Kinetics of the Decomposition of Total Aliphatic Waxes in Olive Oil During Deodorization

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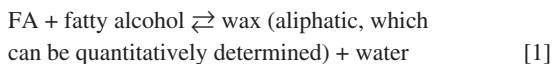
ABSTRACT: Changes in the content of aliphatic waxes during industrial deodorization and/or physical refining of bleached olive oil were studied in an experimental discontinuous pilot plant of 250 kg deodorizer using nitrogen as stripping gas in place of steam. The kinetic constants for the decomposition of waxes during the deodorization process were determined. The reaction orders studied are zero (or can be considered zero) within the working interval. The values of rate constants, activation energy, frequency factor, increment of activation Gibbs free energy, activation enthalpy, and activation entropy are established.

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KEY WORDS: Kinetic, olive oil, physical refining, wax.

During olive oil deodorization (in both chemical and physical processes) there is a change in the content of aliphatic waxes with respect to the bleached oil. When the bleached olive oil reaches the deodorization temperature, the content of aliphatic waxes is maximal (generally, all the possible waxes that can be formed from its content in fatty alcohols). However, throughout the deodorization process there is a diminution of the wax content that is due to the decomposition of waxes and the distillation of the alcohols formed during this process and, in the case of physical refining, the distillation of the FFA present in the oil (1).

The formation–decomposition of waxes during olive oil deodorization is a reaction that takes place at high temperatures (between 180 and 270°C, at maximum) and under vacuum (in general, between 3 and 10 torr of absolute pressure). It is an esterification–deesterification reaction between one FA and a fatty alcohol that can be expressed by

$$\text{FA + fatty alcohol} \rightleftarrows \text{wax (aliphatic, which can be quantitatively determined) + water} \qquad [1]$$

The reaction also can be described as a transesterification reaction between a fatty alcohol and an acylglycerol, and its two phases can be described as

$$\text{MAG, DAG, or TAG + water} \rightleftarrows \text{glycerol, MAG, or DAG + FA} \qquad [2]$$
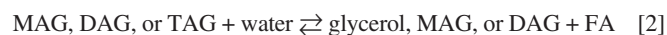
In general, waxes are formed mainly from the FFA. These FA then react as indicated in Equation 1 (second phase of this transesterification reaction).

There are reports in the scientific literature on esterification reactions between FA and short-chain alcohols, because they are used for the qualitative and quantitative determination of such acids as methyl esters by GC. The direct esterification is catalyzed by strong acids and is usually achieved by sulfuric acid/methanol and/or hydrochloric acid/methanol. The transesterification of acylglycerols is catalyzed by strong alkalis, usually alcoholic KOH or sodium methylate. In this kind of reaction the catalyst has a great influence on the reaction rate (2).

Kinetic studies on the esterification reaction between alcohols and organic acids have been performed using short-chain alcohols and short-chain FA (in general, the monosodium-substituted salts of diacids), because they allow one to do the studies with aqueous or $MeOH/H_2O$ solutions. Examples of such researches are the studies performed to determine the effect of salts on the kinetics of formation of monoesters of ethyl malonate, methyl glutarate, and ethyl adipate performed by Sánchez Burgos *et al.* (3,4). These reactions were studied for the first time by Nielsen (5) in 1936 and a previous mention of them can be found in the work of Meyer (6).

The references found in the literature are not relevant for describing the formation–decomposition of aliphatic waxes during the process of deodorizing olive oil. In this case, the substances involved in the reaction are high M.W. alcohols—linear molecules of 18 (or more) carbon atoms—and FA. The reaction takes place in olive oil (which is not an alcoholic, aqueous, or water–alcohol medium), without the use of any catalyst (strong acid or alkali), at temperatures between 180 and 270°C and under vacuum.

With respect to the possibility of changes in the acylglycerol structures, the assays performed by Gracian and Mancha (7) showed clearly that physical refining produces only small changes that, for most edible oils and fats, are of little significance. However, in the case of the olive oil, such changes have great importance because of the strict regulation in relation to their contents (8–10).

These studies cannot be considered as models for the formation of waxes, since they are related only to the transesterification of acylglycerols.

The aim of this work was to study the kinetics of decomposition of waxes during the process of deodorizing olive oil. These parameters are of interest for the olive oil refining industries, which want to develop more efficient processes that lead to improved quality of the treated oils, where limits for wax content are established by European Common Market (EEC) regulations (8,9). In addition, refined oils must contain no more than a minimal proportion of waxes so as to avoid rejection by consumers owing to the turbidity produced by the crystallization of the excess wax. Removal of waxes by crystallization and/or filtration is an expensive process because of the neutral fat losses and the energy necessary to achieve the separation.

EXPERIMENTAL PROCEDURES

Physical refining. Olive oil with a FFA content of 1.85% was bleached in the pilot plant of the Instituto de la Grasa according to the technique described in Reference 1 (0.5% clay-Type OD, Minas de Gador, Almería, Spain; 90°C, 30 min, absolute pressure lower than 30 mm Hg). Batches were taken from a homogeneous mixture of bleached oil. Bleached olive oil was physically refined in a discontinuous deodorizer of 250 kg maximum capacity. The technique and the equipment were described (1,10). The experiment carried out for olive oil described in Reference 1 was planned according to a centered cube 2^3 experimental design (complete factorial design) with three central points. The experimental treatments (Table 1, treatments E-1 to E-11) were performed in random order, and the range of values for each variable was selected according to the optimal values from a previous similar experiment. In each experiment the N_2 flow was introduced into the deodorizer, which was already charged with the corresponding amount of bleached oil. The temperature was raised to 100°C, to ensure heat transfer and protection of the oil, before the refining began. The rate of N_2 flow (±0.04 m³/h), the operating temperature (±0.5°C), and the oil height in the deodorizer (measured by weight ± 0.5 kg) (1) were controlled according to the design levels (Table 1). Time (± 1 min) was computed from the point at which the oil reached the required temperature. Each batch was sampled at 0, 1.5, 3, 4, and 5 h. The N_2 flow was shut down after the batch cooled to 100°C.

Chemical refining. Lampante olive oil (3.9% FFA content) was heated at 40°C for 20 min with 0.2% of commercial phosphoric acid (85%, w/w), and the excess acid was neutralized with sodium hydroxide at the same temperature. After 20 min, the temperature was raised to 90°C to speed soap formation, and the soap was separated by centrifugation 20 min later.

The neutralized oil was washed three times with water and dried. Then it was bleached under the same conditions mentioned above. The deodorization process was performed under the same conditions as in the physical refining but at 180°C. Samples were taken when the oil reached 180°C (*t* = 0) and after 1, 2, 3, and 4 h of processing.

TABLE 1
Experimental Design, Showing the Values of the Variables Studied and Conditions of the Different Deodorization Assays Performed

Flow of N_2[a]	Oil weight (kg)		
[m³(n.c.)t⁻¹ h⁻¹]	240°C	250°C	260°C
1.5	125 (E-1)[b]		125 (E-2)
	157 (E-3)		175 (E-4)
2.0		150 (E-5)	
		150 (E-6)	
		150 (E-7)	
2.5	125 (E-8)		125 (E-10)
	125 (E-9)		125 (E-11)

[a]Notes: n.c. = normal conditions; t = tonnes.
[b]In parentheses are the treatment codes.

Determination of wax content. Wax content was determined according to the EEC regulations for olive oil and pomace oil, Regulations (CEE) no. 2568/91 EEC (8) modified by Regulations (CEE) no. 183/93 (9).

The olive oil sample was prepared with 0.5 mg of oil and 1 mL of internal standard (0.1 mg/mL lauryl arachidate, C_{32}) with a few drops of Sudan I as colorant; because the oil was stored in the freezer, it was necessary to heat it about 30 min at 40–50°C, with vigorous stirring, before taking the sample. Waxes were separated on a silica gel column using hexane/ether (98.5:1.5) as eluent. The first fraction, with a polarity lower than TAG, was concentrated to dryness and then recovered with 4 mL of *n*-heptane. GC analysis was performed by injecting 1 μL of this solution onto a fused-silica capillary column (15 m length, 0.25 mm i.d., and 0.10 μm thickness) with an on-column injector. The chromatographic conditions were: HP chromatograph (model 5890-II) with automatic injector and FID. The temperature program was from 80 to 120°C, at about 30°C/min, and from 120 to 340°C at about 5°C/min. The temperatures of the detector and the injector were 320°C. Hydrogen flow was 25–35 cm³/min and analysis time was 40 min (1).

Analytical error was calculated from the 13 samples of oils with different amounts of analyte. Each sample was divided into two subsamples, and each subsample was injected in duplicate into the gas chromatograph. The error in sample determination was evaluated as ±4% (1).

Kinetic study. To estimate the reaction order, data were adjusted to reactions of order 0, 1, 2, and 3 by the method of least squares. Then residual variances and correlation coefficients were compared. Equations were fitted considering two different situations: (i) Each deodorization assayed was independent; (ii) assays at the same temperature are replications made under similar conditions as the other two independent variables (since these variables have a limited influence on the content of waxes in comparison with the deodorization temperature) (1).

This latter hypothesis implies the inclusion of the variances derived from the other two variables in the total variance of the fitted equation. This implies that, if the equations are fitted independently for each deodorization assay

performed at the same temperature, the fitted curve may be the same, but the confidence intervals corresponding to the experimental points will vary their positions with respect to the curve and, in consequence, the integration constant also will change. To fit the equation in these conditions it is enough to establish that the curves obtained at the same temperature are parallel (i.e., they have the same slope but different constants for $x = 0$). The common slope is thus an estimation of the value of k, expressed as ppm h^{-1}. Once the values of k are known, the other thermodynamic constants can be easily estimated.

RESULTS AND DISCUSSION

The kinetics of the decomposition of aliphatic waxes can be quantified during the deodorization process and the parameters estimated. These results are useful in making an estimation of the content of waxes in refined olive oils.

The reaction rate (v) at a specific time is, according to the law of mass action, directly proportional to the product of the concentrations of the respective substances (r_i) involved in the reaction (c_{ri}). The power to which each concentration is raised is generally an integer (a_i). The constant of proportionality (k) is known as the "specific rate" or "rate constant."

$$v = k \prod c_{ri}^{a_i} \qquad [3]$$

By definition, the order of a reaction is the sum of the powers that appear in Equation 3. At the same time, each power (a_i) is known as a partial order (with respect to the substance, r_i). Several mathematical and/or graphical procedures are available to determine the order, and the order of the reaction adopted is the one that gives the lowest variance and the highest correlation coefficient (11).

The procedures are summarized in Table 2.

Except for the odd exception, the reaction rate increases with temperature. Arrhenius established this dependence (12, 13),

$$k = A \cdot \exp(-E^{\neq}/RT) \qquad [4]$$

in which the constant A is termed the "frequency factor" or "pre-exponential factor" and $E^{\neq}$ is the "activation energy."

Expressing this equation logarithmically,

TABLE 2
Equations for the Estimation of the Kinetic Parameters According to the Reaction Order[a]

Order	Differentiation method	Integration method
0	$dc_{ri}/dt = k$	$k \cdot t = c_{ri}$
1	$dc_{ri}/dt = k \cdot (a - c_{ri})$	$k \cdot t = \ln[a/(a - c_{ri})]$
2	$dc_{ri}/dt = k \cdot (a - c_{ri})^2$	$k \cdot t = [1/(a - c_{ri})] - 1/a$
3	$dc_{ri}/dt = k \cdot (a - c_{ri})^3$	$k \cdot t = [1/(3 - 1)] \cdot [(1/(a - c_{ri})^2] - (1/a^2)]$

[a]Volume: V; concentration: $c_{ri} = mols_{ri}/V$; concentration: $c_{ri} = ppm_{ri} = (mols_{ri} \cdot Pm_p)/(V \cdot p_e)$; M.W. (weighted): Pm_p; specific weight of the oil: p_e; t: time; k: rate constant; a: constant.

$$\ln k = \ln A - E^{\neq}/RT \qquad [5]$$

By estimating the rate constant (k) at different temperatures (T), the values of A and $E^{\neq}$ can be calculated with Equation 6,

$$\ln(c_{ri}) = -E^{\neq}/RT + \ln(t) + \ln(A) \qquad [6]$$

This expression is often written as:

$$\ln(c_{ri}) = -E^{\neq}/RT + B \cdot \ln(t) + \ln(A) \qquad [7]$$

where B (fitting coefficient) must be 1 when the reactions are, or can be considered as, order 0 in the interval of time studied.

For a simple reaction such as wax formation, and since the reaction occurs at constant temperature and pressure throughout the deodorization period, the values of $\Delta G^{\neq}$, $\Delta S^{\neq}$, and $\Delta H^{\neq}$ can be calculated or estimated from the values found for the rate constant (12):

$$-\Delta G^{\neq} = [\ln k - \ln(k_B \cdot T/h)] \cdot RT \qquad [8]$$

and by the equation (13):

$$\Delta G^{\neq} = \Delta H^{\neq} - T \cdot \Delta S^{\neq} \qquad [9]$$

where $\Delta G^{\neq}$ = increment of activation Gibbs free energy; T = absolute temperature; $R = 1.987$ cal $\cdot$ K^{-1} $\cdot$ mol^{-1}; k_B = Boltzmann constant = $1.38026 \cdot 10^{-16}$ erg $\cdot$ K^{-1}; h = Planck constant = $6.6252 \cdot 10^{-27}$ erg $\cdot$ s; k = rate constant; $\Delta H^{\neq}$ = increment of activation enthalpy; $\Delta S^{\neq}$ = increment of activation entropy.

The values of the contents of waxes in the different assays and samples analyzed are shown in Figures 1–4.
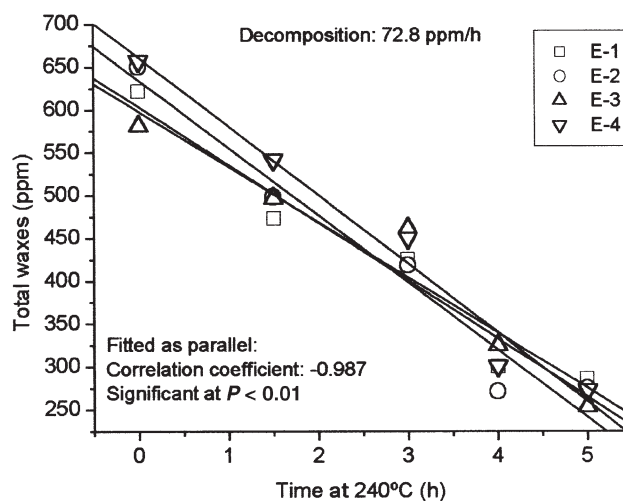

FIG. 1. Contents of total waxes during the refining assays performed at 240°C. Data were fitted to each assay independently, considering a reaction order of zero. Significance was determined by F test of the variance analysis of the regression. For treatment codes see Table 1.
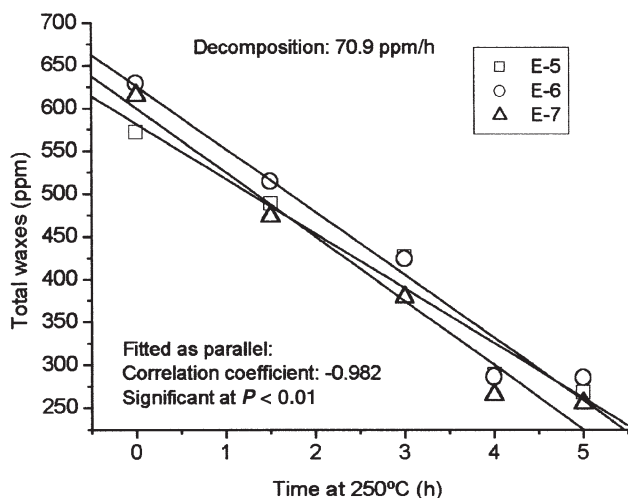
FIG. 2. Contents of total waxes during the refining assays performed at 250°C. Data were fitted to each assay independently, considering a reaction order of zero. For treatment codes see Table 1.

FIG. 4. Contents of total waxes during the refining assays performed at 180°C. Data were fitted to each wax independently, considering a reaction order of zero.

Because of the lack of pertinent prior information the possibility that the order of the reaction is 0, 1, 2, and 3 has been checked. Bearing in mind that the most appropriate order is the one that produces the highest correlation coefficient and lowest variance, the order of reaction for our data can be established as 0. Then the order of the reaction is, within the interval considered, 0.

Figures 1–4 show the fitted curves for each of the assays. It is evident that the diverse curves show similar slopes, confirming the hypothesis that they can be consider as parallel for the calculation of k.

Table 3 shows the estimated values of $\Delta G^{\neq}$ and k, assuming that the assays performed at the same temperature may be considered as replications.
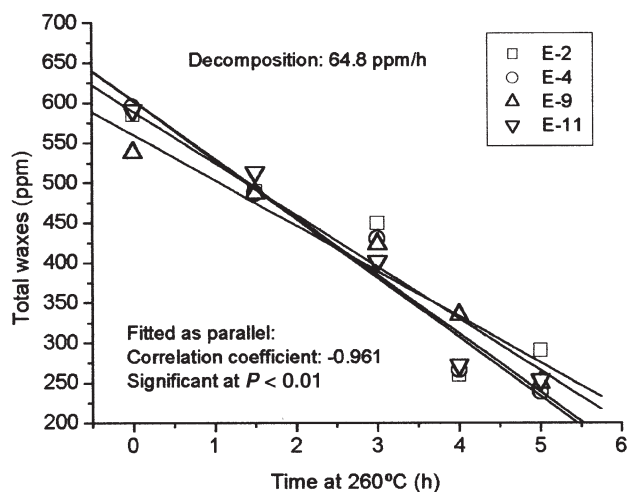

FIG. 3. Contents of total waxes during the refining assays performed at 260°C. Data were fitted to each assay independently, considering a reaction order of zero. For treatment codes see Table 1.
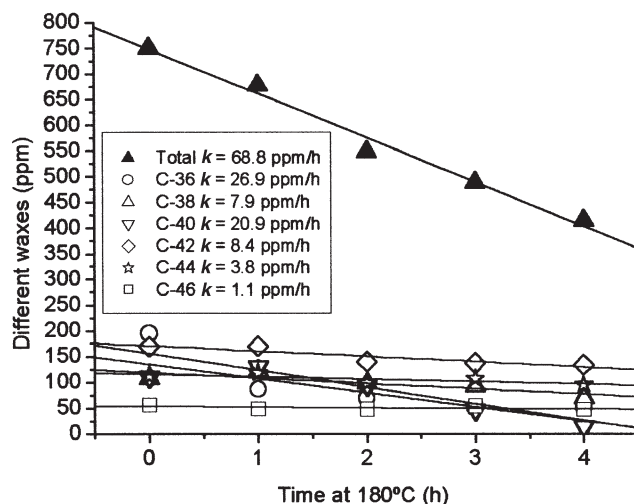
To calculate these data, one must express the k of the reaction in mols/L·s, using 0.826, 0.797, 0.793, and 0.788 g/mL as olive oil density at 180, 240, 250, and 260°C, respectively.

The results suggest that the lower M.W. waxes are more easily decomposed during chemical refining (higher k values) (Table 3). This means that by applying chemical refining, the refined oil will have higher proportion of high M.W. waxes. However, in physical refining, there is no consistent tendency with respect to the M.W. of waxes. Apparently, the higher temperature of the process counteracts the effect of M.W. in the decomposition reaction and produces a similar rate across the M.W. range studied.

$\Delta G^{\neq}$ (Table 3) increases with temperature in all waxes during physical refining, and its values are independent of the M.W. of waxes. In chemical refining $\Delta G^{\neq}$ are lower corresponding to a lower processing temperature.

Estimated values of $E^{\neq}$, A, $\Delta H^{\neq}$, and $\Delta S^{\neq}$, for the values of k found, are shown in Table 4. This table shows that values for $\Delta S^{\neq}$ are similar in the range of wax M.W. studied. In contrast, $\Delta H^{\neq}$ increases with wax M.W. This means that, in the temperature interval studied, the energy to be supplied will depend on the wax M.W.

This work has permitted the estimation of different thermodynamic parameters of wax decomposition during the deodorization of olive oil. For the first time, values of $E^{\neq}$, A, and increments of $\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ have been established.

A good knowledge of wax decomposition kinetics will permit optimization of the processing variables to produce the highest wax decomposition and will avoid any further elimination of wax by crystallization from the deodorized oils before commercialization. Furthermore, elimination of waxes during physical refining results in lower neutral fat losses and lower energy consumption because it will not be necessary to separate them by crystallization.

TABLE 3
Order (according to the hypothesis established) Within the Interval of Temperatures Studied
for the Formation–Decomposition of the Aliphatic Waxes Quantified in the Olive Oil, k, and $\Delta G^{\neq}$

Wax	Type of refining	Temperature (°C)	Order of reaction	k (ppm h^{-1})	k (mol L^{-1} s^{-1})	$\Delta G^{\neq}$ (kcal mol^{-1})
C-36	Physical	240	0	8.7	$5.7 \cdot 10^{-9}$	49.8
	Physical	250	0	8.4	$5.5 \cdot 10^{-9}$	50.8
	Physical	260	0	7.7	$5.1 \cdot 10^{-9}$	52.0
	Chemical	180	0	26.9	$1.7 \cdot 10^{-8}$	42.8
C-38	Physical	240	0	11.9	$7.4 \cdot 10^{-9}$	49.5
	Physical	250	0	11.1	$6.9 \cdot 10^{-9}$	50.5
	Physical	260	0	9.2	$5.5 \cdot 10^{-9}$	52.0
	Chemical	180	0	7.9	$4.7 \cdot 10^{-9}$	44.0
C-40	Physical	240	0	17.0	$1.0 \cdot 10^{-8}$	49.2
	Physical	250	0	15.9	$9.5 \cdot 10^{-9}$	50.2
	Physical	260	0	14.2	$8.5 \cdot 10^{-9}$	51.5
	Chemical	180	0	20.9	$1.2 \cdot 10^{-9}$	43.2
C-42	Physical	240	0	16.0	$9.1 \cdot 10^{-9}$	49.3
	Physical	250	0	16.1	$9.2 \cdot 10^{-9}$	50.2
	Physical	260	0	14.9	$8.5 \cdot 10^{-9}$	51.5
	Chemical	180	0	8.4	$4.6 \cdot 10^{-9}$	44.0
C-44	Physical	240	0	12.5	$6.8 \cdot 10^{-9}$	49.6
	Physical	250	0	11.9	$6.5 . 10^{-9}$	50.6
	Physical	260	0	12.2	$6.7 \cdot 10^{-9}$	51.7
	Chemical	180	0	3.8	$2.0 \cdot 10^{-9}$	44.8
C-46	Physical	240	0	6.6	$3.4 \cdot 10^{-9}$	50.3
	Physical	250	0	7.4	$3.9 \cdot 10^{-9}$	51.1
	Physical	260	0	6.5	$3.4 \cdot 10^{-9}$	52.5
	Chemical	180	0	1.1	$5.5 \cdot 10^{-10}$	45.9
Totals[a]	Physical	240	0	72.8	$4.2 . 10^{-8}$	47.7
	Physical	250	0	70.9	$4.1 \cdot 10^{-8}$	48.7
	Physical	260	0	64.8	$3.8 . 10^{-8}$	49.9
	Chemical	180	0	68.8	$3.8 . 10^{-8}$	42.1

[a]M.W. (weighted) = 602.

TABLE 4
Estimated Values of $E^{\neq}$, A, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ in Physical Refining (240–260°C)

Waxes	$E^{\neq}$ (kcal mol^{-1})	A (mol L^{-1} h^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (kcal mol^{-1})
C-36	−3.014	$2.98 \cdot 10^{-10}$	−8.8	−0.11
C-38	−8.033	$2.87 \cdot 10^{-12}$	−13.8	−0.12
C-40	−4.404	$1.34 \cdot 10^{-10}$	−10.1	−0.12
C-42	−1.837	$1.52 \cdot 10^{-9}$	−7.6	−0.11
C-44	−0.415	$4.47 \cdot 10^{-9}$	−6.1	−0.11
C-46	0.048	$3.73 \cdot 10^{-9}$	−5.9	−0.11
Totals	−2.709	$2.97 \cdot 10^{-9}$	−8.3	−0.11

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