

INVESTIGACION

A regression analysis on the green olives debittering.

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RESUMEN

Análisis de regresión del endulzamiento de aceitunas verdes.

En este artículo se ajusta un modelo de regresión, que da el tiempo de endulzamiento t en función de la concentración de hidróxido sódico C y la temperatura de endulzamiento T , en el endulzamiento de aceitunas verdes de tamaño mediano de la variedad Conservolea. Este modelo tiene la forma simple $t = a_0 C^{a_1} \cdot e^{a_2/T}$, donde a_0 , a_1 y a_2 son constantes. Los valores de a_0 , a_1 y a_2 son determinados por el método de los mínimos cuadrados a partir de un grupo de datos experimentales. El modelo determinado es muy satisfactorio para las condiciones en las que las aceitunas verdes griegas son endulzadas.

PALABRAS-CLAVE: Aceituna verde de mesa – Análisis de regresión – Endulzamiento – Mínimos cuadrados.

SUMMARY

A regression analysis on the green olives debittering

In this paper, a regression model, which gives the debittering time t as a function of the sodium hydroxide concentration C and the debittering temperature T , at the debittering of medium size green olive fruit of the Conservolea variety, is fitted. This model has the simple form $t = a_0 C^{a_1} \cdot e^{a_2/T}$, where a_0 , a_1 and a_2 are constants. The values of a_0 , a_1 and a_2 are determined by the method of least squares from a set of experimental data. The determined model is very satisfactory for the conditions in which Greek green olives are debittered.

KEY-WORDS: Debittering – Green table olive – Least squares – Regression analysis.

1. INTRODUCTION

The olive fruit is unique among the drupes in that it contains, primary in the flesh, the bitter principle oleuropein (8). It is well documented in the literature that oleuropein is not harmful to humans (2). Nevertheless it has to be removed from the flesh, at least partly, otherwise olives are intensely bitter and unsalable.

The technique which is used almost exclusively in debittering green olives is the hydrolysis of oleuropein with sodium hydroxide solution (9). This hydrolysis gives as products glucose, oleanolic acid and 3,4-dihydroxy-ethyl alcohol. The debittering time

is depended on the concentration of the sodium hydroxide solution (lye), the treatment temperature, the fruit variety and the fruit size. Also some others factors, such as maturity stage of the fruit, fruit/lye relationship during the treatment, situation of the cultivar, and type of culture (irrigated or non irrigated trees), may influence results.

Additionally, the lye treated olives have to be reached with water. Efforts to reduce the volume of spent lye and residual water have been made in Spain (6). They resulted in: (I) the reutilization of spent lye after building up its strength to the original level (it has found industrial application even in treating the table olive variety Gordal (3) in Spain), and (II) the complete or partial elimination of washings through the use of food grade HCl for neutralizing (5) the residual alkalinity (additional research must be designed and performed before this technique could be seriously considered for industrial application).

The present work was undertaken to investigate the correlation among the debittering time, the sodium hydroxide concentration and the debittering temperature for the green olives of the Conservolea variety (the main Greek variety). Because the labor cost of processing green olives following the conventional procedure is high, this correlation can be used for the optimization of the green olives debittering without reutilization of the spent lye (it is a usual practice in Greece) or with reutilization of the spent lye (it must be applied today) or with complete or partial elimination of washings (it will be applied in the future).

2. MATERIALS AND METHODS

The investigation covered the year 1989-1990.

2.1. Materials

Green olive fruit of the Conservolea variety was harvested by the beginning of October in the area

of Stylis. The lot was medium sized approximately 201-230 olives per kilogram (commercial name: extra large (1)). It was processed the same day.

Sodium hydroxide solutions (C) 1.0%, 1.2%, 1.4%, 1.6%, 2.0%, 2.4% and 4.0% w/v, at the temperatures (T) of 2°, 5°, 10°, 15°, 20°, 25° and 30°C are used for the green olives lye treatment (debittering).

2.2. Description of the experiment

A portion of the olive fruit lot was distributed in the previous referred sodium hydroxide solution and remained in contact with the lye for a period (t), at the end of which the lye had penetrated about two thirds of the way to the pit in all the fruit treated.

2.3. Control of the green olives debittering

The course of green olives debittering was monitored by withdrawal of sequential olives

samples and by measuring, at definite time intervals, the penetration depth of the sodium hydroxide in the olives. The sodium hydroxide penetration depth in the olives was measured by the red colour, which was created by the addition one or two drops phenolphthalein indicator on the cutted along to the largest axis of the olives.

3. THE EXPERIMENTAL DATA

The experimental values of the green olives (Conservolea variety) debittering time (t), for the various sodium hydroxide concentration (C), at the various temperatures (T), are shown in table I.

4. RESULTS AND DISCUSSION

As the green table olives are debittered, the lye go across two biological media of very different

Table I.
The green olives debittering time (hours).

| $\begin{matrix} T (^{\circ}K) \\ C(NaOH) \\ (\% w/v) \end{matrix}$ | 275 | 278 | 283 | 288 | 293 | 298 | 303 |
|--|-------|-------|-------|-------|-------|-------|-------|
| 1.0 | - | 78.71 | 43.01 | 29.07 | 20.74 | 17.00 | 13.60 |
| 1.2 | 79.05 | 53.89 | 31.79 | 21.76 | 15.89 | 11.90 | 9.35 |
| 1.4 | 55.25 | 38.93 | 21.59 | 16.66 | 11.56 | 9.35 | 5.95 |
| 1.6 | 32.47 | 25.33 | 16.83 | 12.41 | 9.35 | 5.95 | 4.25 |
| 2.0 | 18.19 | 11.56 | 9.35 | 8.08 | 6.55 | 5.10 | 3.40 |
| 2.4 | 12.16 | 9.97 | 7.70 | 6.54 | 5.16 | 3.78 | 2.43 |
| 4.0 | 5.95 | 5.10 | 4.25 | 3.57 | 2.98 | 2.55 | 1.50 |

characteristics. Firstly, the lye cross all the waxy layer of the olive epicarp. Then it penetrates nearly the two thirds of the fruit mesocarp. These penetrations are based on the diffusion laws of Fick (7).

We process directly the experimental data and look to find a regression model, which gives the debittering time t (hours) as a function of the sodium hydroxide concentration C (gr NaOH/100 ml solution) and the debittering temperature T (°K). The

demand regression model has the following form:

$$t = a_0 C^{a_1} e^{a_2/T} \quad (1)$$

because (I) in each debittering temperature, there is a very satisfactory linear regression equation of form $\ln t = d_1 \ln C + d_0$ between the $\ln t$ and $\ln C$, and (II) in each sodium hydroxide concentration, there is a very satisfactory linear regression equation of form $\ln t = h_1 \left(\frac{1}{T}\right) + h_0$ between the $\ln t$ and $1/T$.

The model (1) is intrinsically linear and it can be expressed, by suitable transformation of the variables, in the following standard linear model form:

$$\ln t = b_0 + a_1 \ln C = a_2 \left(\frac{1}{T} \right) \quad (2)$$

where $b_0 = \ln a_0$.

The constants of equation (2) are determined by the method of least squares (4). According to this method, the 95% confidence limits for b_0 , a_0 , a_1 and a_2 are $b_0 = -14.509 \pm 1.771$, $a_0 = e^{-14.509 \pm 1.771}$, $a_1 = -1.674 \pm 0.135$ and $a_2 = 5153.675 \pm 510.624$.

As the fruit size, the epicarp hardness and the mesocarp cohesiveness are increased, the debittering time is also increased. At the debittering of green olive fruit of the Conservolea variety, for fixed debittering temperature, sodium hydroxide concentration and maturity stage of the fruit, the lye penetrates all the mesocarp of small size fruit (351-380 olives per kilogram), about two thirds of the way to the pit of the medium size fruit (201-230 olives per kilogram) and about one second of the way to the pit of the large size fruit (91-100 olives per kilograms), at the same time period. The epicarp hardness and the mesocarp cohesiveness are depended on the fruit variety, the maturity stage of the fruit, the situation of the cultivar and the type of culture (irrigated or non irrigated trees).

For the regression model (2), the values of multiple correlation coefficient R (0.978), of residual mean squares s^2 (0.04) and of rate $s/\ln t$ (0.083) give a very satisfactory correlation between the experimental data $\ln t_i$ and the predicted values $\ln \hat{t}_i$. For the regression model (1), the values of multiple correlation R (0.731), of residual mean square s^2 (41.9) and of rate s/\bar{t} (0.375) give a satisfactory correlation between the experimental data t_i and the predicted values \hat{t}_i . The regression model (1) is very satisfactory for $(C, T) \in D = [1.3\% \text{ w/v}, 2.6\% \text{ w/v}] \times [286^\circ\text{K}, 300^\circ\text{K}]$ (a region in which the Greek green olives are debittered), because the relative values of residual mean square s^2 and of rate s/\bar{t} are $s^2 = 1.824$ and $s/\bar{t} = 0.139$.

If the estimation of constants a_0 , a_1 and a_2 is based on the experimental data of region D, then the regression model (1) will have multiple correlation coefficient $R = 0.923$, residual mean square $s^2 = 0.724$ and rate $s/\bar{t} = 0.087$, and the 95% confidence limits of constants will be $a_0 = e^{-12.290 \pm 2.435}$, $a_1 = -1.702 \pm 0.226$ and $a_2 = 4490.945 \pm 705.851$.

5. CONCLUSIONS

At the debittering of medium size green olive fruit of the Conservolea variety, the debittering time (t , in hours) can be determined by an empirical equation, which gives it as a function of the sodium hydroxide concentration (C in % w/v) and the debittering temperature (T in $^\circ\text{K}$). This equation has the simple form $t = a_0 C^{a_1} \cdot e^{a_2/T}$ and is based on a set of experimental data in the region $[0.9\% \text{ w/v}, 4.1\% \text{ w/v}] \times [275^\circ\text{K}, 305^\circ\text{K}]$. The 95% confidence limits for a_0 , a_1 and a_2 which have been determined by the method of least squares, are $a_0 = e^{-14.509 \pm 1.771}$, $a_1 = -1.674 \pm 0.135$, $a_2 = 5153.675 \pm 510.624$. The determined equation is satisfactory in the region $[0.9\% \text{ w/v}, 4.1\% \text{ w/v}] \times [275^\circ\text{K}, 305^\circ\text{K}]$ and very satisfactory in the region $[1.3\% \text{ w/v}, 2.6\% \text{ w/v}] \times [286^\circ\text{K}, 300^\circ\text{K}]$.

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