Physical refining of edible oils using nitrogen as stripping gas. Process optimization

By **E. Graciani Constante, J.C. Bada Gancedo, F. Rodríguez Berbel** and **Mª V. Ruiz Méndez.**

Instituto de la Grasa, C.S.I.C., Avda. Padre García Tejero nº 4, 41012 Sevilla (Spain).

* The present work has been carried out with the financial support of the CICYT for project ALI 91-0720.

RESUMEN

Refinación física de aceites comestibles utilizando nitrógeno como gas de arrastre. Optimación del proceso.

La utilización de nitrógeno como gas de arrastre en la refinación física de aceites comestibles representa un avance tecnológico con ventajas potenciales, como la posibilidad tanto de recoger destilados de desodorización de alta calidad como de eliminar polución.

Los objetivos del presente trabajo son estudiar, evaluar y optimizar, tanto como sea posible, las variables que intervienen en el proceso (flujo de nitrógeno, temperatura de operación y altura de la capa de aceite en el desodorizador) en función de la calidad de los aceites obtenidos así como de los requerimientos de producción.

Los ensayos se han realizado con aceite de girasol en un desodorizador discontinuo de 200 kg de capacidad. Se ha utilizado un diseño de experimento en cuadrado latino de 4x4, constituido por tres factores a cuatro niveles cada uno.

Los resultados obtenidos han permitido establecer ábacos adecuados para determinar las condiciones más interesantes en las que llevar a cabo el proceso, según la calidad de aceite final deseada y la función objetivo de la factoría. Dichos ábacos son presentados en el trabajo. Los resultados se han contrastado mediante una nueva serie de experiencias.

PALABRAS-CLAVE: Aceite de girasol - Nitrógeno - Refinación física.

SUMMARY

Physical refining of edible oils using nitrogen as stripping gas. Process optimization.

The use of nitrogen as a stripping gas in physical refining of edible oils represents a technological improvement with potential advantages such as the possibilities of recovering high quality deodorized distillates and eliminating pollution.

The objectives of the present paper are to study, evaluate and optimize, as far as possible, independent variables involved in the process (nitrogen flow, operating temperature and the height of the oil layer inside the deodorizer) in reference to the quality of the obtained oils as well as the manufacturing requirements.

All the experiments were carried out with sunflower oil in a discontinuous deodorizer with a 200 Kg capacity. A 4x4 latin square experimental design was used, consisting of three factors, each of which had four different levels.

The results led to the establishment of charts that allow to determine the most suitable conditions in which to carry out the processing in accord with the desired quality of the finished oil and the functional objectives of the factory. These charts are presented in the paper. The results were checked by another set of experiments.

KEY-WORDS: Nitrogen - Physical refining - Sunflower oil.

1. INTRODUCTION

The use of nitrogen as a stripping gas in the physical refining and/or deodorization of edible oils represents a technological advance which is currently being studied and developed (Graciani Constante, E. et al., 1991; Huesa Lope, J. et al., 1990). Its use in the oil refining process depends on various factors, among which the following are the most important:

The cost of nitrogen in comparison to that of steam, which is currently used as the stripping gas in these processes, makes the change-over impossible. At present, certain suppliers of gases for industrial use are taking this fact into account when setting the prices of nitrogen supplies, so as to make them more competitive.

In some cases, adapting the equipment that is already in place in the factory to the new technology involves modifying the evacuation capacity of the stripping gas tubing and of the vacuum equipment. Under the process conditions nitrogen does not condense whereas steam does on the barometric condensers. Thus the volume of gas to be evacuated when nitrogen is used is greater than when steam is used. The two most simple ways of increasing evacuation capacity are:

a) To use steam ejectors of a greater capacity with or without a pump in combination.
b) To install mechanical pumps compatible with the predicted requirement for nitrogen and distillate evacuation.

The choice of the most suitable solution will depend on the prices of the different mecanisms, of the steam produced, of the Kwh, of the fuel, etc.

In some cases and for certain oils, when nitrogen is used as the stripping gas it may be profitable to make use of the volatile products obtained from deodorization. If the technology used allows these to be condensed and obtained with a sufficiently high quality, these may be commercially exploited. The "CRYOCOND" system, used in these trials condenses the distillates onto a cold surface (at a temperature of approximately -24°C.). They can then

be obtained with very little deterioration if they are drained without the temperature rising above 25-30°C, without a loss of vacuum and without the use of life steam to fuse them and strip them from the columns. As the products are natural and in great demand by the pharmaceutical, cosmetic and food industries, they will have a much higher value when isolated under these conditions.

In order to keep the production costs resulting from refining and deodorizing as low as possible, the time which the oils remain in the deodorizers must be short, the working temperatures and gas flows must be such that a high efficiency is achieved and the costs of preparing the oils prior to submitting them to these operations must be as low as possible.

Finally, the characteristics and qualities of the finished oils should be such as to make the oils as commercially profitable as possible.

Other factors to be taken into account are the effects that modification of the distillate condensation and vacuum production equipment will have on the levels of pollution resulting from the wastewaters and from the gases released into the atmosphere and, furthermore, what effects these modifications will have on water consumption.

An overall evaluation, using an objective function, of all the above mentioned factors, will allow an assessment to be made of the economic viability of such a change in technology in any particular factory, as well as of the convenience or not of implanting it.

The objectives of the present work are to study, evaluate and optimize, as far as possible, the physical refining of edible oils using nitrogen as the stripping gas and to determine the influence of fundamental and independent variables within the process (nitrogen flow, the temperature at which the process takes place and the height of the oil layer inside the deodorizer) on the quality of the obtained oils, so that, in accord with manufacturing requirements, work protocols can be established from which production costs and the value of the refined oils obtained can be calculated.

2. EXPERIMENTAL

2.1 Neutralizing distillation and/or physical refining of sunflower oil.

2.1.1. *Oil used*

All assays were carried out using aliquots taken from a homogeneous mixture of two different lots of sunflower oil:

1st) Degummed, neutralized and bleached oil.
One lot of 2000 Kg of chemically-neutralised, degummed oil supplied by an oil plant. This oil had been bleached under vacuum in batches of 200 Kg with bleaching earth (about 0.20% of the quantity of oil) at a temperature of 90 to 100°C for 20 minutes.

2nd) Degummed, un-neutralized and un-bleached oil.
One lot of 1000 Kg of crude sunflower oil from the same supplier as the first. This oil was degummed, using the traditional method, in lots of 200 Kg using commercial phosphoric acid (about 0.20% of the quantity of oil) and water (in the same proportion) at a temperature of 40°C for 20 minutes. The separation of the gums was carried out by centrifugation at 80°C.

The homogeneous mixture of both oils produced a single degummed oil with a degree of acidity of 0.56%. The colour, measured by Lovibond, was 2.5 red units, 35 yellow units and 0.1 blue units. The analytical data are shown in the different tables and graphs under the name "Initial oil" (i.o.).

For the assays to confirm the obtained results, a mixture of sunflower oil was prepared. This mixture consisted of 2000 Kg of the oil which had been degummed, chemically neutralised and bleached using the same conditions as those described previously and 1000 Kg of crude oil which had been degummed and bleached also using the previously described conditions. Its colour measured by Lovibond was 2 red units, 20 yellow units and 0.1 blue units, and it had an acidity of 0.54 %.

2.1.2. *Deodorizer*

A discontinuous cylindrical deodorizer, with an internal diameter of 63 cm, was used. This had a maximum functional capacity of 220 Kg of oil with an inlet for the stripping gas in the form of a loop situated in its lower part (at some 10 cm from the base of the vessel) with a radius of 18.5 cm. The loop was equipped with 80 orifices oriented towards the bottom at an angle of 45° with respect to the vertical.

2.1.3. *Vacuum and distillate condensation apparatus.*

The apparatus used has been described in a previous publication (Graciani Constante, E., 1991). This consisted of a vacuum system made up of a ROOTS pump, capable of evacuating 500 m^3/h, in series with a model 433 HUCKEPACK pump capable of evacuating 250 m^3/h. For the condensation and collection of distillates a "VACUOFROST" system was used. This consisted of CRYOCOND refrigerated condensation columns. These columns, which had already been tested and which are described in the previously cited work, allow the condensation of the greater part of the distillates through contact with the cold surface(-24°C). In the tests reported here, the problems previously found and described by Graciani Constante, E. et al. (1991) did not arise, since there was no condensation of solid fatty acids. The formation on the cold surface of a layer of condensates which form a barrier between the surface and the circulating gases, can lead to less condensation and can induce major changes in the vacuum at the head of the deodorizer as a result of an increase in the temperature of the gases to be evacuated.

2.1.4. *Stripping gas: its control.*

Injection of the stripping gas-nitrogen of a suitable quality-was regulated at some 15-20 cm from the deodorizer by means of a mass meter (with a mean error of between 0.2 and 0.5%) that operated at an absolute pressure of 2 bars and at room temperature. The nitrogen flow rates used in every case are reported in Table I. The absolute quantity of nitrogen introduced into the deodorizer can be calculated from the flow rate used, from the quantity of oil introduced and from the duration of the assay.

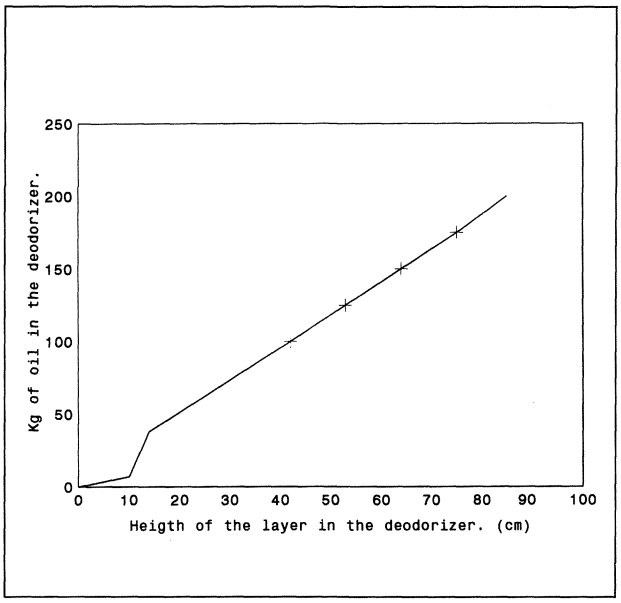
Note: One cubic metre of nitrogen under normal conditions (0 °C and at a pressure of one atmosphere) is equivalent to 44.625 moles, or 1.25 Kg of nitrogen, and is comparable to 0.803 Kg of steam.

2.1.5. *Level of oil inside the deodorizer.*

This level depends on the quantity of oil to be deodorized in each assay. The different levels used are shown in Graph 1.

2.1.6. *Deodorization process.*

In all of the operations, once the oil (at room temperature) has been introduced into the deodorizer (also at room temperature and under vacuum), heating begins using a stream of a suitable liquid heated to a maximum temperature some 5°C higher than that set for the test being conducted. In this way localised heating of the oil was avoided. The heating system is regulated by the temperature of the oil in the deodorizer, which ensures that the operating temperature has a maximum variation of 1.0°C.



Graph 1
Height of the oil layer in the deodorizer as a function of the quantity of oil.

Table I
Operation Conditions used in the different assays

N_2 Flow (m^3/T·h) (*)	Operation Temperature (°C). (**) 240	248	256	265
0.8	175 Kg Oil (***) E_1 t = 0.75 h p = 3.75 mmHg	150 Kg Oil E_2 t = 0.67 h p = 3.75 mmHg	125 Kg Oil E_3 t = 0.75 h p = 3.75 mmHg	100 Kg Oil E_4 t = 1.00 h p = 4.00 mmHg
1.4	150 Kg Oil E_5 t = 0.75 h p = 3.50 mmHg	125 Kg Oil E_6 t = 0.50 h p = 4.00 mmHg	100 Kg Oil E_7 t = 0.60 h p = 3.50 mmHg	175 Kg Oil E_8 t = 1.25 h p = 5.00 mmHg
2.0	125 Kg Oil E_9 t = 0.60 h p = 5.00 mmHg	100 Kg Oil E_{10} t = 0.92 h p = 4.00 mmHg	175 Kg Oil E_{11} t = 1.08 h p = 6.00 mmHg	150 Kg Oil E_{12} t = 1.25 h p = 6.00 mmHg
3.0	100 Kg Oil E_{13} t = 0.67 h p = 6.00 mmHg	175 Kg Oil E_{14} t = 0.83 h p = 5.20 mmHg	150 Kg Oil E_{15} t = 0.92 h p = 6.00 mmHg	125 Kg Oil E_{16} t = 1.00 h p = 6.00 mmHg

Notes:
(*) Measurement accuracy = ± 0,2 %
(**) Measurement accuracy = ± 1° C
(***) Measurement accuracy = ± 300 g. Taken Samples = 1l

E_a Experiment n.º a
t time (in hours) necessary to reach the operating temperature. Nitrogen was introduced at 90°C - 100°C
p Deodorizer head pressure (in millibars)

Introduction of the stripping gas starts when the temperature of the oil is between 90 and 100°C. Zero time is the time when the oil reaches the operating temperature. From this moment onwards the operating conditions are maintained constant for 5 consecutive hours, during which time samples are taken. Subsequently, the oil is cooled as rapidly as possible and once it has reached a temperature of between 110 and 80°C the flow of the stripping gas is stopped.

The cooled oil obtained without any type of additive is considered to be the finished product.

The operating conditions used in each trial are summarized in Table I.

2.2 Sampling

Using a suitable device, samples of the oils were taken from inside the deodorizer during the experiment without altering the operating conditions (except for the small decrease in the oil content in the deodorizer which was taken into account in the calculations). In all cases the samples taken were of between 0.8 and 0.9 l. The samples were cooled under the same vacuum conditions as those pertaining during the experiment, in a sample colector, but without any passage of nitrogen. Once they had reached room temperature, they were removed to the outside. All samples were stored at between -22 and -24°C.

Samples were taken at 0, 1.5, 3, 4, and 5 hours, and one was taken of the finished oil as well.

Several 1 l bottles of bioriented PVC were filled with the finished oil and these were stored for one year in the dark at room temperature prior to their analysis.

Samples of the original oil were taken prior to introduction into the deodorizer.

2.3 Sample analysis.

- Acidity. UNE norm 55011
- Peroxide index. UNE norm 55023
- p-anisidine index. UNE norm 55127
- Total oxidation index: twice the peroxide index plus the p-anisidine index.
- Determination of the composition in fatty acids in position two of the triacylglycerols. UNE norm 55079.
- Tocopherol determination. UNE norm 55073 and by HPLC. An analytical column with a 4 mm internal diameter and 250 mm long was used. The packing material was silica (5 μm) and the mobile phase was hexane-isopropanol (99:1) at a flow rate of 0.9 ml/min. A fluorescence detector was used (excitation wavelength 290 nm; emission wavelength 330 nm)
- Stability by Rancimat at 98°C and with an air flow of 18 l/h.
- Lovibond colour, 5 1/4" test-tubes.
- Determination of sterols. Norm UNE 55019. Internal standard: cholesterol.
- Organoleptic characteristics: judged by specialists.

2.4 Calculation of efficiency

In all cases, the efficiency of distillation of the fatty acids present in the oils was determined using the formula established theoretically for technological distillation operations using a stripping gas(Vian, A., et al., 1964):

$$E_{1\text{-}2} = \frac{p}{p_e\,(N + C_1 - C_2)}\left(C_1 - C_2 + A \ln \frac{C_1}{C_2}\right)$$

$E_{1\text{-}2}$ represents the efficiency of the neutralizing distillation between times 1 and 2.

N is the number of moles of stripping gas passing through the deodorizer during the time of operation.

C_1 and C_2 are moles of acids present in the oil at times 1 and 2.

A moles of oil; if, during the time period under consideration, we take several samples of oil. A is the weighted mean number of moles of oil present during the experiment.

p represents the vapour pressure at the head of the deodorizer.

p_e is the mean value of vapour pressure of the fatty acids present in the oil. This, in accordance with the literature consulted (Graciani Constante, E., *et al.*,1991; Weast, A.C., 1984; Paquot, C., *et al.*, 1962) was measured at 28 mm Hg, 32 mm Hg, 44 mm Hg and 60 mm Hg for the temperatures, 240, 248, 256 and 265°C, respectively.

2.5 Experimental design

A 4 x 4 latin square design was used, consisting of three factors, each of which had four different levels (Dugué, D., 1969) (Table I).

2.6 Statistical analysis

Results were studied by an analysis of variance (Dugué, D., 1969; Barella i Miró, A., 1977) and the fits were obtained by the least squares method (Davies, O.L., 1966).

2.7 Confirmation of the results

To confirm the results obtained from the established design, 13 new experiments were designed. The characteristics of each of the deodorizations carried out are summarized in Table VI.

Table VI
Operation Conditions used in the assays performed to confirm the previous results.

N_2 Flow (m^3/T·h) (*)	Operation Temperature (°C). (**) 230	240	248	256	265
1.4		100 Kg Oil E_{17} t = 0.75 h p = 3.00 mmHg	175 Kg Oil E_{18} t = 1.00 h p = 3.00 mmHg	175 Kg Oil E_{19} t = 1.50 h p = 4.50 mmHg	100 Kg Oil (***) E_{20} t = 1.00 h p = 3.00 mmHg
2.0		100 Kg Oil E_{21} t = 0.75 h p = 3.00 mmHg	175 Kg Oil E_{22} t = 0.83 h p = 3.00 mmHg	100 Kg Oil E_{23} t = 1.00 h p = 2.50 mmHg	100 Kg Oil E_{24} t = 1.16 h p = 2.50 mmHg
2.0		175 Kg Oil E_{25} t = 0.83 h p = 3.00 mmHg		175 Kg Oil E_{26} t = 1.25 h p = 3.75 mmHg	
3.0	100 Kg Oil E_{27} t = 0.50 h p = 3.00 mmHg		100 Kg Oil E_{28} t = 0.67 h p =3.00 mmHg		
4.0	100 Kg Oil E_{29} t = 0.50 h p = 3.00 mmHg				

Notes
(*) Measurement accuracy = ± 0,2 %
(**) Measurement accuracy = ± 1° C
(***) Measurement accuracy = ± 300 g. Taken Samples = 1l

E_a Experiment n.º a
t time (in hours) necessary to reach the operating temperature. Nitrogen was introduced at 90°C - 100°C
p Deodorizer head pressure (in millibars).

3. RESULTS AND DISCUSSION

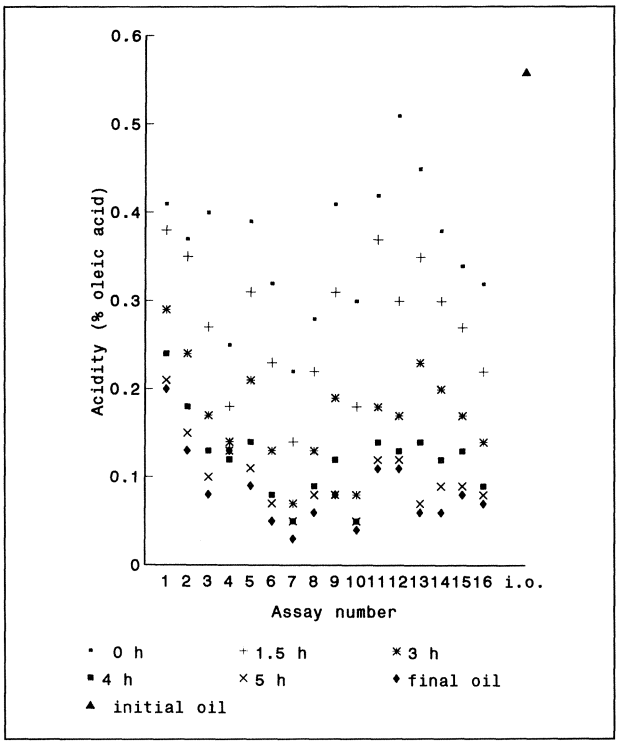
3.1 Results obtained in the design of experiments

The values measured for percentage acidity, peroxide index, p-anisidine index, total oxidation index, alfa-tocopherol content, gamma-tocopherol content and oil stability for every sample taken are shown in Graphs 2, 3, 4, 5, 6, 7 and 8, respectively. In Table II data on the composition of the fatty acids present in position two of the triacylglycerols are shown and in Table III the colour measurements taken from the different sampled oils are summarised.

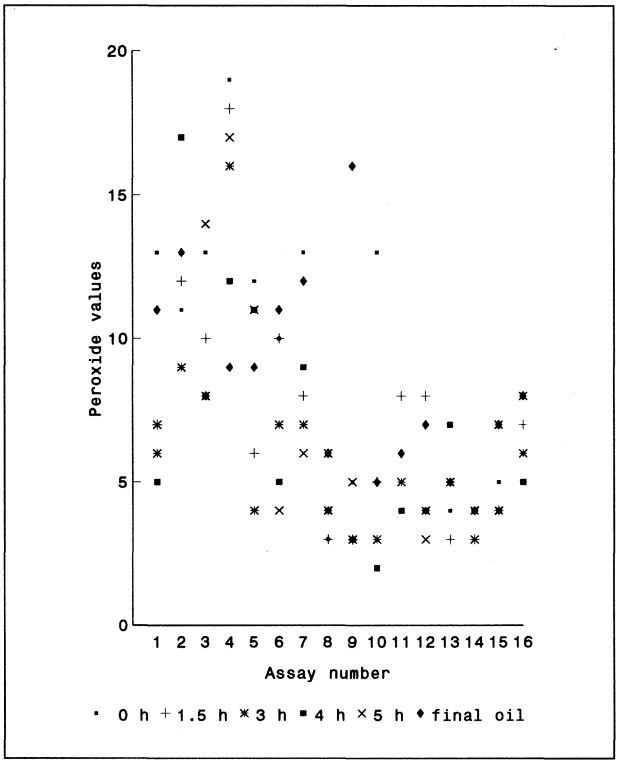
All oils obtained, with the exception of those from assays 1 and 2, were judged, by the different experts consulted, to have totally positive organoleptic characteristics and to be suitable for normal consumption.

3.2 Evaluation of the results and conclusions obtained from the results of the experimental design.

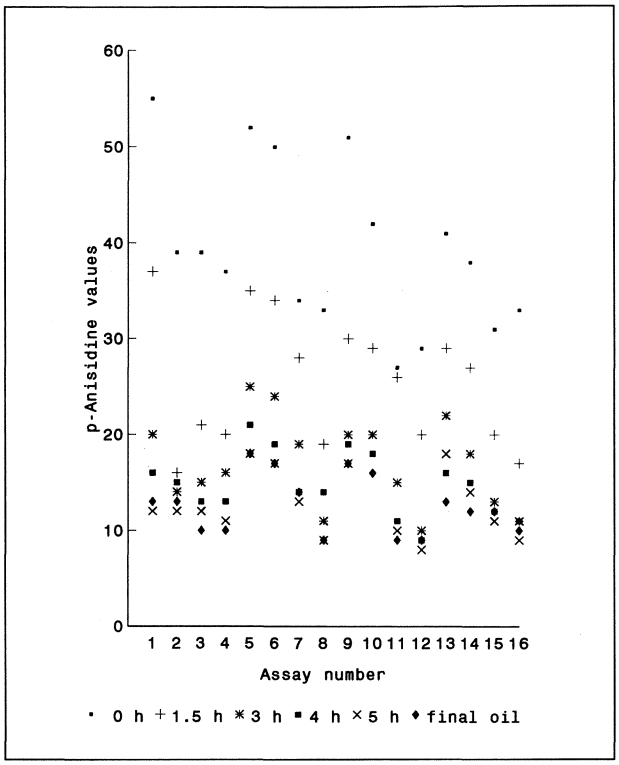
Statistical analysis of the results, according to the experimental designed, allows one to evaluate the contribution of any of the independent variables to the total variance and the influence that each independent variable has on the dependent variable (Table IV).



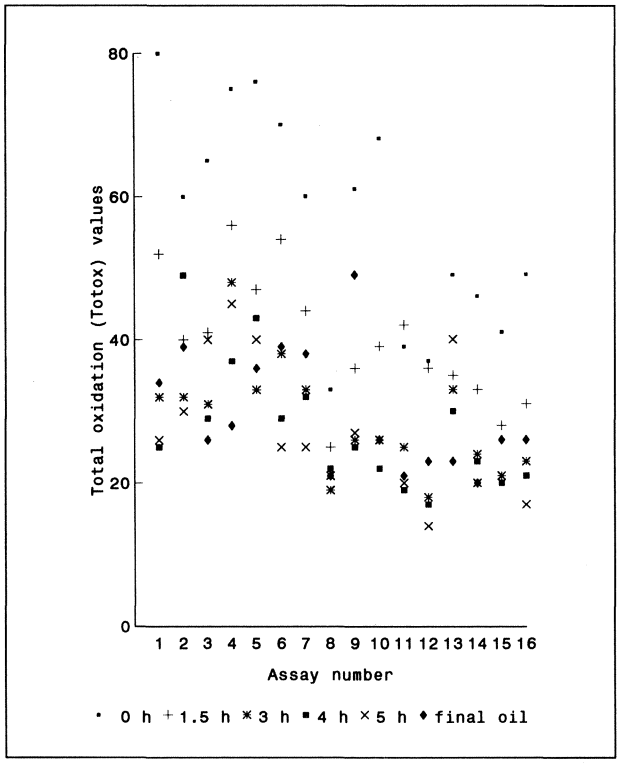
Graph 2
Acidity (% oleic acid) of the oils obtained.



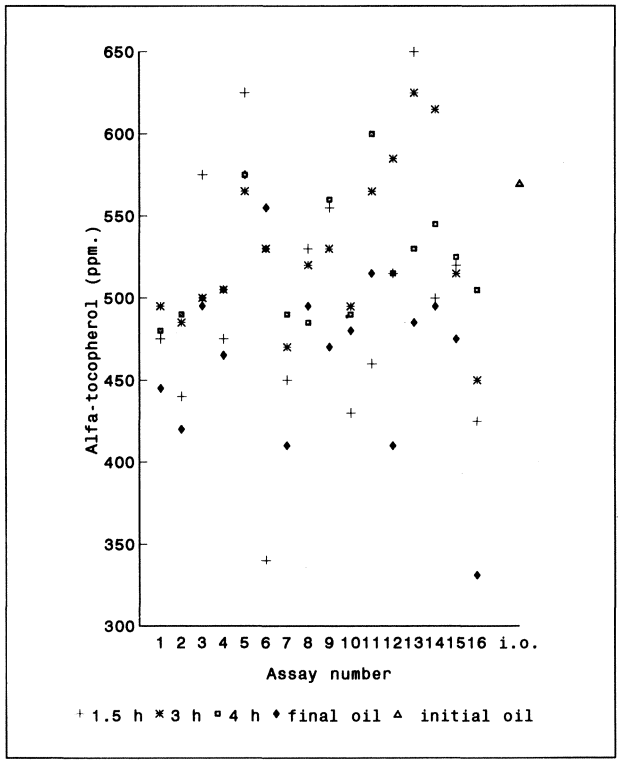
Graph 3
Peroxide values of the oils obtained.



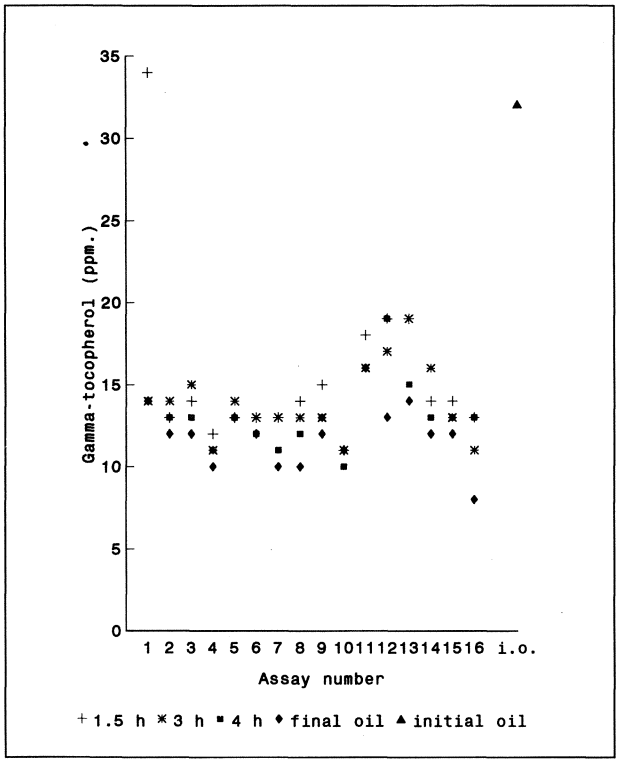
Graph 4
P-Anisidine values of the oils obtained.



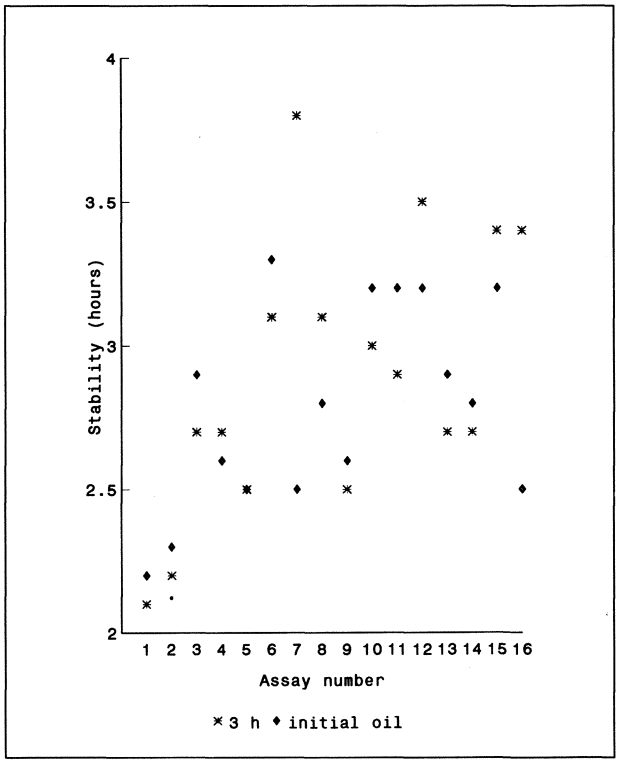
Graph 5
Total oxidation (Totox) values of the oils obtained.



Graph 6
Alfa-tocopherol contents of the oils obtained.



Graph 7
Gamma-tocopherol contents of the oils obtained.



Graph 8
Stabilities of the oils obtained.

Table II
Results of the neutralizing distillation: Composition of fatty acids in the ß position of the acylglycerols

N_2 Flow ($m^3/T \cdot h$)	Time (h)	Operation Temperature 240°C 16:0	18:1	18:2	248°C 16:0	18:1	18:2	256°C 16:0	18:1	18:2	265°C 16:0	18:1	18:2
		175 Kg of oil			150 Kg of oil			125 Kg of oil			100 Kg of oil		
0.8	3	0.61	30.1	69.1	0.42	32.1	66.8	0.97	30.9	67.8	0.70	31.7	67.3
	Final	0.78	31.4	66.8	0.67	31.3	67.0	1.17	33.2	65.2	1.51	32.6	64.5
		150 Kg of oil			125 Kg of oil			100 Kg of oil			175 Kg of oil		
1.4	3	0.46	31.5	67.4	0.53	32.6	65.9	0.55	32.6	66.8	1.38	33.4	64.7
	Final	0.62	30.7	67.4	0.87	31.1	67.1	1.04	33.6	64.5	1.12	31.6	64.7
		125 Kg of oil			100 Kg of oil			175 Kg of oil			150 Kg of oil		
2.0	3	0.34	32.1	67.2	0.57	32.3	66.6	1.04	33.6	64.5	1.12	31.6	66.4
	Final	0.72	34.2	64.3	0.96	31.6	66.4	1.31	32.5	65.7	1.50	34.7	62.4
		100 Kg of oil			175 Kg of oil			150 Kg of oil			125 Kg of oil		
3.0	3	0.52	31.3	67.3	0.66	32.2	66.6	0.58	32.8	66.2	1.04	33.4	64.3
	Final	0.56	32.5	66.4	0.66	32.2	66.4	1.05	32.0	66.1	1.42	32.5	63.7

% of fatty acid in ß position of the acylglycerols of the initial oil.
16:0 = 0.49%; 18:1 = 32.0%; 18:2 = 67.4%

Table III
Results of the neutralizing distillation: Lovibond colour

N_2 Flow (m^3/T·h)	Time (h)	Operation Temperature															
		240°C				248°C				256°C				265°C			
		R	Y	B	N	R	Y	B	N	R	Y	B	N	R	Y	B	N
		175 Kg of oil				150 Kg of oil				125 Kg of oil				100 Kg of oil			
	0	2.1	21			3.0	30			3.0	26		0.2	3.0	30		
	1.5	2.4	24			2.7	27		0.1	3.0	30			3.0	30		
0.8	3	3.0	30	0.7		2.7	27		0.1	3.0	30	0.1		3.3	33		0.1
	4	2.6	20		0.1	3.0	30			3.0	30			3.7	30		
	5	3.0	30			3.0	30			3.0	30		0.1	4.1	35		
	Final	3.0	30	0.2	0.1	3.3	33		0.2	3.3	33		0.1	3.7	35		0.1
		150 Kg of oil				125 Kg of oil				100 Kg of oil				175 Kg of oil			
	0	3.0	19		0.1	3.5	30		0.1	3.0	30			2.6	30		
	1.5	3.0	30			3.0	30			3.4	35			3.0	30		
1.4	3	3.0	30			4.0	40			3.0	30			3.0	30		
	4	3.1	30		0.1	3.4	35		0.2	3.5	30		0.1	3.0	30		
	5	3.0	30			3.4	30		0.1	3.2	30		0.1	3.0	30		0.1
	Final	3.5	35			3.4	30		0.1	4.0	20		0.1	3.5	30		0.1
		125 Kg of oil				100 Kg of oil				175 Kg of oil				150 Kg of oil			
	0	3.1	35			3.5	35		0.1	3.1	30						
	1.5	3.0	30	0.2		3.1	30			2.9	20			3.3	35		0.1
2.0	3	3.0	30			3.1	30			2.9	29		0.1	3.0	30	0.1	
	4	3.0	30			3.4	35			2.7	27		0.2	3.5	35	0.1	0.1
	5	3.5	35		0.1	3.7	35		0.1	3.0	30			3.8	35		
	Final	3.7	35	0.1	0.1	3.6	35		0.1	3.5	35		0.1	4.1	35		
		100 Kg of oil				175 Kg of oil				150 Kg of oil				125 Kg of oil			
	0	3.6	35		0.1	3.5	35			3.0	30			3.7	16		0.2
	1.5	2.8	28		0.2	3.3	30		0.1	3.0	30			4.0	40	0.2	
3.0	3	3.5	30			3.5	35		0.2	3.0	30			4.0	40	0.3	
	4	3.5	35			3.5	35		0.1	3.0	30			4.0	40		
	5	3.5	35		0.1	3.3	30		0.2	3.0	30			4.0	40		
	Final	3.8	35			3.3	33			3.5	30		0.1	4.4	40		

Initial oil (i.o.) Colour units: 2.5 R (Red); 35 Y (Yellow); 0.1 B (Blue); N (Neutral)

The experimental design does not allow a statistical analysis of the interactions among the different independent variables to be made; the variance values due to the interactions are accumulated in the residual variance. For this reason, the functions applied to fit the results, cannot have xy, xz or yz terms (x, y and z representing the three independent variables).

In the present study, to obtain representative functions of the assays carried out, a second degree function, lacking the terms previously mentioned, has been adopted: x represents the flow of nitrogen in m^3 per metric tonne and per hour; y, the operating temperature in °C; z, the height in cm (suitably weighted) of the oil layer in the deodorizer. The results obtained can be seen in Table V. Using a complete second degree function as a fit would give rise to lower variance values and to higher correlation coefficients than those obtained, given that the minor square method is used to verify the fit. However, for reasons previously explained, the value of these functions in explaining the results is less than that of the fit functions used here.

Tables IV and V also include the results of the calculations of efficiency of the different fractional distillation operations using a stripping gas to eliminate the free fatty acids present in the oils; i.e, the efficiency of the physical refining of the oils.

Table IV
Influence of the independent variables on the results

Results	Nitrogen Flow		Temperature (Snedecor Law (F) and Significance)		Height of oil layer	
Vacuum	12.5	99.0%	2.5		0.9	
Pre-heating time	2.7		14.4	99.0%	5.0	99.5%
Acidity at 0 hour	1.7		1.1		1.4	
Acidity at 1.5 h	0.2		0.9		2.4	
Acidity at 3 h	8.3	97.5%	11.5	99.0%	8.6	97.5%
Acidity at 4 h	15.7	99.0%	4.3	90.0%	10.7	99.0%
Final oil acidity	7.6	97.5%	1.7		1.2	
Efficiency between 0 - 1.5 h	1.2		0.05		2.4	
Efficiency between 0 - 3 h	10.7	99.0%	5.1	95.0%	1.6	
Efficiency between 0 - 4 h	7.9	97.5%	9.0	97.7%	3.5	90.0%
Efficiency between 1.5 - 3 h	7.8	97.5%	6.3	97.5%	0.5	
Efficiency between 3 - 4 h	18.7	99.0%	1.9		2.1	
Efficiency between 4 - 5 h	0.4		3.2		0.3	
Efficiency from begining to 3 h	74.4	99.0%	24.6	99.0%	17.7	99.0%
Efficiency from begining to end	5.3	95.0%	6.8	97.5%	1.7	
Peroxide value at 0 h	4.2	90.0%	0.08		1.7	
Peroxide value at 1.5 h	4.2	90.0%	1.3		0.8	
Peroxide value at 3 h	5.4	95.0%	1.2		1.5	
Peroxide value at 4 h	3.6	90.0%	0.05		1.7	
Final oil Peroxide value	1.8		0.7		1.6	
p-Anisidine value at 0 h	1.9		14.8	99.0%	1.7	
p-Anisidine value at 1.5 h	1.3		5.9	95.5%	0.7	
p-Anisidine value at 3 h	2.1		11.7	99.0%	1.9	
p-Anisidine value at 4 h	3.7	90.0%	14.8	99.0%	0.8	
Final oil p-Anisidine value	3.7	90.0%	12.9	99.0%	2.6	
Totox value at 0 h	3.4	90.0%	2.2		1.3	
Totox value at 1.5 h	1.9		0.3		0.3	
Totox value at 3 h	3.0		0.4		2.0	
Totox value at 4 h	3.9	90.0%	1.1		1.8	
Final oil totox value	1.3		1.5		1.3	
ß-position on 16:0 at 3 h	0.2		7.5	97.5%	2.3	
Final oil ß-position on 16:0	2.2		24.5		0.4	
ß-position on 18:1 at 3 h	2.3		2.1		0.2	
Final oil ß-position on 18:1	1.3		1.2		0.4	
ß-position on 18:2 at 3 h	2.8		3.3	90.0%	0.5	
Final oil ß-position on 18:2	1.5		7.5	97.5%	0.6	
Oil stability at 3 h	7.1	97.5%	9.0	97.5%	1.5	
Final oil stability	8.1	97.5%	14.1	99.0%	0.2	
α-Tocopherol at 1.5 h	0.2		2.3		0.3	
α-Tocopherol at 3 h	1.1		0.6		0.6	
α-Tocopherol at 4 h	1.0		0.6		0.3	
Final oil α- Tocopherol	0.7		0.8		0.4	

Table V
Values for the parameters corresponding to the different fits applied
$a x + b y + c z + d x^2 + e y^2 + f z^2 + g$ = Value for the dependent variable

Dependent variable	a	b	c	d	e	f	g	Variance
Acidity								
0 h	$-1.27.10^{-1}$	0.393	$2.81.10^{-2}$	$2.45.10^{-4}$	$5.23.10^{-3}$	$-1.99.10^{-4}$	15.85	$5.23.10^{-1}$
1.5 h (*)	$-8.00.10^{-2}$	-0.080	$1.26.10^{-2}$	$1.51.10^{-4}$	$2.23.10^{-2}$	$-7.94.10^{-5}$	10.46	$1.74.10^{-3}$
3 h (*)	$-1.25.10^{-1}$	-0.182	$8.93.10^{-3}$	$2.41.10^{-4}$	$4.62.10^{-2}$	$-5.67.10^{-5}$	16.17	$4.50.10^{-4}$
4 h (*)	$-8.86.10^{-2}$	-0.166	$5.43.10^{-3}$	$1.72.10^{-4}$	$3.95.10^{-2}$	$-2.84.10^{-5}$	11.47	$4.72.10^{-4}$
Final oil	$-9.48.10^{-2}$	-0.133	$8.93.10^{-4}$	$1.87.10^{-4}$	$2.87.10^{-2}$	$-5.67.10^{-6}$	12.14	$6.36.10^{-4}$
Efficiencies of vaporization								
Initial oil - 3h	0.467	-0.106	$-7.90.10^{-3}$	$-9.37.10^{-4}$	$-2.59.10^{-2}$	$1.70.10^{-5}$	-56.79	$3.39.10^{-3}$
Initial - Final oil	0.239	-0.175	$-2.33.10^{-2}$	$-4.96.10^{-4}$	$1.38.10^{-2}$	$-2.33.10^{-4}$	-28.33	$3.63.10^{-3}$
0 h - 1.5 h	0.098	0.194	$1.71.10^{-2}$	$-1.93.10^{-4}$	$-6.86.10^{-2}$	$-2.21.10^{-4}$	-12.44	$1.18.10^{-2}$
0 h - 3 h	0.374	0.257	$1.41.10^{-2}$	$-7.50.10^{-4}$	$-9.51.10^{-2}$	$-1.59.10^{-4}$	-46.48	$4.74.10^{-3}$
0 h - 4 h	0.282	0.165	$2.91.10^{-2}$	$-5.77.10^{-4}$	$-7.01.10^{-2}$	$-3.28.10^{-4}$	-34.54	$4.53.10^{-3}$
1.5 h - 3 h	0.647	0.323	$1.06.10^{-2}$	$-1.30.10^{-3}$	$-1.23.10^{-1}$	$-9.08.10^{-5}$	-80.05	$7.18.10^{-2}$
3 h - 4 h	0.054	0.023	$5.49.10^{-2}$	$-1.55.10^{-4}$	$-2.26.10^{-2}$	$-5.22.10^{-4}$	-4.73	$1.78.10^{-2}$
Efficiencies of vaporization calculated by means of theoretical fits.								
Initial oil - 3 h	0.489	-0.120		$-9.81.10^{-4}$	$-2.17.10^{-2}$		-59.85	$1.32.10^{-2}$
Initial - Final oil	0.219	-0.164		$-4.58.10^{-4}$	$9.89.10^{-2}$		-25.35	$1.51.10^{-2}$
0 h - 3 h (*)	0.374	0.259		$-7.50.10^{-4}$	$-9.51.10^{-2}$		-46.21	$1.03.10^{-2}$
0 h - 4 h (*)	0.282	0.165		$-5.77.10^{-4}$	$-7.01.10^{-2}$		-33.85	$7.58.10^{-2}$
1.5 h - 3 h (*)	0.647	0.323		$-1.30.10^{-3}$	$-1.23.10^{-1}$		-79.75	$2.06.10^{-2}$
3 h - 4 h (*)	0.055	0.024		$-1.55.10^{-4}$	$-2.26.10^{-2}$		-3.11	$3.61.10^{-2}$

Notes: x Operation temperature, (°C)
y Nitrogen flow, ($m^3/T \cdot h$)
z Height of the layer within the deodorizer, (cm)
(*)The relevant charts can be consulted: Graphs 9, 10, 11, 12, 13, 14, 15.

The vacuum obtained at the deodorizer head in the different operations performed depends, to a great extent, only on the flow rate of nitrogen used in the assay (Table IV). However, the quantity of stripping gas evacuated by the pumps depends as much on the flow rate used as on the height of the oil layer (with significance levels of 97.5 and 99%, respectively).

One interpretation of this fact is that, as the vacuum produced by the pumps only depends on the flow rate of the stripping gas even though, in some assays, the absolute amount of gas to be evacuated is greater for lower than for higher flow rates, there are other variables that also have an influence on the process of elimination of the stripping gas. Among these the following have to be considered: the design of the nitrogen distributors; the design of the distillate condensers; the temperature gradient of the distillates and of the stripping gas up to the distillate condensers, etc. A suitable design to ensure the evacuation of the nitrogen and the condensation of the distillates should take into account the fact that the oleins have, or should have, a high value in certain oils.

We wanted to study the behaviour of the oxidation products (peroxides, etc.) during the process and to verify the influence of the different independent variables on them. To do this, we worked with the mixture described in (2.1.1) which already has peroxide compounds from the unbleached oil component.

With regards to the degree of oxidation and the stability of the refined oils obtained (Graphs 3, 4, 5 and 8 and Table IV), it can be seen that the peroxide values depend on the gas flow; that the p-anisidine values depend on the operating temperature and that the total oxidation values do not depend on the value of any of the three independent variables studied. The values reached for these indices after 1.5 h of experimentation, are good in almost all cases. The overall stability of the oils depends as much on the flow rate of the gas as on the temperature at which the operation is performed and the values obtained can be considered adequate except when the conditions employed in assays E_1 and E_2 are used.

Within the range of variability studied for the different independent variables, the tocopherol contents of the

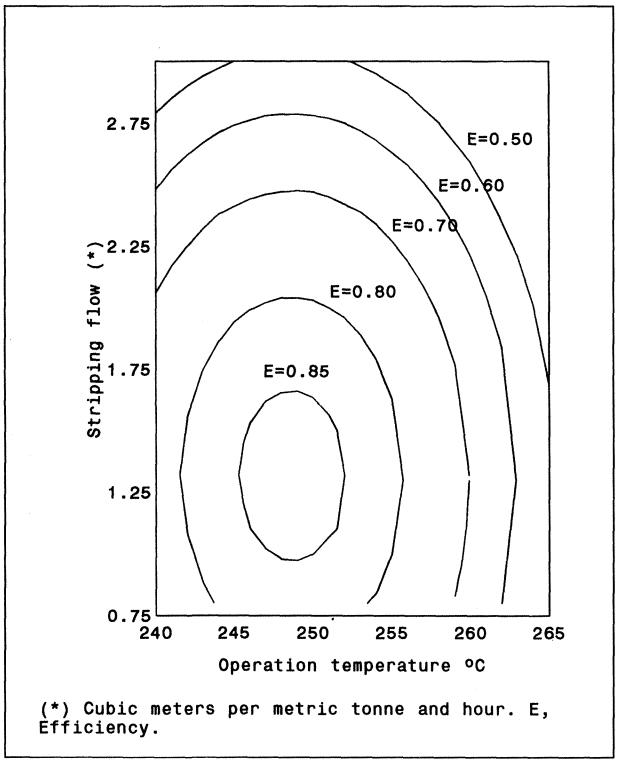
different oils (Graphs 6 and 7) do not depend on any of these variables (significance > 90%) (Table IV). In oils subjected to the operating temperatures for up to four hours there were no significant losses of tocopherol. In the worst of cases the loss did not represent more than 23% of the initial oil content. In the majority of cases the losses did not reach 15%. Heating for longer than four hours induced a significant loss in the tocopherol content of the oils; these losses being greater, the higher the temperature used. In the worst of cases, these losses reached up to 50%. Generally, the losses of gamma-tocopherol were greater than those of beta-tocopherol.

The colour of the oils (Table III) did not suffer any reduction as a result of the different treatments when, as in the present case, the initial oil was intensely coloured. The values obtained for the different colour measurements made on the oils subjected to treatments lasting 3 h under the conditions of the assay show that there was an increase in the red component, compared to the level in the initial oil, while there was a decrease in the yellow component. The resulting oils had a higher intensity of reds and yellows than those treated for 3 h. A slight decrease in the yellow coloration was only seen when this was compared with the level in the initial oil.

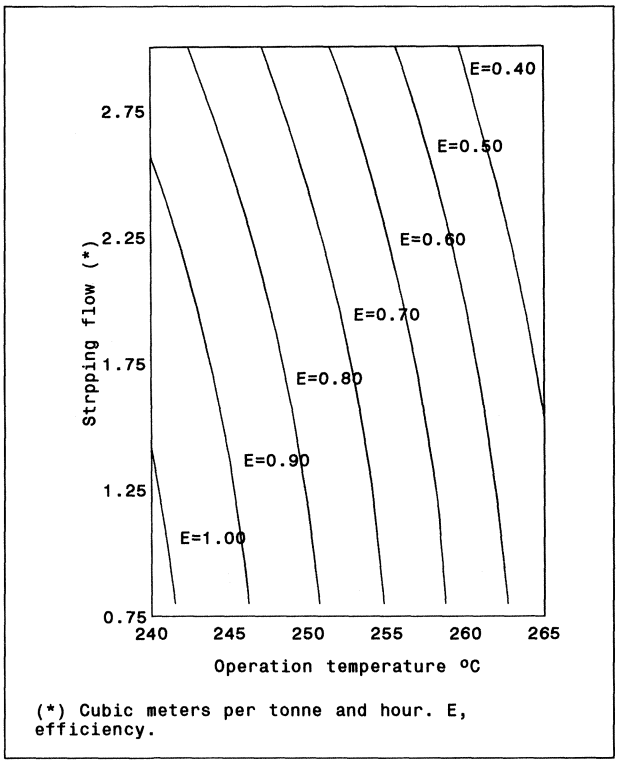
When evaluating the results obtained for the deacidification of the oils as a function of the treatments to which the oils were subjected, it is necessary to take into account the fact that operating at temperatures above 220°C favours thermolysis of the acylglycerols (Nawar, W.W., 1985) and the formation of ester bonds among the free hydroxyl groups and the fatty acids present in the oils. As a result of these reactions, changes occur in the composition of the fatty acids in the beta position of the triacylglycerols (Gracián, J. *et al.*, 1971). To reduce these changes to undetectable levels in the deodorized oils, it is necessary to work under conditions which prevent these two reactions from taking place, either by using lower operating temperatures or by performing the distillation of the fatty acids so efficiently that they are eliminated before they can take part in these esterification reactions.

The results obtained from the analysis of the composition of the fatty acids in the beta position in the triacylglycerols (Table II) indicate that such an alteration is a function of temperature for the 16:0 and 18:0 acids, with degrees of significance of 90% and 99%, respectively - Table IV - and that the alteration is greater the longer the duration of the physical refining process. In the same way it can be seen that the alterations are fewer in those experiments where the efficiency of stripping with nitrogen is high.

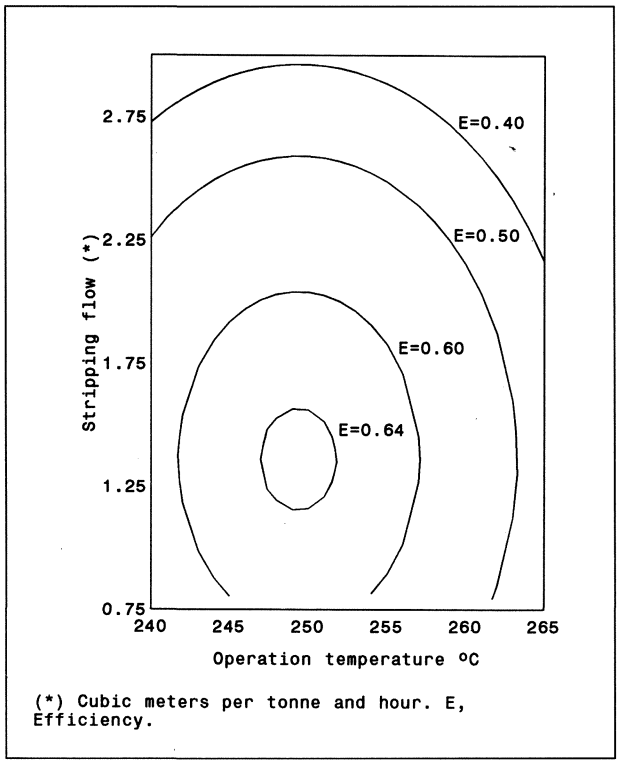
The efficiency values corresponding to the first hour and a half of operation are generally very low, except in those operations in which the final oils obtained have a degree of acidity equal to or lower than 0.5%. This may be because, initially, those volatile components responsible for odour and flavour are eliminated together with the distilled fatty acids.



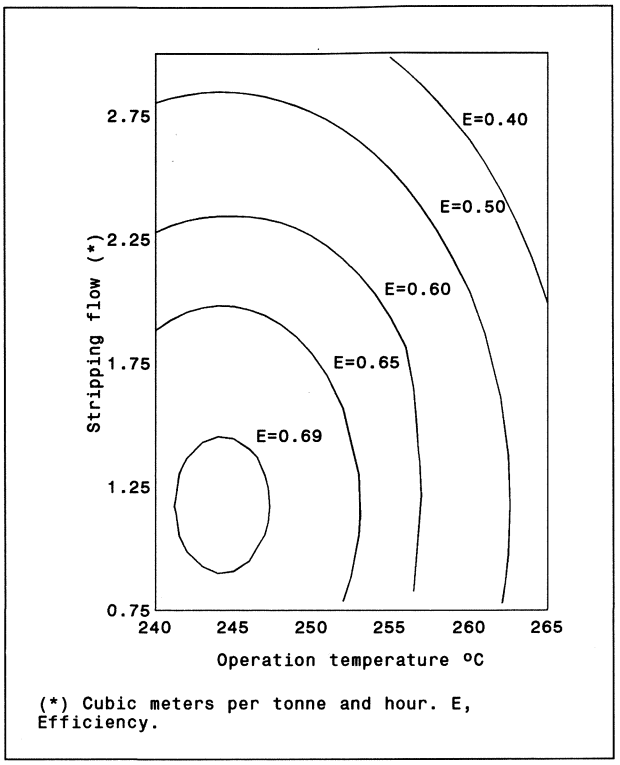
Graph 9
Chart corresponding to the fits applied to the experimental efficiencies between 1.5 - 3 hours.



Graph 10
Chart corresponding to the fits applied to the experimental efficiencies between 3 - 4 hours.



Graph 11
Chart corresponding to the fits applied to the experimental efficiencies between 0 - 3 hours.



Graph 12
Chart corresponding to the fits applied to the experimental efficiencies between 0 - 4 hours.

All the efficiencies calculated for operating times between 1.5 and 4 h are higher. The efficiencies corresponding to the final hour of operation, between 4 and 5 h, again fall sharply, which may be accounted for by a decrease in the presence of those fatty acids capable of being distilled.

It is worth nothing that in these operations, apart from the first hour and a half, higher efficiencies of neutralizing distillations are obtained than those measured in a previous paper (Graciani Constante, E., 1991) on the distillation of 16:0 fatty acids in deodorized soy oil. Different ways of introducing the nitrogen have been tried. In the present work the loop has already been described in the experimental section, while in the work of Graciani Constante (1991) a mammoth pump was used.

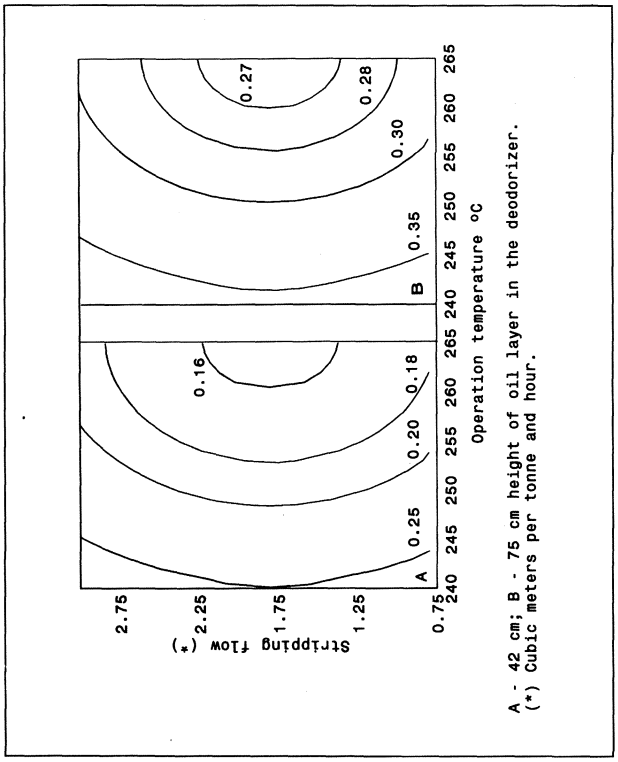
Table IV shows how, in most cases, the efficiency depends only on the working temperatures and on the nitrogen flow, especially when these have been calculated for different partial intervals of the neutralizing distillation process.

Graphs 9, 10, 11 and 12 are the resulting curves, when the fits corresponding to the efficiencies of the fatty acid distillation operations are calculated independently of the height of the oil layer and according to the data for the acidity of the final oils in all of the performed assay. The remaining fits for the efficiencies are shown in Table V. In this table the obtained fits when the height of the oil layer was taken into account are also shown.

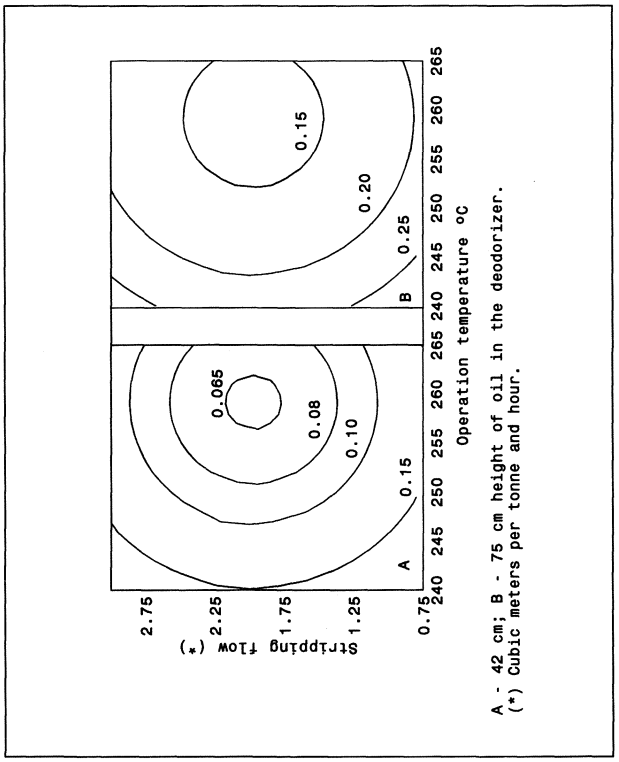
In the zone corresponding to the working area, the shapes of the representative curves of the efficiencies are analogous to the theoretical ones presented by Lorf, S.C. (1990), although the obtained fits here are second degree.

Graphs, 13, 14 and 15 show the fits for the results of the free acidity in the oils submitted to 1.5, 3 and 4 h of treatment at the operating temperature. All the fit functions for this variable (Table V) show how the resulting acidity depends on the three independent variables (Table IV) with high significance values, except at the start of the operations. The residual acidity of the final oils only depends on the nitrogen flow. The latter has to be capable of eliminating the acidity that is continually produced when the heating time of the oils is too long and there is a high number of thermolytic reactions to prevent these reactions from producing alterations in position 2 of the triacylglycerols.

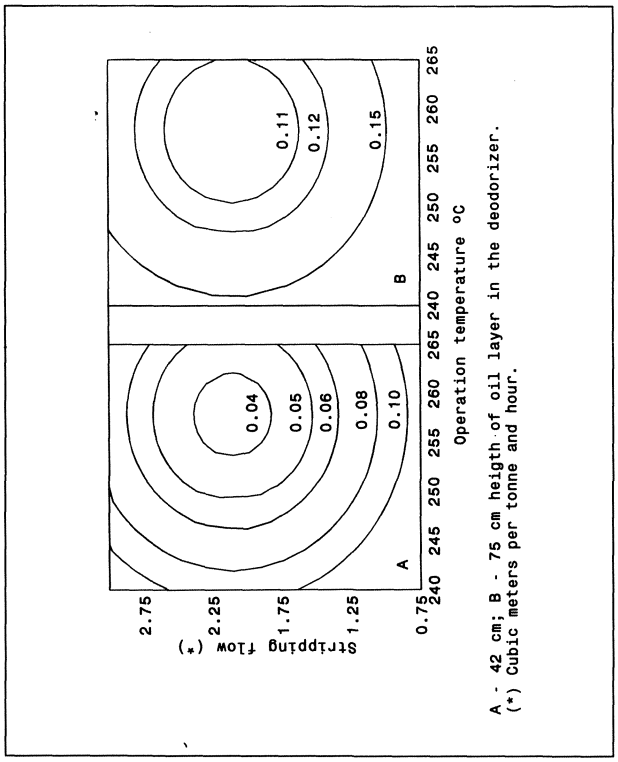
A synthesis of all of the results obtained for the efficiencies of the different operations and for the acidity values of the oils, together with the data for the other variables studied gives sufficient information for us to arrive at an optimum plan of work once the objective of the physical refining of the oils is established.



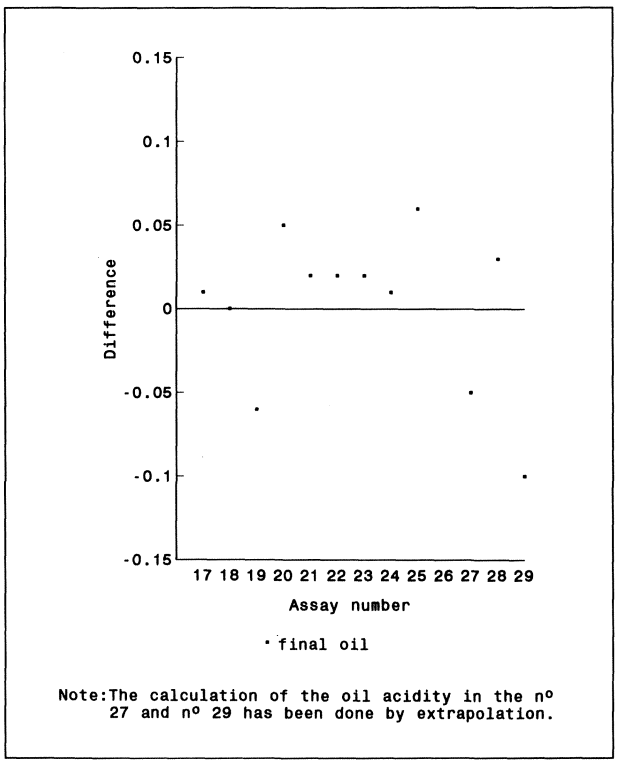
Graph 13
Chart corresponding to the fits applied to the acidity values after 1.5 hour at operation temperature.



Graph 14
Chart corresponding to the fits applied to the acidity values after 3 hours at operation temperature.



Graph 15
Chart corresponding to the fits applied to the acidity values after 4 hours at operation temperature.



Graph 16
Differences between the measured acidity values and calculated ones using the fits.

3.3 Evaluation of the results obtained from the assays carried out to confirm the experimental design.

In Table VII, the acidity degree in each sample taken and, in Graph 16, the differences found between the mean degree of acidity and that expected (from the predictions made using the fits (Table V) or using the graphs to these (Graphs 13, 14 and 15)) for the deodorized oils are shown. Generally, the experimental and predicted results agree or differ only slightly. The mean deviation between the mean acidity and the calculated acidity is 0.02 % with an error of plus or minus 0.01 units. In approximately a quarter of all of the measurements taken, the experimental results are 0.03 % better than those expected.

In trials E_{27} and E_{29}, carried out using different conditions from those tested in the proposed experimental plan, the degree of acidity of the final oils obtained are completely satisfactory.

Table VIII summarizes the mean Lovibond colour measurements of the oils. In general it was not possible to conclude that the bleached, deodorized oils increased or decreased in colour to any significant degree as a result of the temperature to which they had been exposed nor as a result of the duration of the assay. The final oils had very similar colours to the oils entering the deodorizers.

Table VII
Acidity of oils after the different treatment times

Time (h)	Oil Acidity												
	E_{17}	E_{18}	E_{19}	E_{20}	E_{21}	E_{22}	E_{23}	E_{24}	E_{25}	E_{26}	E_{27}	E_{28}	E_{29}
0	0.38	0.36	0.37	0.27	0.39	0.40	0.31	0.24	0.41	0.35	0.43	0.38	0.43
1										0.26			
1.5	0.32	0.30	0.30	0.22	0.29	0.33	0.22	0.11	0.39		0.26	0.19	0.31
2										0.19			
3	0.19	0.15	0.28	0.15	0.17	0.23	0.10	0.08	0.30	0.16	0.18	0.12	0.18
4	0.14	0.13	0.20	0.14	0.12	0.14	0.06	0.08	0.22	0.13	0.12	0.08	0.14
5	0.11	0.11	0.16	0.13	0.09	0.11	0.05	0.07	0.17	0.11	0.09	0.07	0.11
6										0.10			
7										0.09			
8										0.09			
9										0.07			
10										0.08			
Final oil	0.09	0.10	0.16	0.11	0.08	0.10	0.04	0.06	0.17		0.09	0.07	0.10

E_a. Experiment a

Table VIII
Results of the Lovibond colour of the oils in the assays performed to confirm the previous results.

N_2 Flow (m^3/T.h)	Time (h)	Operation Temperature (°C)																	
		230				240				248				256				265			
		R	Y	B	N	R	Y	B	N	R	Y	B	N	R	Y	B	N	R	Y	B	N
1.4	3					E_{17} 2.5	20		0.2	E_{18} 2.9	20		0.3	E_{19} 2.0	20		0.1	E_{20} 2.4	20		0.3
	5					2.7	20		0.3	2.6	20		0.3	2.0	20		0.1	2.1	20		0.3
2.0	3					E_{21} 2.1	20		0.3	E_{22} 2.4	20		0.3	E_{23} 2.0	20		0.3	E_{24} 2.3	23		0.3
	5					2.0	20		0.3	2.2	20		0.3	2.4	24		0.3	2.1	21		0.3
2.0	3					E_{25} 2.3	23		0.3					E_{26} 2.0	20		0.1				
	5					2.1	21		0.3					2.3	20		0.2				
3.0	3	E_{27} 2.3	23		0.3					E_{28} 2.5	20		0.3								
	5	2.3	23		0.3					2.3	20		0.3								
4.0	3	E_{29} 2.4	20		0.3																
	5	2.5	20		0.3																

– Initial oil (i.o.) Colour units: 2.0 R (Red); 20 Y (Yellow); 0.0 B (Blue); 0.1 N (Neutral)

– E_a: Experiment number a

4. CONCLUSIONS

The experiments performed indicate that:

For oils with a high intensity of colour, physical refining with nitrogen as the stripping gas does not produce any decrease in the colour compared to the initial values under the conditions of the present experiments. When speaking about the bleached oils, the colour of the deodorized oils is analogous to those of the bleached oils.

Physical refining of the oils using nitrogen as the stripping gas produces oils with as good a quality as might be required.

Generally speaking, the physical refining operation using nitrogen as the stripping gas should be carried out at temperatures between 250 and 260°C, with a nitrogen flow rate between 1.4 and 2.3 m^3/T·hour and with the oil layer at a height of 40-50 cm. These values are similar to those reported in the literature for deodorizing or physically refining with steam (Athanassiadis, A., 1991) and allow physical refining in a short time, giving rise to well deacidified oils with good organoleptic characteristics and with the other quality attributes suitable for commercialisation. The two types of charts proposed can be consulted.

If oils with very low degrees of acidity are required, it is advisable not to raise the temperature too high and to use the maximum proposed nitrogen flow rates. Consult the corresponding charts.

The total amount of nitrogen needed can be calculated from the previously given formula in a suitably modified form:

$$N' = 0.16\, A' \frac{p}{Ep_V} (C'_1 - C'_2 + 0.29 \ln \frac{C'_1}{C'_2}) - (C'_1 - C'_2)$$

E is the efficiency of the neutralizing distillation (see charts).

N' the required amount of nitrogen in m^3.

C'_1 and C'_2 are, respectively, the degrees of acidity in the oils before and after the operation.

A' is the number of metric tonnes of oil.

p is the pressure at the head of the deodorizer (mm Hg).

P_V is the vapour pressure of fatty acids (mm Hg).

These conclusions are applicable to the experiments performed in the present work. Their application to other apparatus for physical refining involves a certain degree of extrapolation.

COLLABORATION

The collaboraters in the present work are:

The companies: Carburos Metálicos S.A. and Busch Ibérica S.A.

Mr. Enrique Pinto Garcia, staff member of the Structural Unit "Procesos Industriales y Medio Ambiente" (Industrial Processes and the Enviroment), in the installations of the modifications, perfecting and working, of The Pilot Refining Plant.

ACKNOWLEDGMENTS

The authors express their thanks to the technicians of the above companies for their help and advice; to Miss Maria del Carmen Arévalo Mendoza, Mrs. Esperanza Oliveras Moreno and Mr. Manuel Serrano García for the analyses carried out; and to the Factory of ACEPROSA at Seville for supplying the oils.

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(Recibido: Septiembre 1993)