J Amer Oil Chem Soc (2007) 84:479–487
DOI 10.1007/s11746-007-1057-1

ORIGINAL PAPER

Optimization of Deacidification of Mixtures of Sunflower Oil and Oleic Acid in a Continuous Process

M. M. Prieto González · J. C. Bada · M. León · E. Graciani

Received: 28 February 2005 / Revised: 21 December 2006 / Accepted: 09 March 2007 / Published online: 24 April 2007
© AOCS 2007

Abstract Mixtures of refined sunflower seed oil and oleic acid were deacidified using nitrogen as stripping gas in a pilot-plant scale continuous deodorizer. To optimize the process, two different levels were tested for the classical operating parameters of oil temperature, nitrogen flow rates, oil mass flow rates and initial free fatty acid contents. In addition, two heating procedures were tested, including one using separate electrical heating of the oil and gas distillates to maintain the same temperature in both parts of the deodorizer, and another in which only the oil was heated and controlled, resulting in a temperature difference between the oil and the gas distillates. The statistical technique of blocking with paired comparisons was used to analyze the final free fatty acid content, rate of free fatty acid loss with respect to the processed oil flow rate, free fatty acid content in the distillates recovered by condensation, and efficiency. The results showed that the oil temperature and maintaining the same temperature in the oil and the gas distillates produced the most relevant effects, having a positive effect on most of the responses.

M. M. Prieto González (✉)
Universidad de Oviedo, Campus de Viesques,
Edificio de Energía, Carretera de Villaviciosa, s/n,
33204 Gijón, Spain
e-mail: manuelap@uniovi.es

J. C. Bada
Instituto de Productos Lácteos de Asturias,
33300 Villaviciosa, Spain

M. León · E. Graciani
Instituto de la Grasa, 41012 Sevilla, Spain

Keywords Edible oil distillates · Efficiency · Free fatty acids · Nitrogen · Physical refining · Sunflower oil · Continuous refining

Introduction

Operating conditions in batch deodorization are described by the values inside the deodorizer, including pressure in the gas distillate phase, oil temperature, stripping gas flow, and depth of the oil. The stripping gas that has traditionally been used is dry saturated steam. However, the use of nitrogen as stripping gas was suggested a number of years ago [1], and the performance of both gases was comparable [2–4]. The oil temperature, nitrogen flow rate and depth of the oil layer that lead to the best experimental results have previously been discussed with respect to the physical refining of sunflower seed oil in a 200-Kg capacity discontinuous deodorizer [5].

In ideal distillation, the temperature of the vapor and liquid phases are assumed to be the same. Unfortunately, however, this is not always true, at least in some classical batch or plate-column deodorizers, the problem being greater for small installations. The reasons could be deficient insulation, conductivity effects of the materials in the equipment downstream from the deodorizer that may cool the upper part of the deodorizer, and thermodynamic flow effects. These factors, in conjunction with the normal low flow rate of the gases and the low specific heat capacity of the gas distillates, leads to a decrease in the gas temperature. If the gas temperature is not maintained, the cooled vapor may condense back to the liquid phase, resulting in decreased deacidification efficiency.

The effect of temperature distribution inside the deodorizer on efficiency was initially demonstrated by

Deffense [6] after carrying out laboratory evaluations using a mixture of soybean oil and stearic acid (4% w/w) and live steam as stripping gas. Recent studies in a pilot-plant scale batch deodorizer installation (30-L, made of stainless steel) by Prieto et al. [7] and Bada et al. [8] have also shown the benefits of controlling the temperature of the gas distillate. Maintaining the temperature in the gas distillate zone inside the deodorizer the same as that of the oil greatly affects deodorization time (which was reduced by one-half), efficiency (which was more than two-fold greater), final free fatty acid content in the oil, and the quality of the deodorized oil.

The process in industrial plants is generally continuous, and is quite different from the batch process. Until now, however, research efforts in optimizing deodorization have focused mainly on batch systems. The present research on continuous processes was undertaken bearing in mind the interest of the results obtained in the batch process and the lack of data on continuous processes.

The present paper deals with optimizing the performance of physical refining of edible oils in a continuous deodorizer considering the operating conditions including heating the gas distillate zone inside the deodorizer to the same temperature as the oil (UH = 1) or not heating (UH = 0). In the latter case, the temperature in the gas distillates in the upper part of the deodorizer was lower than the oil temperature; oil temperature inside the deodorizer (T_o); nitrogen ($\dot{V}_{N_2}$) volumetric flow rate; free fatty acid content in the oil at the deodorizer inlet (IFFA); and volumetric flow rate of the oil to the deodorizer ($\dot{V}_o$).

The following responses are defined to describe distillation:

- Free fatty acid content at the deodorized outlet (OFFA) represents the acidity obtained at the deodorizer outlet at steady state.
- Removed free fatty acid per unit of treated oil (RFFAu) gives the proportion of the mass flow rate of free fatty acid removed from the oil with respect to the mass flow rate of the treated oil, which was used to take into account both the removed fatty acid mass flow rate and the oil mass flow rate. For the sake of simplicity, this was called acidity removed per unit of treated oil.
- Free fatty acid in the recovered distillates (FFAC) indicates the effectiveness of oil droplet recovery. The lower the FFAC, the greater the oil losses. For sake of simplicity, this is called acidity of recovered distillates.
- Vaporization efficiency (E) is determined by the formula that was theoretically established by Vian [9] for technological distillation operations with a stripping gas for the case of high free fatty acid contents,

$$E = \frac{\frac{P_d \dot{M}_o}{P_{ole}} \ln \frac{\dot{M}_{IFFA}}{\dot{M}_{OFFA}} + \frac{P_d}{P_{ole}} \left(\dot{M}_{IFFA} - \dot{M}_{OFFA} \right)}{\dot{M}_{N_2} + \dot{M}_{IFFA} - \dot{M}_{OFFA}} \qquad (1)$$

where E is the vaporization efficiency calculated to take into account the inlet and outlet free fatty acid content in the oils; P_d (mm Hg) was the pressure at the head of the deodorizer; P_{ole} (mm Hg) was the vapor pressure of the major compound in the distillates, oleic acid was used for the present study; $\dot{M}_o$ was the mol flow rate of oil (average molecular weight, 880 g); and $\dot{M}_{N_2}, \dot{M}_{IFFA}$ and $\dot{M}_{OFFA}$ ere the mol flow rates of the stripping gas and free fatty acids content in the oil (average molecular weight, 282 g) at the deodorizer inlet and the outlet, respectively.

All these responses will be obtained for the process steady state, which was maintained for at least 3 h.

Experimental Procedures

Deodorizer Description

The deodorizer was made of AISI 316 L stainless steel, the interior parts shown in detail in Fig. 1. The vessel was cylindrical (250 mm diameter and 600 mm high) with a hemispherical bottom and a flat top. The nominal volumetric flow rate was 5 L/h, although the flow rate may be adjusted to between 2 and 8 L/h. The device was internally divided into three zones by three vertical plates (baffles) welded to the surface of the cylinder and to the semi-spherical bottom of the deodorizer. The stripping gas flow rate was controlled independently in each zone to obtain better distribution of nitrogen inside the deodorizer. Nitrogen was introduced into each of these zones by means of a perforated horizontal tube (two rows of holes at 45° to the tube axis and oriented towards the bottom). The size of the holes ranged between 0.5 and 1 mm. The nitrogen

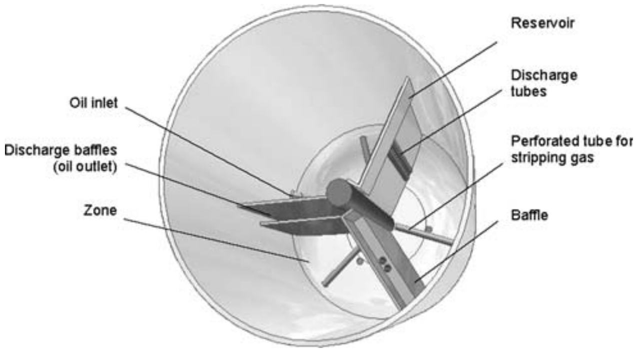

Fig. 1 Internal parts of the deodorizer

tubes were placed as near as possible to the bottom of the deodorizer and as close as possible to the center.

The depth of the oil layer in each of the three deodorizer zones was defined on the basis of the value employed for the discontinuous deodorizer in Prieto et al. [7]. This depth was used for the first deodorizer zone, where filling of the deodorizer commences. The depth of the oil layers in the three zones was in descending order, from the first to the third. These differences in depth made it possible for the oil to move from one zone to another by natural overflow. Other considerations taken into account in the design of the deodorizer were those of obtaining sufficient residence time for the oil and of guaranteeing as far as possible that the fluid did not stratify. Each zone was thus filled from the bottom-up. The first zone was filled by introducing the oil at the lowest point of the deodorizer. The oil moved upward until reaching the top of the lowest baffle in the zone, where there was a small oil reservoir provided with a vertical descent discharge tube. This discharge tube introduced the oil into the second zone near the bottom, so that the second zone was also filled from the bottom-up. The same procedure was repeated in filling the third zone. There was a discharge zone at the outlet of the third zone formed by two parallel discharge baffles that channeled the oil to a discharge point in the semi-spherical bottom. The oil volume contained in the deodorizer at stable state was 13 L. There was accordingly a zone in the deodorizer that contained the distillate gases with a height of 250 mm.

The deodorizer was heated electrically by specially designed ceramic brackets installed on the outside of the vessel, around the zone filled with the oil. The heating power was calculated so as not to reach 300 °C in order to prevent polymerization. Heating strips were used to heat the outside of the deodorizer in the zone occupied by the gas distillates.

A drift eliminator was present at the top of the deodorizer (continuous or batch) that recovered the oil droplets. The oil was cooled at the deodorizer outlet under vacuum until it reached <90 °C.

Figure 2 shows the general diagram of the installation employed. The deodorizer was continuously fed with the mixture to be deodorized and the stripping gas, and the deacidified mixture and gas distillates were produced. The gas distillates were partially condensed and recovered in the horizontal two-pass shell-and-tube heat exchanger cooled with water at a water inlet temperature of 18 °C (condenser). The uncondensed gases were introduced into a vertical two-pass shell-and-tube heat exchanger cooled with silicone oil at an inlet temperature of –40 °C (freezer). The required vacuum was achieved by connecting the outlet of the vertical heat exchanger to a vacuum pump (manufactured by MPR, model PIL6-11, Spain) via a droplet eliminator. The entire installation, except for the vacuum pump, was thermally isolated from the surrounding atmosphere by means of 40-mm-thick mineral fiberglass.

The temperatures of the oil and gas distillate and the pressure at the head of the deodorizer were measured and automatically recorded. The temperatures were measured using Pt-100 probes, calibrated in the range of 0–300 °C, with an accuracy of ±1 °C. Pressure was measured with a membrane measurement device (Fisher–Rosemount, model 3051CA), ±0.0075% span accuracy, calibrated between 0.5 and 20 mm Hg. The nitrogen flow rate was measured using a mass flow rate meter (model F-110 C, Bronkhorst, High-Tech, The Netherlands), ±1% sensitivity, calibrated from 0 to 100 l/h at 2 bar pressure and 20 °C. The nitrogen injection pressure was established using a pressure regulator calibrated between 1 and 7 bar (Argón, Spain, model 404, ±0.1 bar sensitivity). The temperatures of the oil and gas distillates were maintained with an accuracy of ±1 °C, at the established values using two controllers (Shimaden Co., LTD, Tokyo, Japan, model SR60) that were separately

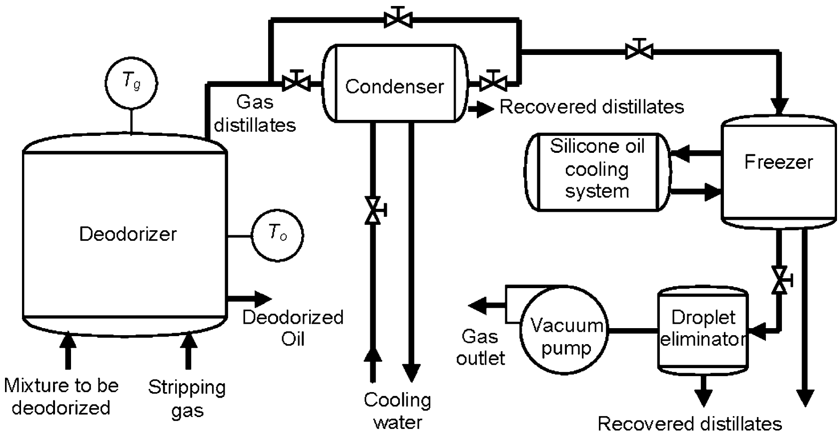

Fig. 2 Schematic diagram of the experimental installation

connected to their corresponding Pt-100 probe and electrical heating system.

Deodorization Trials

For each trial, 75 L of oil was continuously introduced into the deodorizer. The oil was made up of mixtures of refined sunflower seed oil (0.1% w/w free fatty acid, Pulisol, S.A. Aceites de Carrión, Toledo,Spain) and oleic acid (90% w/w purity, Merck, Darmstadt, Germany). The initial free fatty acid content of the refined sunflower oil was increased by adding oleic acid to obtain the desired initial free fatty acid control for each trial.

The oil was introduced into the deodorizer once the desired vacuum was obtained (2–4 mm Hg absolute pressure). Once the oil reached about 90 °C, a small flow of nitrogen was injected to remove the oil in order to prevent inappropriate wall temperatures. Full nitrogen flow for the trial commenced when the oil reached 180 °C. On reaching the desired operating conditions, samples were taken from the deodorizer and the condenser every 30 min to determine the evolution of deacidification and distillate recovery. Acidity was determined for each sample, according to standard AOCS methods [10] until reaching steady state and subsequently until completing at least 3 h under steady-state operation.

The chosen operating conditions for the trials were close to those used in the discontinuous deodorizer of Prieto et al. [7]. Two working levels were established for each variable: stripping gas flow rate ($\dot{V}_{N_2}$: 20 and 35 L/h; injected at 2 bar pressure and ambient temperature); and oil temperature (T_o: 240 and 260 °C). Trials were performed for each temperature, either maintaining the same temperature in the gas distillate and in the oil (heating the upper part of the deodorizer and controlling its temperature, UH = 1), or not (the heating of the upper part of the deodorizer was switched off, UH = 0); inlet free fatty acid content (IFFA: 2.5 and 7% w/w), and oil flow rate ($\dot{V}_o$: 5 and 3 L/h).

We preferred to work within a broad interval of the OFFA contents of the deodorized oils to be able to draw conclusions regarding the effect of operating conditions. For that reason, our objective was not to deacidify the oils to commercial edible oil refining standards.

Results and Discussion

The effects of heating procedure, temperature in the oil, nitrogen flow rate, inlet free fatty acids content and oil flow rate were determined. Tables 1, 2 and 3 show the results arranged to apply the block formation technique [11] in order to confirm observations by establishing the corresponding confidence coefficients.

Table 1 shows the results for the factor of heating the gas distillates or not, UH = 1 and UH = 0, respectively. The responses are specified in Column 1: outlet free fatty acid contents, OFFA (% w/w); removed free fatty acid per unit of oil entering the deodorizer, RFFAu (w/w); free fatty acid content in the recovered distillates in the condenser, FFAC (% w/w); and vaporization efficiency, *E* (%). Columns 2–5 define the operating conditions, which were maintained the same in the trials being compared (UH = 1 and 0). The values obtained for the responses (Columns 6 and 7) and their differences (Column 8) change only as a result of the heating procedure.

Case UH = 0: the pressure in the deodorizer was 1.7 ± 5 mm Hg. For this deodorizer, the temperatures of the gas distillate depended on the temperature of the oil: the mean temperature difference (gas distillates-oil) being 56.9 °C for the higher oil temperature and 47.7 °C for the lower oil temperature.

Case UH = 1: the mean pressure in the deodorizer was 1.8 ± 0.4 mm Hg. As in the previous case, the oil temperatures were kept very close to the established values, with differences of ±0.5 and ±1 °C for the higher and lower oil temperatures, respectively. The temperatures of the gas distillates were very close to that of the oil, with mean differences of 0.2 and 1 °C for the higher and lower values of oil temperature, respectively.

Comparing the results for UH = 0 and UH = 1, we observed that the outlet acidity values were lower when the gas distillates were heated. For UH = 0, the gas distillate temperature was lower than that of the oil and this difference caused refluxing of the free fatty acid into the oil. Refluxing could be partly avoided if the distillates were removed rapidly, which could be done by increasing the nitrogen flow rate. However, maintaining the same temperature in both the oil and the gas distillates gave good deacidification at lower nitrogen flow rate. The required vacuum equipment would also be smaller. In addition to the lower the stripping flow rate, the lower the oil losses as a result of the decreased the drag force over the oil droplets and the greater the efficiency, according to the expression of Vian [9]. These effects can be observed in the second and ninth rows for UH = 1, responses of acidity of the recovered distillates and efficiency, respectively.

The importance of the heating procedure depended on the oil temperature. For equal nitrogen flow rates (e.g., comparing the first and second rows) the differences in the outlet acidity due to the application of heating were greater at the lower oil temperature. This behavior may be explained by taking into account the fact that the vapor pressure of fatty acids increased as the temperature of the oil, and hence of the distillates, increased.

The heating procedure also had a positive effect on the amount of acidity removed per unit of oil treated and on

Table 1 Heating procedure factor: block formation and critical confidence coefficients

Heating procedure factor: block formation

Response	IFFA (% w/w)	T_o (°C)	$\dot{V}_{N_2}$(L/h)	$\dot{V}_o$(L/h)	UH = 0	UH = 1	d_i
OFFA (% w/w)	2.5	240	20	5	0.983	0.135	–0.848
	2.5	260	20	5	0.260	0.160	-0.100
	7	240	20	5	0.630	0.392	–0.238
	7	260	20	5	0.317	0.200	–0.117
	7	240	35	5	1.350	0.206	–1.144
	7	260	35	3	0.460	0.085	–0.375
	2.5	240	35	3	0.323	0.044	–0.279
	2.5	260	35	3	0.095	0.050	–0.045
	2.5	260	35	5	0.380	0.090	–0.290
RFFAu (w/w)	2.5	240	20	5	3.104	5.621	2.517
	2.5	260	20	5	6.770	7.059	0.289
	7	240	20	5	17.416	18.026	0.610
	7	260	20	5	18.218	18.514	0.296
	7	240	35	5	16.416	18.499	2.083
	7	260	35	3	18.688	18.806	0.118
	2.5	240	35	3	5.702	5.888	0.186
	2.5	260	35	3	6.368	7.377	1.009
	2.5	260	35	5	5.535	7.262	1.727
FFAC (% w/w)	2.5	240	20	5	97.786	97.063	–0.723
	2.5	260	20	5	93.640	95.313	1.673
	7	240	20	5	101.893	100.697	–1.196
	7	260	20	5	100.507	99.833	–0.674
	7	240	35	5	102.030	101.187	–0.843
	7	260	35	3	98.847	98.433	–0.414
	2.5	240	35	3	97.975	95.537	–2.438
	2.5	260	35	3	94.877	93.380	–1.497
	2.5	260	35	5	94.550	94.203	–0.347
E (%)	2.5	240	20	5	14.343	46.355	32.012
	2.5	260	20	5	20.209	22.545	2.336
	7	240	20	5	37.599	45.165	7.566
	7	260	20	5	24.499	59.281	34.782
	7	240	35	5	27.122	16.327	–10.795
	7	260	35	3	14.442	16.327	1.885
	2.5	240	35	3	6.369	23.656	17.287
	2.5	260	35	3	4.680	12.196	7.516
	2.5	260	35	5	11.590	17.705	6.115

Critical confidence coefficients

Response	d_{avg}	SD	t_{n-1}	$(1 - \alpha_{ctn-1})$ 100	M_r (%)
OFFA (% w/w)	–0.3818	0.371	–2.9108	99.02	–63.97
RFFAu (w/w)	0.9817	0.908	3.0584	99.22	17.12
FFAC (% w/w)	–0.7177	1.104	–1.8379	89.66	–0.72
E (%)	10.9671	14.695	2.1109	93.22	94.99

efficiency for all the assayed nitrogen flow rates and oil temperatures evaluated. Efficiency values doubled, on average, when the upper part of the deodorizer was heated. Although the acidity of the recovered distillate was slightly lower, the values were very high for all trial conditions, with values between 93 and 101% w/w. This

Table 2 Oil temperature factor: block formation and critical confidence coefficients

Oil temperature factor: Block formation

Response	IFFA (% w/w)	UH	$\dot{V}_{N_2}$(L/h)	$\dot{V}_o$(L/h) (L/h)	T$_o$ = 240 °C	T$_o$ = 260 °C	d_i
OFFA (% w/w)	2.5	0	20	5	0.983	0.260	–0.723
	2.5	1	20	5	0.135	0.160	0.025
	2.5	1	35	5	0.120	0.090	–0.030
	2.5	1	35	3	0.044	0.050	0.006
	7	0	20	5	0.630	0.317	–0.313
	7	1	20	5	0.392	0.200	–0.192
	7	1	35	5	0.206	0.159	–0.047
	7	1	35	3	0.087	0.085	–0.002
	2.5	0	35	3	0.323	0.095	–0.228
RFFAu (w/w)	2.5	0	20	5	3.104	6.770	3.666
	2.5	1	20	5	5.621	7.059	1.438
	2.5	1	35	5	5.687	7.262	1.575
	2.5	1	35	3	5.888	7.377	1.489
	7	0	20	5	17.416	18.218	0.802
	7	1	20	5	18.026	18.514	0.488
	7	1	35	5	18.499	18.619	0.120
	7	1	35	3	18.800	18.806	0.006
	2.5	0	35	3	5.702	6.368	0.666
FFAC (% w/w)	2.5	0	20	5	97.786	93.640	–4.146
	2.5	1	20	5	97.063	95.313	−1.750
	2.5	1	35	5	96.191	94.203	−1.988
	2.5	1	35	3	95.537	93.380	−2.157
	7	0	20	5	101.893	100.507	−1.386
	7	1	20	5	100.697	99.833	–0.864
	7	1	35	5	101.187	99.283	−1.904
	7	1	35	3	100.413	98.433	−1.980
	2.5	0	35	3	97.975	94.877	−3.098
E (%)	2.5	0	20	5	14.343	20.209	5.866
	2.5	1	20	5	46.355	22.545	−23.810
	2.5	1	35	5	31.532	17.705	−13.827
	2.5	1	35	3	23.656	12.196	−11.460
	7	0	20	5	37.599	24.499	−13.100
	7	1	20	5	45.165	59.281	14.116
	7	1	35	5	34.946	25.596	−9.350
	7	1	35	3	20.656	16.327	–4.329
	2.5	0	35	3	6.369	4.680	−1.689

Critical confidence coefficients

Response	d_{avg}	SD	t_{n-1}	$(1 - \alpha_{ctn-1})$ 100	M_r (%)
OFFA (% w/w)	–0.1671	0.240	−1.9669	91.53	–28.97
RFFAu (w/w)	1.1389	1.111	2.8999	99.01	24.04
FFAC (% w/w)	−2.1414	0.961	–6.2997	99.99	−2.18
E (%)	–6.3981	11.376	−1.5907	84.97	−20.06

result indicates that oil losses were very small in all trials. The latter percentage of over 100% was the result of determining the free fatty acid contents using the molecular weight for oleic acid as the reference when there are compounds with lower molecular weights in the distillates.

Table 3 Nitrogen flow rate factor: block formation and critical confidence coefficients

Nitrogen flow rate factor: block formation

Response	IFFA (% w/w)	T_o (°C)	UH	$\dot{V}_o$(L/h)	$\dot{V}_{N_2} = 20\text{L/h}$	$\dot{V}_{N_2} = 35\text{L/h}$	d_i
OFFA (% w/w)	2.5	240	1	5	0.135	0.120	–0.015
	2.5	240	1	3	0.925	0.044	–0.881
	2.5	260	0	5	0.260	0.380	0.120
	2.5	260	1	5	0.160	0.090	–0.070
	7	240	0	5	0.630	1.350	0.720
	7	240	1	5	0.392	0.206	–0.186
	7	260	1	5	0.200	0.159	–0.041
	2.5	260	0	3	1.042	0.095	–0.947
	7	260	1	3	0.480	0.085	–0.395
RFFAu (w/w)	2.5	240	1	5	5.621	5.687	0.066
	2.5	240	1	3	5.318	5.888	0.570
	2.5	260	0	5	6.770	5.535	–1.235
	2.5	260	1	5	7.059	7.262	0.203
	7	240	0	5	17.416	16.416	–1.000
	7	240	1	5	18.026	18.499	0.473
	7	260	1	5	18.514	18.619	0.105
	2.5	260	0	3	3.580	6.368	2.788
	7	260	1	3	18.640	18.806	0.166
FFAC (% w/w)	2.5	240	1	5	97.063	96.191	–0.872
	2.5	240	1	3	98.117	95.537	–2.580
	2.5	260	0	5	93.640	94.550	0.910
	2.5	260	1	5	95.313	94.203	–1.110
	7	240	0	5	101.893	102.030	0.137
	7	240	1	5	100.697	101.187	0.490
	7	260	1	5	99.833	99.283	–0.550
	2.5	260	0	3	95.347	94.877	–0.470
	7	260	1	3	97.100	98.433	1.333
E (%)	2.5	240	1	5	46.355	31.532	–14.823
	2.5	240	1	3	24.502	23.656	–0.846
	2.5	260	0	5	20.209	11.590	–8.619
	2.5	260	1	5	22.545	17.705	–4.840
	7	240	0	5	37.599	27.122	–10.477
	7	240	1	5	45.165	34.946	–10.219
	7	260	1	5	59.281	25.596	–33.685
	2.5	260	0	3	4.260	4.680	0.420
	7	260	1	3	6.257	16.327	10.070

Critical confidence coefficients

Response	d_{avg}	SD	t_{n-1}	$(1 - \alpha_{ctn-1})$ 100	M_r (%)
OFFA (% w/w)	–0.1883	0.510	–1.044	67.29	–
RFFAu (w/w)	0.2373	1.141	0.588	42.73	–
FFAC (% w/w)	–0.3013	1.184	–0.72	50.78	–
E (%)	–8.1132	12.125	–1.893	90.49	–4.01

The results of applying of the block formation technique used to obtain the critical confidence levels for the responses are presented at the bottom of Table 1. The average increase or decrease in response with respect to the value for its lower level is also shown (M_r). The average difference $d_{avg} = \sum d_i/n$ (where *n* is the number of data) and the sample standard deviation SD = $\sqrt{\sum(d_i - d_{\text{avg}})^2/(n-1)}$ were calculated for each response. The n differences of each factor (d_i) were assumed to be samples of an approximately normal population of mean zero. Thus, $d_{\text{avg}}/\text{SD}/\sqrt{n}$ followed a Student t distribution with $(n - 1)$ degrees of freedom t_{n-1}. One-sided or two-sided significance tests were used to obtain the critical significance level α_{ctn-1} and the critical confidence coefficient $(1 - \alpha_{ctn-1})$. This technique was also applied to the rest of the factors.

It can be appreciated that when the gas distillates were heated, the outlet free fatty acid content diminished and the amount of free fatty acids removed increased. This can be stated with a very high degree of confidence, 99 and 99.2%, respectively. The average decrease for the outlet acidity was 63.97% and the average increase for acidity removed per unit of oil treated was 17.12%. It can likewise be stated with a 89.66% degree of confidence that the acidities in the recovered distillates decreased when heating was applied, although this decrease was very low on average, 0.72%. As regards efficiency, this increased with a confidence coefficient of 95%, that, the average increase was 93.22%, which meant that it nearly doubled.

Table 2 shows the block formation for the oil temperature factor, along with the differences in response. The critical confidence coefficients for all responses are shown at the bottom of the table. It can be appreciated that efficiency decreased at higher oil temperature, and this can be stated with a quite high degree of confidence of 85%, the average decrease being 20%. This behavior was expected from the vaporization efficiency expression: when the oil temperature increases, the efficiency is negatively affected. The confidence coefficients were higher for all other responses, the highest being for acidity of recovered distillate, followed by acidity removed by unit of oil treated, and the outlet acidity. The effect was positive in improving the distillation process for the outlet acidity and the acidity removed per unit of oil treated, with average values of 29.0 and 24.0%, respectively. There was, however, a negative effect for acidity of the recovered distillate, in that the acidity in the recovered distillate decreased when the oil temperature increased, although the average decrease was only 2.18%.

Table 3 shows the block formation along with the differences in response for the nitrogen flow rate. The influence of the effect is not very clear, as low critical confidence coefficients were found, except for efficiency, which was negatively affected, with an average value of 4.01%. A more in-depth analysis of outlet acidity and acidity removed per unit of oil treated in the upper part of Table 3 shows that in most assays, except for the conditions in the third and fifth rows, increased nitrogen flow rate produced a decrease in acidity. Despite the values obtained for the calculated confidence coefficients, the authors believe that the nitrogen flow rate had a positive effect on outlet acidity; this finding was also observed in the discontinuous deodorizer and other trials. The same consideration may be made for acidities of recovered distillates, with respect to the increase in the nitrogen flow rate leading to a decrease in the response, this effect being negative.

The study of inlet free fatty acid content and oil flow rate was performed in a similar way; however, the tables of block formation and critical confidence coefficients are not presented. With respect to the inlet free fatty acid content factor, the confidence coefficients were high for all responses except for outlet acidity; the effect was positive on acidity removed per unit of oil treated, acidity of recovered distillate and efficiency, with average values of 217, 5.03 and 69.9%, respectively. As regards the oil flow rate factor, the influence of the effect was not clear, due to the low critical confidence coefficients, with the exception of efficiency, for which we found to have a positive effect resulting in an average increase of 189%.

In order to ensure that the block formation technique was appropriately applied, which implies that there is non-iteration between factors, 2^{5-1} factorial designs were applied (five factors and two levels) [11], although the results are not presented in this paper. We found that there were no significant interactions between the factors. This technique provided additional evidence of the positive effect of increasing the nitrogen flow rate on the outlet free fatty acids response.

Acknowledgments This work was funded by The Spanish National Research and Development Program (Projects: ALI-95-0517 and AGL 2001-3583) and the University Institute for Industrial Technology of Asturias (IUTA). We thank Silvia González, Javier Sánchez and Esperanza Olivera for their technical support in the trials and the analyses performed.

References

1. Norris F (1985) Deodorization. In: Applewhite TH (ed) Baileýs industrial oil and fat products, vol 3. Wiley, New York, pp 897–930
2. Ruíz-Menéndez MV, Márquez-Ruíz G, Dobarganes MC (1996) Comparative performance of steam and nitrogen as stripping gas in physical refining of edible oils. J Am Oil Chem Soc 73:1641–1645
3. Ruíz-Méndez MV, Garrido-Fernández A, Rodríguez Berbel FC, Graciani E (1996) Relationships among the variables involved in the physical refining of olive oil using nitrogen as stripping gas. Fett/lipid 98:121–125
4. Camacho L, Ruíz Méndez MV, Graciani E (1999) Changes in olive oil components during deodorization and/or physical refining at pilot plant scale using nitrogen as stripping gas. Fett/lipid 101:38–43
5. Graciani E, Bada JC, Rodríguez F, Ruíz-Méndez MV (1994) Physical refining of edible oils using nitrogen as stripping gas. Process Optimization. Grasas y Aceites 45:132–146

6. Deffense E (1994) Refinación con vapor: comparación de la Teoría con la Práctica, Dossier Oleo, pp 49–57
7. Prieto MM, Bada C, Graciani E, Lombardía I (1999) A comparative study of two heating procedures in the physical refining of edible oils. J Am Oil Chem Soc 76(12):1471–1476
8. Bada JC, Prieto Prieto MM, Xiberta J, Graciani E, León M (2002) Application of two heating methods in physical refining of high-FA olive and sunflower oils. J Am. Oil Chem Soc 79(3):209–214
9. Vian A, Ocón J (1964) In: Elementos de Ingeniería Química, Aguilar, Madrid, p 657
10. Official methods and recommended practices of the American oil chemists' society, 5th edn. In: Firestone (ed), AOCS, Champaign, 1998, Methods Cd 3d–63
11. Box GEP, Hunter WG, Hunter JS (1978) in Statistics for experimenters. An introduction to design, data analysis, and model building. Wiley, New York, pp 93–106 and 306–374