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THERMOANALYTICAL, KINETIC AND RHEOLOGICAL PARAMETERS OF COMMERCIAL EDIBLE VEGETABLE OILS

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Abstract

Thermoanalytical, kinetic and rheological parameters of commercial edible oils were evaluated. The thermal decomposition of the oils occurred in three steps, due to polyunsaturated, monounsaturated and saturated fatty acids decomposition, respectively. According to the temperature of the beginning of the decomposition, the following stability order was observed: corn (A)>corn>sunflower (A)>rice>soybean>rapeseed (A)>olive>rapeseed>sunflower (A – artificial antioxidants). Kinetic parameters were obtained using Coats–Redfern and Madhusudanan methods and presented good correlation. According to the activation energy of the first thermal decomposition event, obtained of Coats–Redfern' method, the following stability order is proposed: sunflower>corn>rice>soybean>rapeseed>olive. In relation to rheological properties, a Newtonian behavior was observed and no degradation occurred in the temperature range studied.

Keywords: edible oils, kinetic, rheology, thermal decomposition

Introduction

Commercial edible oils, very appreciated on cooking, have required the development of new analytical methods to evaluate its processing and storing conditions [1]. When manipulated in a non-adequate way, these products get deteriorated, oxidation being the main decomposition reaction. Oil oxidation occurs through a free radical mechanism, due to hydroperoxides and peroxides decomposition in low molecular mass aldehydes and acids [2].

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Many methodologies have been proposed to evaluate commercial oil quality [1]. The majority of these methods submit a sample to conditions that accelerate oxidation normal process. Degradation is evaluated by mass gain and organoleptic measurements. Peroxides and other oxidation products may be determined by chemical or spectral analysis. Actually, thermoanalytical methods as differential scanning calorimetry (DSC) and thermogravimetry (TG) have received considerable attention [3–10]. These methods are advantageous in relation to the conventional ones because they present a higher precision and sensitivity as well as use smaller amount of sample and the results are obtained faster [11, 12]. Besides these methods, rheological properties study is a simple tool used as a way of determining the solution, suspension and mixture behavior [13].

In this work, thermoanalytical (specific heat, stability decomposition temperature and decomposition enthalpy) and kinetic (activation energy, frequency factor and reaction order) of commercial edible oils were determined by using DSC and TG. Rheological properties were evaluated during heating and cooling of the oils.

Experimental

The commercial edible oils used in this work, were: soybean, sunflower, olive, rapeseed, corn and rice. All oils are produced by Brazilian industries. The compositions are presented in Table 1.

The edible oils were characterized by thermal analysis (TG/DTG and DSC) and rheological measurements.

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 20ºC min^{-1}, sample mass of 8.0±0.5 mg, in the temperature range of 25–800ºC. From this data, a kinetic study was done, using equations described in [14], solved using integral methods proposed by Coats–Redfern [15] and Madhusudanan [16].

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

Vegetable oils	Fatty acids			Artificial antioxidants
	monounsaturated	polyunsatured	saturated	
Olive	71.3	12.7	16.0	–
Rapeseed (A)	65.2	29.3	5.5	citric acid/E vitamin
Rapeseed	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	–

(A) presence of artificial antioxidants

DSC curves were obtained in a DSC (DSC-50, Shimadzu), in nitrogen atmosphere (50 mL min^{-1}), using aluminum crucibles, heating rates: 5, 10 and 20ºC min^{-1}, sample mass of 8.0±0.5 mg, in a temperature range of 25–500ºC. From this data, apparent specific heat capacity of edible vegetable oils was determined.

Rheological measurements were realized in a rheometer (LV-DVII, Brookfield), in a temperature range of 10–80ºC. Measurements were carried out in many shear rates, during heating and cooling of the vegetable oils.

Results and discussion

Thermogravimetric analysis

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 600ºC, with no residues after thermal treatment up to 800ºC.

According to TG/DTG data was verified that the mass loss values corresponded, for the majority of samples, the percentage of fatty acid described in Table 1 [17, 18]. In the thermal decomposition events, it was observed that the first event (200–380ºC) is due to polyunsaturated fatty acid decomposition – this is the most important step to determine the edible oils thermal stability order. According to the temperature of the

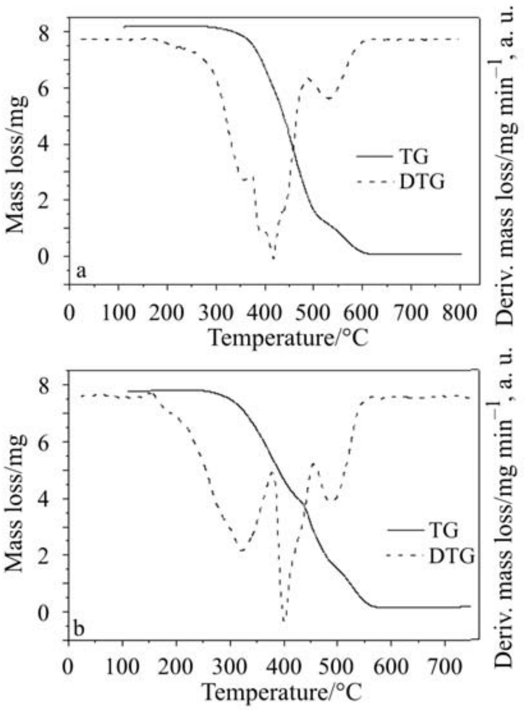

Fig. 1 TG/DTG curves of sunflower oil a – with antioxidant b – without antioxidant

beginning of the thermal decomposition, the following stability order is established: corn (A)>corn>sunflower (A)>rice>soybean>rapeseed (A)>olive>rapeseed>sunflower. It may be seen that thermal stability of edible vegetable oils depends on the presence of artificial antioxidants.

During heating, triglycerides, that constitute 96–98% of edible oils, produce volatile compounds that are constantly removed by the vapor formed during heating. These products are mainly formed by thermal reactions of the unsaturated fatty acids [1].

The beginning of the oxidation of edible vegetable oils is characterized by oxygen absorption by fatty acid chain, leading to the formation of oxidation products as peroxides [1]. This behavior is generally identified by an increase in the sample initial mass. For sunflower oil samples analyzed under air atmosphere, a small mass gain was observed in DTG curve, indicating that thermal decomposition process involved oxygen absorption and volatile liberation. For sunflower oils containing antioxidants no mass gain is observed and reaction occurs only with volatile liberation.

The second thermal decomposition event (380–480ºC) is due to monounsaturated fatty acids decomposition. During this reaction, double bonds are broken leading to saturation in triglyceride molecules that constitute edible oils. The third thermal decomposition event, in the temperature range of 480–600ºC, is due to saturated fatty acids thermal decomposition.

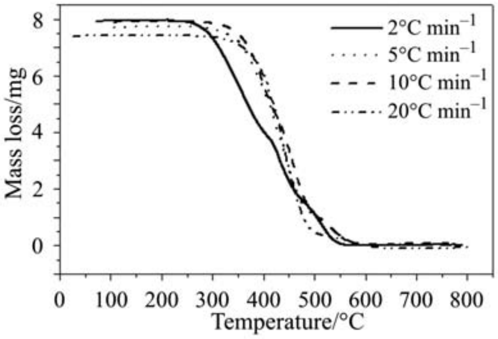

Fig. 2 TG curves of soybean oil at different heating rates

To verify the dependence of the thermogravimetric curve profile with experimental conditions, different heating rates were used (2, 5, 10 and 20ºC min^{-1}), as shown in Fig. 2. It may be observed that the increase in heating rate leads to a moving in the initial decomposition temperature. In the analysis done with the rates of 2, 5 and 10ºC min^{-1}, a thermal decomposition process occurred in three events. On the other hand, when a heating rate of 20ºC min^{-1} was used, only two events were observed. This is probably due to a superposition of the events, due to the high heating rate.

DSC analysis

DSC curves of the edible vegetable oils presented similar profiles, with endothermic and exothermic transitions, as shown in Fig. 3.

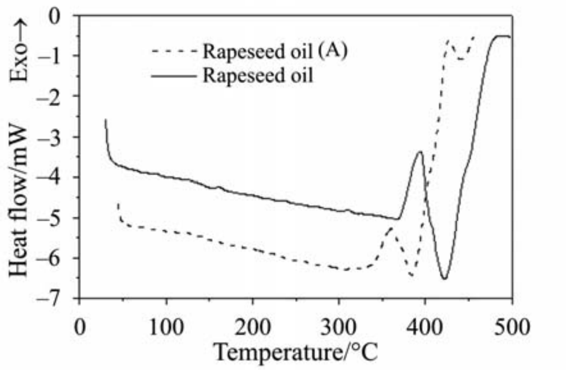

Fig. 3 DSC curves of rapeseed oil with and without artificial antioxidant

Exothermic transitions are probably due to polymerization of fatty acids that constitute edible oils. Endothermic transitions are due to thermal decomposition of saturated and unsaturated fatty acids. These results are in agreement with TG.

In the study of the variation of calorimetric profile of sunflower oil as a function of heating rate, it may be observed that the higher the heating rate, the more dislocated the temperature of thermal transition. The increase in heating rate leads to an enlargement and consequently increase of the area of the peaks related to the thermal decomposition events.

The enthalpies calculated from DSC curves are related to polymerization and decomposition molar enthalpies. Results indicate that these enthalpies are right related to fatty acids composition of the edible vegetable oils.

Heat capacity

Curves of standard apparent specific heat capacities in liquid phase of the corn oils are presented in Fig. 4.

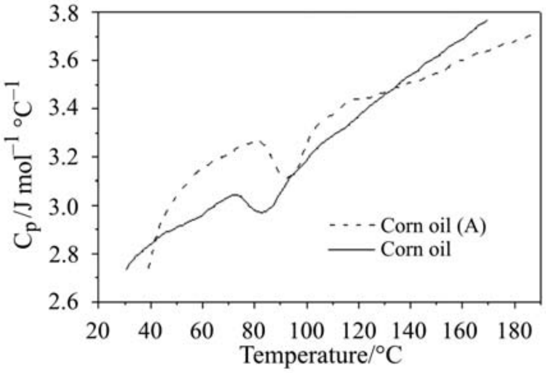

Fig. 4 C_p curves of corn oils

Apparent specific heat capacities of commercial edible oils at different temperatures are presented in Table 2.

Table 2 Apparent specific heat capacities of edible vegetable oils, according to DSC

Temperature/°C	Apparent specific heat capacities/J mol^{-1} °C^{-1}					
	olive	soybean	corn	rice	sunflower	rapeseed
40	2.721	2.269	2.039	1.860	1.833	1.833
60	2.890	2.470	2.250	2.032	2.030	2.008
80	3.052	2.531	2.319	2.089	2.076	2.059
100	3.092	2.547	2.346	2.109	2.070	2.077
120	3.293	2.646	2.462	2.201	2.152	2.165
130	3.337	2.669	2.490	2.218	2.164	2.187
150	3.590	2.728	2.561	2.260	2.197	2.240
170	3.778	2.784	2.640	2.310	2.236	2.284
190	3.910	2.780	2.655	2.347	2.241	2.320

Specific heat capacities values did not vary very much for the oil samples analyzed. Calculated C_p values are in accordance with values related in literature for other vegetable oils [20].

Kinetic parameters

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 [15, 16], 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 Tables 3 and 4.

According to the activation energy of the first thermal decomposition event, obtained of Coats–Redfern' method, the following stability order is proposed: sunflower>corn>rice>soybean>rapeseed>olive.

Rheological behavior

Rheological behavior of the edible vegetable oils may be observed in Fig. 5, that presents a linear relation between shear stress and shear rate.

As it may be observed in Fig. 5, the edible vegetable oils analyzed presented Newtonian behavior [19, 20]. As temperature increases, a decrease in viscosity is being observed. This rheological behavior is similar to the results observed by Geller [21] to some vegetable oils and triglycerides in its pure state. Figure 6 shows the viscosity (η) variation as a function of temperature to rice oil. It may be observed that viscosity val-

Table 3 Kinetic parameters of the thermal decomposition events of edible vegetable oils, calculated by TG, using Coats–Redfern equation

Events	Kinetic parameters	Edible oils					
		soybean	corn	rice	olive	rapeseed	sunflower
1	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
	A/s^{-1}	$1.3\cdot10^{5}$	$6.8\cdot10^{5}$	$1.8\cdot10^{5}$	$2.9\cdot10^{2}$	$5.4\cdot10^{7}$	$1.7\cdot10^{7}$
	r	1	1	0.999	0.999	1	0.999
	sd	0.023	0.125	0.001	0.003	0.025	0.001
2	n	2.07	2.04	1.86	1.89	2.11	2.08
	E_a/kJ mol^{-1}	290.13	349.39	264.88	270.05	271.09	208.81
	A/s^{-1}	$6.7\cdot10^{26}$	$7.2\cdot10^{23}$	$2.5\cdot10^{17}$	$5.5\cdot10^{7}$	$5.8\cdot10^{17}$	$2.7\cdot10^{13}$
	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
3	n	1.91	1.93	1.87	1.96	2.13	1.98
	E_a/kJ mol^{-1}	337.720	274.21	329.08	277.71	370.33	307.43
	A/s^{-1}	$1.3\cdot10^{20}$	$3.8\cdot10^{17}$	$1.6\cdot10^{19}$	$1.0\cdot10^{29}$	$2.2\cdot10^{22}$	$4.5\cdot10^{17}$
	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 4 Kinetic parameters of the thermal decomposition events of edible vegetable oils, calculated by TG, using Madhusudanan equation

Events	Kinetic parameters	Edible oils					
		soybean	corn	rice	olive	rapeseed	sunflower
1	n	1.07	1.11	0.97	0.99	1.06	0.94
	E_a/kJ mol^{-1}	94.12	94.42	91.82	78.88	88.88	106.61
	A/s^{-1}	$1.9\cdot10^{5}$	$1.9\cdot10^{6}$	$1.5\cdot10^{5}$	$6.29\cdot10^{2}$	$8.4\cdot10^{4}$	$1.7\cdot10^{7}$
	r	0.999	1	0.999	0.999	1	0.999
	sd	0.006	0.0023	0.234	0.005	0.456	0.001
2	n	2.04	2.10	1.87	1.91	2.05	2.03
	E_a/kJ mol^{-1}	273.63	333.07	265.97	272.16	279.81	205.28
	A/s^{-1}	$3.7\cdot10^{25}$	$4.1\cdot10^{22}$	$3.2\cdot10^{17}$	$8.45\cdot10^{17}$	$2.9\cdot10^{18}$	$1.5\cdot10^{13}$
	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
3	n	1.90	1.98	1.96	1.87	2.12	1.88
	E_a/kJ mol^{-1}	324.99	279.24	328.08	293.24	374.24	296.88
	A/s^{-1}	$1.8\cdot10^{19}$	$8.9\cdot10^{15}$	$1.4\cdot10^{22}$	$1.12\cdot10^{29}$	$4.3\cdot10^{22}$	$8.9\cdot10^{16}$
	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

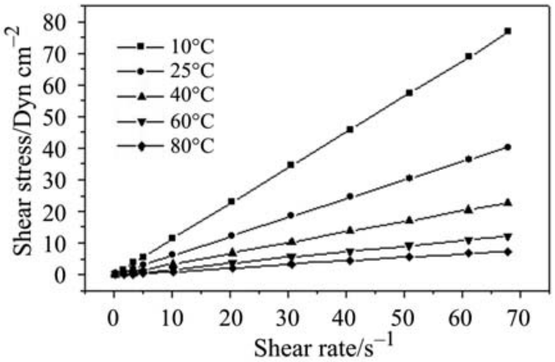

Fig. 5 Relation between shear stress and shear rate, during rapeseed oil heating

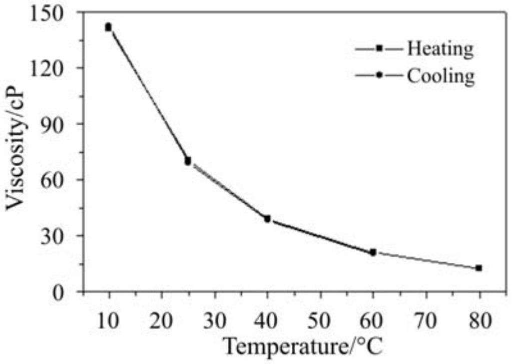

Fig. 6 Viscosity variation of rice oil according to temperature

ues during heating and cooling are similar, indicating that edible vegetable oils do not degrade in the temperature range studied.

Generally, the liquid viscosity depends on its temperature and composition. In some cases, it may also depend on shear rate, shear time, as well as on previous history of samples [13]. In relation to temperature, viscosity of edible vegetable oils decrease as temperature increases. This is due to the higher thermal movement among molecules, besides the reduction of intermolecular bond force, making flux between them easier and reducing viscosity. This behavior was also observed by Kahn and Forster [19, 20].

Conclusions

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 by conventional techniques and the presence of artificial antioxidant may also be detected. Rheological properties of vegetable edible oils are similar in the temperature range 10–80ºC, during heating and cooling, indicating that no thermal degradation occurred in this temperature range.

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