

## KINETIC STUDY OF THERMAL BREAKDOWN OF TRIGLYCERIDES CONTAINED IN EXTRA-VIRGIN OLIVE OIL

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Thermal decomposition of extra-virgin olive oil (EVOO) was investigated by thermogravimetry (TG) and derivative thermogravimetry (DTG) up to 550°C at different heating rates (from 5 to 12.5°C min<sup>-1</sup>). The thermal degradation study of four unsaturated or saturated esterified C18 fatty acids with glycerol (i.e., glyceryl-tristearate (C18:0), -trioleate (C18:1), -trilinoleate (C18:2) and -trilinolenate (C18:3)) was also carried out under the same experimental conditions.

A deconvolution procedure applied only to the first two overlapping steps of EVOO and C18:1 enabled the activation energy of decomposition to be determined both by the Kissinger and the Ozawa–Flynn–Wall isoconversional method for the two deconvoluted steps of EVOO and C18:1, as well as for the only single step of the other three C18 triglycerides. Practically constant activation energy for the first deconvoluted step of EVOO and C18:1 and for the single step of C18:0 was found in good agreement with the results obtained with the Kissinger method, while a similar increasing trend was observed for the second decomposition step of EVOO and C18:1 and for the single steps of C18:2 and C18:3 triglycerides.

**Keywords:** C18 pure triglycerides, extra-virgin olive oil, kinetic analysis, thermal decomposition

### Introduction

Vegetable oils and fats are triesters of glycerol commonly made up of fatty acid molecules, the most representative of which with 18 carbon atoms. Together with proteins and carbohydrates they represent fundamental food substances that play an important role as source of energy in a diet [1]. Commercial edible oils have been studied by different authors [2–6] using thermal analysis to measure several physico-chemical properties related to their oxidation and stability behaviour. Within the framework of a study addressing the development of a kinetic model of the ageing process affecting extra-virgin olive oil we initially investigated the breakdown kinetics of the natural antioxidants (polyphenols) contained in it [7]. In the present study, on the other hand, we also took into consideration the study of the thermal breakdown of the principal compounds of the oily matrix, namely the triglycerides, in an oxidizing atmosphere (air).

In this case the study was carried out by means of thermal analysis (TG and DTG). Several publications involving thermal analysis are available on this subject [8–12], although the kinetic data regarding the oxidative process of triglycerides and olive oil are incomplete and are often contradictory [11, 12], in some cases the data have even been interpreted incorrectly [12].

### Experimental

#### Materials and samples

Glyceryl tristearate, glyceryl trioate, glyceryl trilinoleate and glyceryl trilinolenate of analytical grade were obtained from Sigma Aldrich. All extra-virgin olive oil samples examined, purchased from local shops, and produced by the most important Italian olive oil producers, were in sealed glass bottles.

#### Instrumentation

The TG measurements were carried out at different heating rates (from 5 to 12.5°C min<sup>-1</sup>) using TG 50 Mettler TG equipment with a TC10-TA processor. All thermal analysis runs were performed on 7–12 mg of sample from room temperature up to about 550°C under a 100 cm<sup>3</sup> min<sup>-1</sup> stream of air.

#### Kinetic procedure

Solid state decomposition kinetics is usually described by the following basic equation:

$$d\alpha/dt = k(T)f(\alpha) \quad (1)$$

where  $\alpha$  is the degree of reaction defined as  $\alpha = (w_i - w_T)/(w_i - w_f)$  (being  $w_i$  and  $w_f$  the initial and final mass loss, while  $w_T$  is the mass loss at temperature  $T$ ),

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$f(\alpha)$  is the model function, which assumes different mathematical forms depending on the reaction mechanism [13] and  $k(T)$  is the specific rate constant, whose temperature dependence is commonly described by the Arrhenius equation:

$$k(T) = A \exp(-E/RT) \quad (2)$$

where  $E$  is the activation energy,  $A$  is the pre-exponential factor,  $R$  the gas constant and  $T$  the absolute temperature. Moreover, taking into account that under non-isothermal conditions the heating rate is  $\beta = dT/dt$ ,  $d\alpha/dt = d\alpha/(dT/\beta)$ , where  $t$  is the time; combining Eqs (1)–(2), gives:

$$d\alpha/dT = (A/\beta) \exp(-E/RT) f(\alpha) \quad (3)$$

The proposed kinetic analysis, based on dynamic model-free methods using data obtained at different fixed heating rates,  $\beta$ , seems to be the most reliable approach. Due to the complexity of the decomposition patterns of the examined materials the kinetic study was carried out using the Kissinger equation [14]:

$$\ln(\beta/T_m^2) = \ln(AR/E) + (-E/R)(10^3/T_m) \quad (4)$$

where  $T_m$  is the DTG peak temperature at a given  $\beta$  value,  $A$  the pre-exponential factor,  $E$  the activation energy and  $R$  the gas constant. This equation gives a single activation energy from the slope of Eq. (4) for each step involving mass loss.

Kinetic study of decomposition steps was also performed using the isoconversional method of Ozawa–Flynn–Wall (OFW) [15, 16], which is based on the integral form of Eq. (1) in accordance with the following isoconversional equations

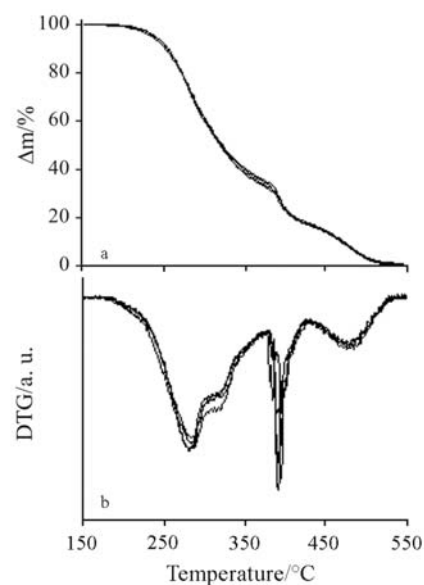
$$\ln(\beta)_\alpha = \ln[(A_\alpha R)/E_\alpha] - \ln g(\alpha) - 5.3305 - 1.052(E_\alpha/R)(1/T_\alpha) \quad (5)$$

Once TG data had been processed the corresponding activation energy values were derived from the slope of Eq. (5) for each value of the extent of reaction  $\alpha$ , if Doyle's approximation [17]:  $\ln p(x) \approx -5.3305 - 1.052x$ , where  $x = E/RT$  and ( $20 \leq x \leq 60$ ) is valid over the entire range of  $\alpha$ .

## Results and discussion

### Thermal behaviours

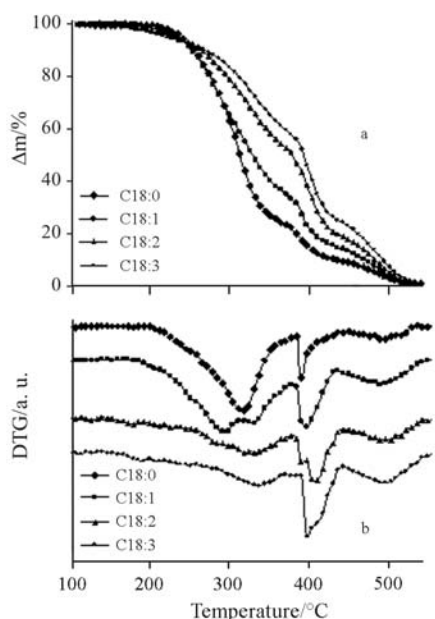
The thermal behaviour of four different commercially available extra-virgin olive oils (EVOOs) is shown in Fig. 1. Identical TG and DTG profiles (Fig. 1a and b, respectively) are obtained. Thus, for the subsequent experiments only one of them was selected to represent all commercial EVOOs. Moreover, from the DTG curves two superimposed steps of mass loss were found between about 160 and 370°C, followed by a third sharp step at around 370°C and a fourth final broad step between 410 and 555°C. Our investigation was focused mainly on the decomposition process between 160 and 370°C, which can be ascribed to the thermal decomposition of the saturated and unsaturated carboxylic chains, while around 370°C a fast combustion of the evolved volatile components probably occurs, followed by oxidation of the carbonaceous residues [11]. Unfortunately, different hypotheses have been suggested in literature [11, 12] regarding the two higher temperatures steps for commercial edible oils and, to a



**Fig. 1** a – TG and b – DTG curves of four different commercial EVOO samples in a stream of air at a heating rate of  $5^\circ\text{C min}^{-1}$

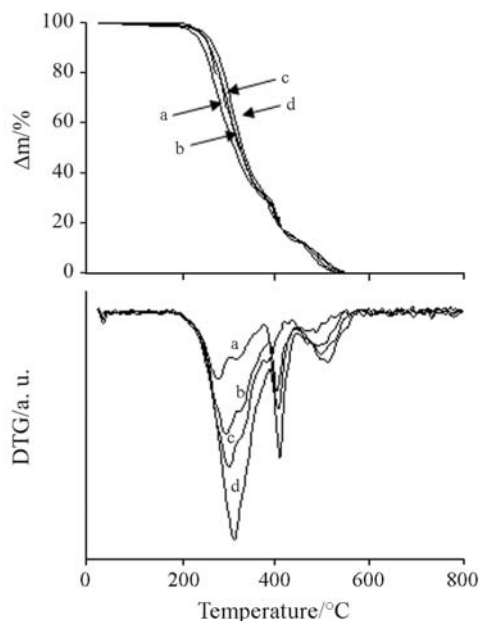
**Table 1** Triglycerides considered in this study and their contents in EVOO expressed in ranges of percent by mass

Compound	Structural characteristics No. of C atoms and insaturations	mass/mass% in EVOO
Glyceryl tristearate	C18:0	0.5–5.0
Glyceryl trioleate	C18:1	55.0–83.0
Glyceryl trilinoleate	C18:2	3.5–21.0
Glyceryl trilinolenate	C18:3	0.0–0.9



**Fig. 2** a – TG and b – DTG curves of the four C18 triglycerides investigated in a stream of air at a heating rate of  $5^{\circ}\text{C min}^{-1}$

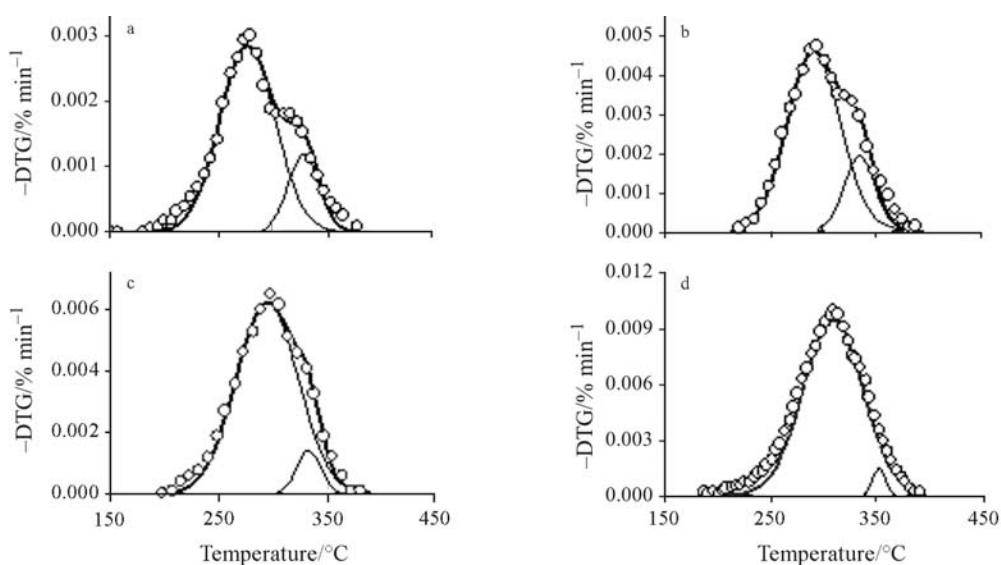
certain extent, also for the first two overlapping steps involving the oxidative degradation of unsaturated and saturated triglycerides that occurs in the range  $160\text{--}370^{\circ}\text{C}$ . Therefore, the thermal behaviour of some of the principal compounds contained in the EVOOs was investigated in the range  $160\text{--}370^{\circ}\text{C}$  to distinguish the step ascribable to the oxidative degradation of the saturated chain from that due to the unsaturated chain of triglycerides. To this end, four pure C18 triglycerides (i.e., glyceryl-tristearate (C18:0), -trioleate (C18:1), -trilinoleate (C18:2) and -trilinolenate (C18:3)) were considered. The mean



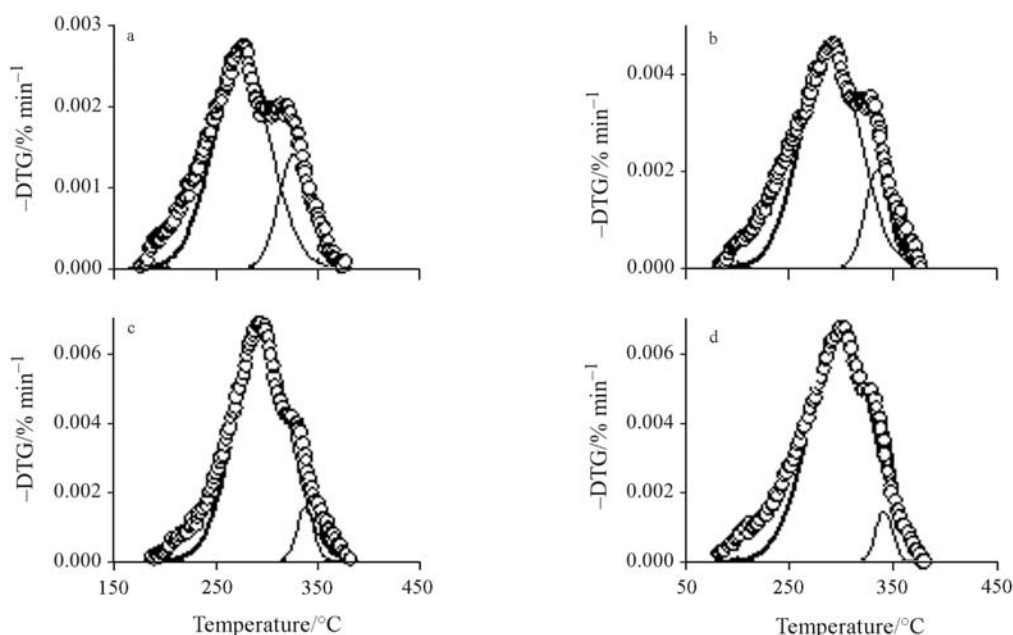
**Fig. 3** TG and DTG curves of EVOO at different heating rates in a stream of air: a – 5; b – 8; c – 10; d –  $12.5^{\circ}\text{C min}^{-1}$

ranges of percent content by mass of these triglycerides usually found in EVOOs are listed in Table 1, while the TG and DTG curves are reported in Fig. 2.

The TG and DTG curves of the saturated C18:0 show a single decomposition step between  $160$  and  $370^{\circ}\text{C}$ , localized between the two superimposed steps occurring in the unsaturated C18:1; the latter two steps are very similar to those exhibited by EVOOs in the same temperature range (Fig. 1a and b). However, this result does not clarify which of the two overlapping steps may be ascribed to the decomposition of



**Fig. 4** Deconvolution of DTG peaks for the thermal degradation of EVOO at different heating rates: a – 5; b – 8; c – 10; d –  $12.5^{\circ}\text{C min}^{-1}$

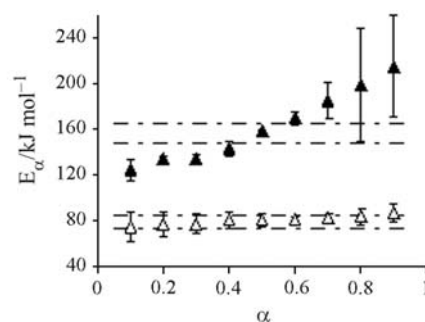


**Fig. 5** Deconvolution of DTG peaks for the thermal degradation of C18:1 at different heating rates: a – 5; b – 8; c – 10; d – 12.5 °C min<sup>-1</sup>

the unsaturated and saturated moieties of the triglycerides. To definitively solve this problem a kinetic analysis of these two partially overlapping processes was undertaken by carrying out several TG measurements at different heating rates. To this end, by way of example, the TG and DTG curves recorded under identical experimental conditions but at different heating rates for comparable size of the same EVOO sample are shown in Fig. 3. Identical measurements were also carried out for each of the four pure triglycerides studied; it was possible to evidence two partly separated steps only for C18:1. Therefore, in Figs 4 and 5, the deconvolution of the first two partially overlapping peaks of the DTG curves, recorded at the four heating rates examined for the thermal degradation of EVOO and C18:1, i.e. the main components of EVOO (Table 1), was performed because they overlapped. For the C18:0, as expected, only one DTG peak was found, while for C18:2 and C18:3 no overlapping DTG peaks were evidenced over the same temperature range. In these cases only the second peak was actually clearly distinct. The deconvolution of DTG curves was therefore not performed in these two cases. However, in order to carry out the kinetic analysis using the Kissinger method, the DTG peak temperature was subsequently determined at each given  $\beta$  value and included in Eq. (4) for the two thermal degradation steps of EVOO and C18:1 as well as for the single degradation step of the other three triglycerides examined.

#### Kinetic data

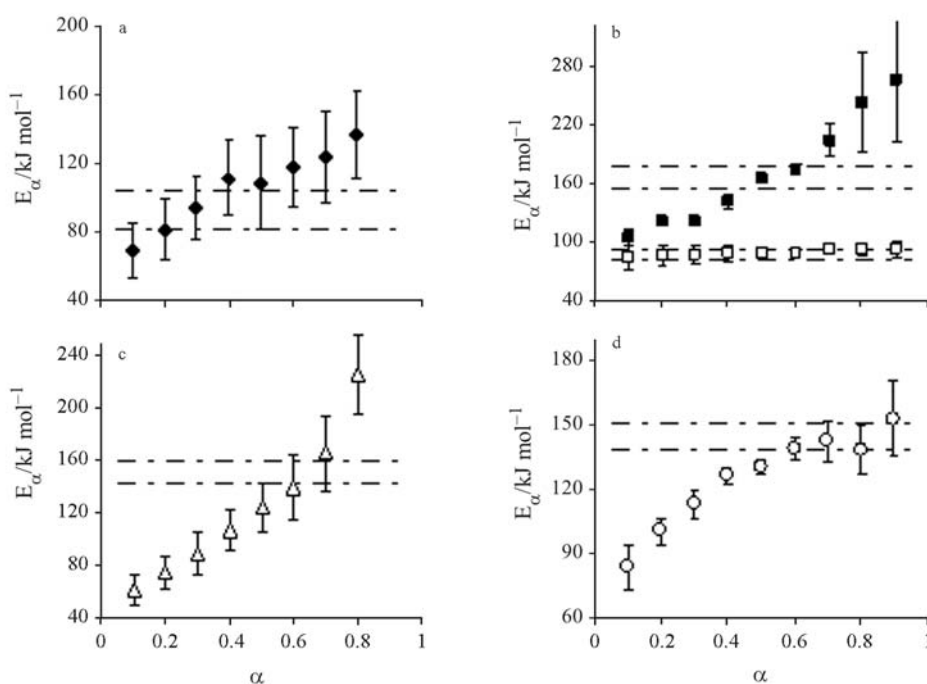
The corresponding kinetic parameters ( $E$  and  $\ln A$  values, respectively) were obtained from the slopes and intercepts of these equations and are reported in Table 2. For EVOO and C18:1, for which two overlapping steps take place in the temperature range examined, the  $E$  and  $\ln A$  values ascribed to the first step are very similar and significantly lower than those of the second step. In addition, the  $E$  and  $\ln A$  values for the single degradation step of the saturated C18:0 are in good agreement with the corresponding values for the first step of both the EVOO and C18:1 samples. In addition, a good agreement was also found with scarcely kinetic data reported in literature [12] for the process occurring at lower temperature range for commercial edible oils. This result allows us to claim that this first step, which occurs at lower temperatures



**Fig. 6** Activation energy trend as a function of  $\alpha$  for the degradation of EVOO

**Table 2** Kinetic data: Arrhenius parameters for the main thermal degradation steps of EVOO and the examined triglycerides derived using the Kissinger method

Compound	I step (160–350°C)		II step (250–370°C)	
	$E/\text{kJ mol}^{-1}$	$\ln A/\text{min}^{-1}$	$E/\text{kJ mol}^{-1}$	$\ln A/\text{min}^{-1}$
EVOO	78±6	15.0±1.2	156±9	30.1±1.8
C18:0	88±7	16.4±1.3		
C18:1	85±5	16.8±1.2	167±11	32.2±1.9
C18:2			151±8	30.4±1.8
C18:3			145±6	27.7±1.6

**Fig. 7** Activation energy trend as a function of  $\alpha$  for the degradation of a – C18:0, b – C18:1, c – C18:2 and d – C18:3

and shows lower activation energies, is probably due to the decomposition of the saturated chain of the triglycerides, while the  $E$  and  $\ln A$  values for the single degradation step of unsaturated C18:2 and C18:3 are in close agreement with those related to the second degradation step of EVOO and C18:1. This step was therefore attributed to the thermal degradation of unsaturated chains of triglycerides. Since the decomposition of EVOO probably has a more complex nature than that described by the Kissinger method, which provides only a single pair of kinetic parameters, the kinetic analysis was also performed using the OFW method. To this end, the temperature associated with a particular degree of conversion  $\alpha$  was determined at each given  $\beta$  value. The corresponding  $E$  value at any given  $\alpha$  value is derived from the slope of the  $\ln \beta$  vs.  $T^{-1}$  equation (Eq. (5)). The  $\alpha$  dependency of  $E$  for each degradation step of EVOO and triglycerides is shown in Figs 6 and 7, respectively. The obtained trends show that the mechanism of degradation for the

saturated chain moiety of triglycerides remains practically unchanged over the whole process, while the one related to the unsaturated chain changes significantly over the entire process. The activation energy actually increases sharply during the degradation and seems to fit the  $E$  value obtained using the Kissinger method (i.e., the values included between the dashed lines of Figs 6 and 7) reasonably well only in the second half or at the end of the process.

## Conclusions

The results of this study confirm that thermal analysis techniques are able to evaluate the thermal stability and the degradation pattern of commercial EVOOs using very small amounts of sample and shorter time analysis with respect to conventional techniques. The comparison of TG and DTG curves of the single pure C18 triglycerides studied with those of the EVOO has



confirmed the hypothesis provided in this paper about the thermal degradation mechanisms related to the different steps of mass loss observed in the corresponding TG/DTG curves of EVOO. This interpretation is substantially in agreement with the one at least partially proposed by Dweck and Sampaio [11]. In particular, the degradation steps ascribable to the unsaturated and saturated chains of the triglycerides, occurring in commercial EVOO samples as a consequence of heating in an oxidizing atmosphere were evaluated.

Finally, the activation energies attributed to the first two degradation steps of EVOO and of the pure C18 triglycerides studied were determined using two model-free kinetic methods. The most significant variation of activation energy during the evolution of the process is observed for the degradation of unsaturated chains.

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