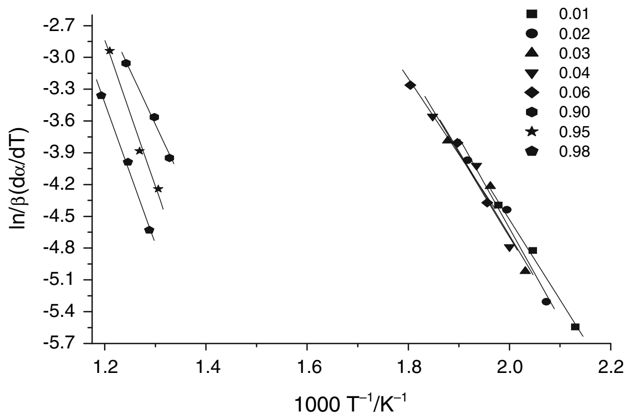

Fig. 6 Plot of Friedman method for degradation activation energy of soybean oil without antioxidants at varying degree of conversion

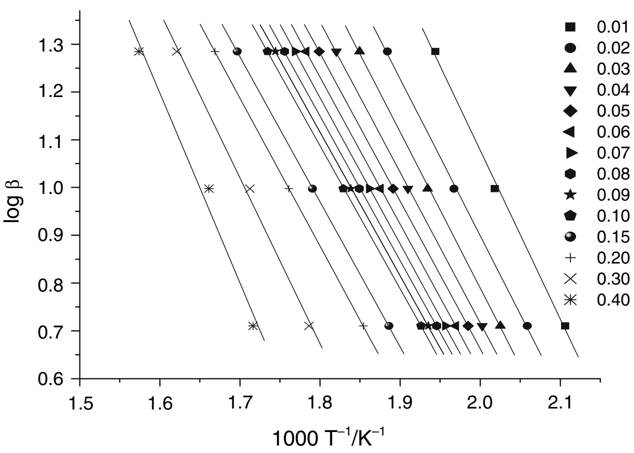

Fig. 7 Plot of O-F-W method for degradation activation energy of sunflower oil with antioxidants at varying degree of conversion

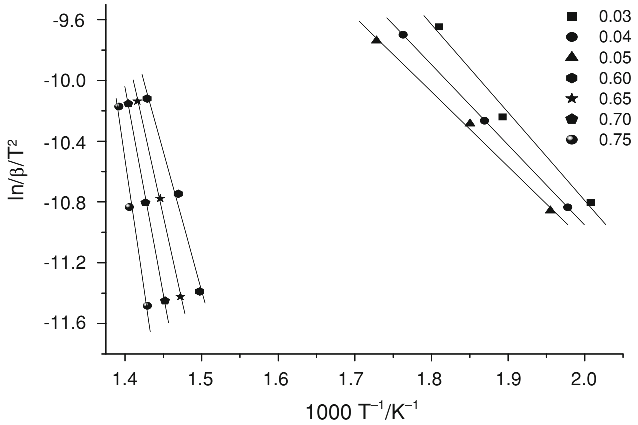

Fig. 8 Plot of Coats–Redfren method for degradation activation energy of blend oil with antioxidant at varying degree of conversion

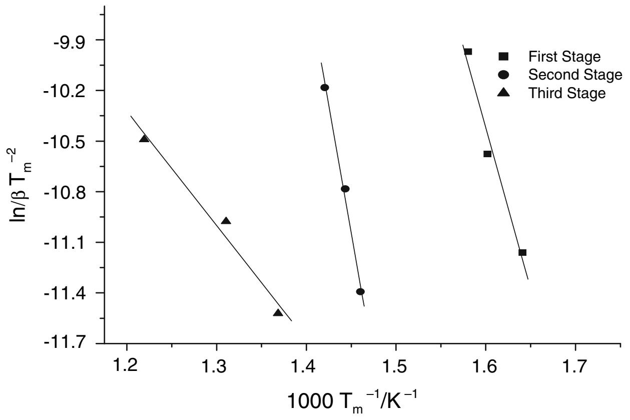

Fig. 9 Plot of Kissinger method for degradation activation energy of sunflower oil with antioxidants at varying degree of conversion

are showing a general trend of activation energy in going from virgin oil to oil containing alpha-tocopherol, sole oil to combination of oils.

The values of activation energy by all the methods are comparatively larger for the oils containing alpha-tocopherol. For example, for the Coats–Redfern (modified) and O-F-W methods, the first stage activation energies are 51.8 ± 3.0 (52.5 ± 0.8), 66.0 ± 10.0 (91.7 ± 5.4), 40.7 ± 6.3 (42.2 ± 5.7) and 55.4 ± 3.6 (58.3 ± 0.7), 71.3 ± 9.4 (98.3 ± 5.1), 49.2 ± 7.6 (50.4 ± 6.6) for SF−(SF+), SB−(SB+) and SF−/SB−(SF+/SB+), respectively. This suggests that oil containing alpha-tocopherol has higher thermal stability than that of the virgin oil.

In addition, the value of second-stage activation energy is higher than that of first stage and third stage. However, the third degradation stage has some peculiar observation. In this stage the oils with/without antioxidant have same activation energies. This is obviously due to the reason that the antioxidant that has to thermally stabilize the oil is decomposed at the end of second step of degradation.

Results were also evaluated in terms of improvement in the performance of edible oils by sole or combination treatment. In case of blends of soybean and sunflower, it is observed that the decomposition temperatures are slightly on the higher side than the sole oils (Table 1). This fact is also supported by the observation that the activation energies of first and second stage of blends were higher than the sole oils. For example, for the Friedman method, the second stage activation energies are 199.3 ± 21.4, 191.4 ± 21.4 and 261.5 ± 28.2 kJ mol^{-1} for SF+, SB+ and SF+/SB+, respectively. The values of activation energy obtained from Coats–Redfern (modified) method are in good agreement with those obtained using O-F-W and Friedman methods; however, they are smaller than the Coats–Redfern method (single heating rate) as given in literature [3, 4, 17].

Table 2 Comparison of kinetic parameters obtained from the present study with the literature values

Oil	Stage	Friedman		O-F-W		Coats–Redfern modified		Kissinger		Literature value [3, 4, 17]
		E/kJ mol^{-1}	*R* (SD)	*E*/kJ mol^{-1}	*R* (SD)	*E*/kJ mol^{-1}	*R* (SD)	*E*/kJ mol^{-1}	*R* (SD)	*E*/kJ mol^{-1}
SF+	I	55.1 ± 1.3	0.9979 (0.0333)	58.3 ± 0.7	0.9996 (0.0080)	52.5 ± 0.8	0.9993 (.01168)	47.9 ± 8.3	0.9848 (0.1426)	92.7
	II	199.3 ± 21.4	0.9940 (0.1673)	187.4 ± 29.8	0.9785 (0.1241)	190.7 ± 22.1	0.9822 (0.1366)	251.3 ± 21.3	0.9964 (0.0795)	288.3
	III	116.4 ± 20.9	0.9707 (0.2158)	121.5 ± 2.2	0.9849 (0.0736)	115.4 ± 23.6	0.9815 (0.1702)	56.2 ± 8.3	0.9870 (0.1284)	355.9
SF−	I	52.7 ± 2.5	0.9988 (0.0411)	55.4 ± 3.6	0.9966 (0.0283)	51.8 ± 3.0	0.9974 (0.08852)	34.2 ± 1.33	0.9992 (0.0301)	86.8
	II	174.0 ± 9.6	0.9897 (0.1622)	156.9 ± 10.0	0.9946 (0.0386)	157.4 ± 9.1	0.9832 (0.1338)	–	–	208.1
	III	115.5 ± 27.6	0.9794 (0.2067)	118.0 ± 23.1	0.9680 (0.1062)	–	–	179.0 ± 23.2	0.9916 (0.1182)	307.4
SB+	I	96.5 ± 7.4	0.9949 (0.0783)	98.3 ± 5.1	0.9989 (0.0209)	91.7 ± 5.4	0.9972 (0.0674)	193.9 ± 8.0	0.9992 (0.0362)	92.8
	II	191.4 ± 21.4	0.9878 (0.1035)	203.4 ± 27.8	0.9932 (0.0504)	202.1 ± 22.1	0.9921 (0.1285)	175.2 ± 0.8	0.9961 (0.0038)	290.1
	III	104.6 ± 25.9	0.9989 (0.0404)	115.6 ± 2.2	0.9964 (0.0332)	107.1 ± 23.6	0.9953 (0.723)	85.2 ± 8.3	0.9990 (0.0462)	337.4
SB−	I	65.5 ± 16.5	0.9745 (0.2077)	71.3 ± 9.4	0.9899 (0.0563)	66.0 ± 10.0	0.9801 (0.1265)	134.7 ± 4.1	0.9939 (0.1003)	–
	II	172.8 ± 17.9	0.9536 (0.3192)	196.0 ± 1.1	0.9279 (0.1872)	–	–	155.6 ± 21.2	0.9899 (0.1293)	–
	III	103.1 ± 10.7	0.9944 (0.0853)	113.4 ± 11.7	0.9940 (0.0435)	109.2 ± 10.1	0.9882 (0.1253)	81.4 ± 24.0	0.9583 (0.2438)	–
SF+/SB+	I	62.3 ± 13.1	0.9569 (0.2364)	50.4 ± 6.6	0.9469 (0.2665)	42.2 ± 5.7	0.9754 (0.1656)	29.5 ± 7.8	0.9659 (0.1922)	–
	II	261.5 ± 28.2	0.991 (0.2002)	230.8 ± 39.5	0.9786 (0.0858)	201.8 ± 50.1	0.9732 (0.2086)	166.6 ± 4.5	0.9748 (0.2049)	–
	III	–	–	–	–	–	–	133.9 ± 3.2	0.9802 (0.1769)	–
SF−/SB−	I	54.0 ± 13.7	0.9787 (0.2252)	49.2 ± 7.6	0.9898 (0.0606)	40.7 ± 6.3	0.9872 (0.1258)	105.9 ± 23.5	0.9762 (0.1941)	–
	II	238.9 ± 13.0	0.9941 (0.1582)	178.6 ± 16.1	0.9889 (0.05152)	189.2 ± 11.1	0.9962 (0.0632)	44.4 ± 8.5	0.9225 (0.3062)	–
	III	–	–	–	–	–	–	–	–	–

Similar results are obtained from TG data discussed in previous section, hence showing a good correlation between TG and kinetics studies. The decomposition activation energy measured in this study can help one to understand the thermal decomposition stability of alpha-tocopherol used in edible oil industries.

Conclusions

Comparison between the results obtained in the present study with those reported in literature has been made. According to the initiation temperature of degradation in thermogravimetric curves, the following thermal stability sequence was observed: sunflower + soybean > sunflower > soybean. Edible oils with antioxidant have higher decomposition temperatures than those without antioxidant. Similar trends have been seen in respect of activation energies for the different degradation stages. However, in case of the third degradation stage, a peculiar behavior has been observed. In this stage the oils with/without antioxidant have same activation energies. Consequently, it can be concluded that the role of antioxidant at higher temperatures is nearly accomplished. The activation energy of second degradation stage is higher than the first degradation stage. This is incomplete agreement with the reported literature values. Besides, our results are based on multiple heating rates and therefore they are thought to be more accurate and reliable.

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