Comparative Performance of Steam and Nitrogen as Stripping Gas in Physical Refining of Edible Oils

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ABSTRACT: Olive, sunflower, and soybean oils were physically refined in a discontinuous laboratory system with either nitrogen or steam as stripping gas during the deodorization step. Comparative assays were also carried out on olive oil in a 10-MT discontinuous industrial plant. Vaporization efficiency of free fatty acids was calculated, and quality of refined oils and composition of deodorizer distillates were analyzed. Results indicated that, in all assays, the efficiency of free fatty acid distillation was higher when nitrogen was used. The amount of nitrogen needed was much lower than that of steam for refined oils of similar high quality. The results also suggested that the amount of stripping gas had a clear influence on the composition of deodorizer distillates because lower quantities of triglycerides and unsaponifiable matter were found when nitrogen was employed.

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KEY WORDS: Distillates, efficiency, nitrogen, oil quality, physical refining, steam.

The use of nitrogen as stripping gas during the deodorization step of the refining process was suggested in the past (1), but live steam has been traditionally used. Due to the improvements in vacuum systems and the competitive price of incondensable gases, nitrogen has been proposed recently as an alternative to the use of live steam (2–5). The suggested amounts of nitrogen range between 5 and 10 times lower than those of steam; potential advantages include the possibility of reducing pollution and recovering high-quality deodorizer distillates.

The vaporization efficiency is expressed as the ratio of partial pressure to the equilibrium pressure. It attempts to measure the completeness to which stripping gas is saturated with the volatile matter when in contact with the oil, and some theoretical equations to predict optimum deodorization conditions have been developed (1,6). The vegetable oil matrix, however, is a nonideal solution, and the vaporization efficiency of volatile compounds strongly depends on oil composition, equipment, and operating conditions. However, when a series of tests are conducted in a single deodorizing system, it is adequate for relative measurements (7).

In this paper, vaporization efficiency of free fatty acids (FFA) has been compared by using either steam or nitrogen as stripping gas. Olive, sunflower, and soybean oils were physically refined in discontinuous laboratory equipment, under operating conditions proposed in the literature with the same molar concentration of both gases for different periods of time. Finally, olive oils were subjected to physical refining in the laboratory and in a discontinuous industrial plant to compare oil quality and the composition of the by-products obtained.

EXPERIMENTAL PROCEDURES

Samples and treatments. Four groups of assays were carried out under the following conditions: (i) Samples of olive, sunflower, and soybean oils were supplied by an industrial Spanish manufacturer as crude oils. Standard conditions for the laboratory discontinuous equipment were used for degumming and bleaching to obtain bleached oils (8), which constituted the initial samples for this study.

Bleached oils were deodorized in a glass discontinuous laboratory deodorizer: 700 g of oil were introduced in a round-bottomed, three-necked flask and heated with a hemispherical mantle with a thermoregulator. Foil-covered ceramic fiber tapes were used for insulation of the equipment to prevent reflux effects. The flask was connected to dry-ice traps and further to a vacuum pump. Vacuum was measured in the vapor outlet by means of an Edwards vacuum meter (Anorsa, Madrid, Spain) (range 0.01–10 Torr).

The source of steam consisted of 50-mL graduated cylinders, filled with distilled deaerated water, held at 25°C in a water bath, and connected directly to a U-shape tube introduced in a thermal oil bath at 100°C. An inlet tube with a stopcock led the incoming steam to the bottom of the deodorizer flask that contained the heated oil, and the stripping gas was distributed through a glass frit (20 mm diameter, 1 µm pore size).

Injection of the nitrogen was regulated with accuracy of ± 0.5 mL/min by a Gilmont Flowmeter Model 1200 (Cole-Parmer, Chicago, IL). The same inlet system was used for steam and nitrogen, to maintain the same equipment design.

Deodorization was conducted for 3 h under a vacuum of 3 Torr. The temperature was 260°C, and the stripping gas flow was 2%/h and 0.3%/h for steam and nitrogen, respectively .

(ii) To refined olive oil was added 2% stearic acid, and the mixture was subjected to redeodorization. Six different as-

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says, starting from 200 g of oil and injecting 0.3 mol of steam or nitrogen, were carried out in different periods of time, i.e., 0.5, 1, and 2 h, under 2 Torr vacuum at 260°C.

(iii) Four bleached olive oils of different initial FFA content were physically refined. The operations were conducted for 3 h under a vacuum of 3 Torr at 260°C. The steam and nitrogen flows of every assay were set based upon the results obtained from the previous experiments (data detailed later in Table 4).

(iv) Four batches of bleached olive oil were physically refined in a 10-MT discontinuous industrial deodorizer with either steam or nitrogen in duplicate assays. Each operation was conducted for 4.5 h under a vacuum of 3 Torr. The vacuum system, consisting of a booster and three ejector steps, was modified by adding two new ejector steps in parallel. Temperature was 250°C, and the stripping gas flow was 0.5%/h and 0.1%/h for steam and nitrogen, respectively.

Analytical determinations. Determinations of FFA, oil stability index with a 679 Rancimat apparatus (Metrohm Ltd., Herisau, Switzerland), peroxide value, and unsaponifiable matter were carried out in oil samples before and after deodorization according to AOCS standard methods (9). Tocopherol evaluation was carried out by high-performance liquid chromatography with the method proposed by IUPAC (10).

Distillate composition was evaluated by thin-layer chromatography–flame ionization detector (TLC–FID) (11). Briefly, samples were dissolved in hexane (20 mg/mL), and 1 µL was spotted on Chromarods SIII (IATRON Laboratories, Tokyo, Japan). The rods were developed in hexane/diethyl ether/acetic acid 98:2:1 for 40 min and scanned in an IATROSCAN MK-5 TLC–FID Analyzer (IATRON Laboratories). Response factors were applied to the main groups of compounds: triglycerides, FFA, hydrocarbons, and sterols. Reproducibility and other details were described in a previous publication (11).

Quantitative evaluation of FFA in distillates was carried out by gas–liquid chromatography (GLC) after methylation with diazomethane (12) to evaluate hydrolytic reactions. Distillates were carefully recovered from the traps with 3 × 50 mL of an ethyl ether solution of heptadecanoic acid (5 mg/mL), used as internal standard for quantitative purposes. Fatty acid methyl esters (FAME) were purified by TLC with hexane/diethyl ether/acetic acid (80:20:1, vol/vol/vol) as the mobile phase. The major band, corresponding to FAME, was scraped, and the sample was eluted with diethyl ether. GLC analyses were carried out in a Hewlett-Packard 5890 gas chromatograph series II (Pittsburgh, PA). A column, 30 m long, 0.32 mm i.d., 0.25 µm film thickness, packed with Supelcowax 10 (Supelco, Bellefonte, PA) was used at 180°C.

RESULTS AND DISCUSSION

The vaporization efficiency of FFA was determined by the formula that was established theoretically for technological distillation operations with a stripping gas (1):

$$E_{1-2} = \frac{P \bullet O}{P_v \bullet S} \ln\left(\frac{FFA_1}{FFA_2}\right) \bullet 100 \qquad [1]$$

where: E_{1-2}, vaporization efficiency of the FFA between times 1 and 2; S is the moles of stripping gas; FFA_1 and FFA_2 moles of FFA at time 1 and 2; O is moles of oil (865 g as average molecular weight); P is the vapor pressure at the head of the deodorizer; and P_v is the mean value of vapor pressure of the FFA (35 Torr at 260°C). The equation refers to FFA because they are the major compounds distilled during deodorization in physical refining.

Table 1 summarizes the FFA of the initial and final olive (OO), sunflower (SFO), and soybean (SBO) oils used in the initial assays, and the resulting efficiencies. Vaporization efficiency values were markedly higher when nitrogen was used, although higher FFA levels remained in sunflower oil and olive oil samples, which would indicate that the amount of nitrogen was not sufficient to reduce FFA to standard levels for high-quality refined oils (<0.1%). A vaporization efficiency above 100% was obtained for sample OO1. As it has been pointed out (7), values much higher than 100% can be found in physical refining of oils due to their high content of FFA.

Apart from differences in physical characteristics of steam and nitrogen, two facts could have influenced the results obtained: First of all, different amounts of steam and nitrogen were used in the assays, and the equation states that the

TABLE 1
Efficiency of FFA Vaporization with Steam and Nitrogen as Stripping Gas During Deodorization of Edible Oils[a]

		Steam		Nitrogen	
Sample	i FFA[b] (% oleic)	f FFA (% oleic)	E (%)	f FFA (% oleic)	E (%)
OO1	6.45	0.04	15.1	0.08	135.3
OO2	1.01	0.05	8.9	0.10	71.3
SFO1	1.46	0.17	6.4	0.20	61.3
SFO2	0.76	0.06	7.5	0.12	56.9
SBO1	0.81	0.14	5.2	0.07	75.5
SBO2	1.32	0.11	7.4	0.07	90.5

[a] Operation conditions: oil, 700 g; pressure, 3 Torr; temperature, 260°C; time, 3 h; steam flow, 2%/h; nitrogen flow, 0.3%/h.

[b] Abbreviations: i FFA, initial free fatty acids; f FFA, final free fatty acids; E, vaporization efficiency; OO, olive oil; SFO, sunflower oil; SBO, soybean oil.

TABLE 2
Influence of the Deodorization Period on the Efficiency of FFA Vaporization[a]

	Steam		Nitrogen	
Time (h)	f FFA[b] (% oleic)	E (%)	f FFA (% oleic)	E (%)
0.5	0.20	11.0	0.03	19.8
1	0.29	9.3	0.04	18.4
2	0.34	8.5	0.04	18.4

[a]Operation conditions: oil, 200 g; temperature, 260°C; pressure, 2 Torr; initial free fatty acids, 2.15% oleic; gas amount, 0.3 mol.
[b]For abbreviations, see Table 1.

amount of stripping gas required is inversely proportional to the vaporization efficiency. Thus, where the amount of steam used in these assays had been in excess, this would be reflected in an apparent worse performance. In turn, a low amount of nitrogen used could have contributed to enhance vaporization efficiency.

On the other hand, hydrolytic or thermolytic reactions give rise to FFA and cannot be excluded (13–15). In case of significant hydrolysis, the injected amount of steam would have to remove the initial FFA plus the FFA originated during physical refining. This fact would result in a lower value of efficiency, because only the initial and the final values of FFA are considered in the equation.

To clarify these points, new experiments were conducted with refined olive oil that contained 2% of added stearic acid. The same molar amounts of steam and nitrogen were injected for different periods of time. Also, in the 2-h experiments, FFA were quantitated in both the final oils and the distillates, to achieve a more direct evaluation of hydrolytic reactions.

Table 2 lists the final FFA content and vaporization efficiency in the six experiments of physical refining that were carried out with 0.3 mol of steam (5.4 g) and nitrogen (7.4 g) in 0.5 h, 1 h, and 2 h. With respect to the previous assays, a lower efficiency was obtained for nitrogen, indicating that lower amounts should have been used, while similar values were obtained for steam. Nevertheless, vaporization efficiency was higher, almost double, for nitrogen than for steam in all experiments. Finally, although vaporization efficiency tended to decrease with longer periods of heating, differences were not considerable.

Table 3 shows the results of a mass balance for FFA at 2 h. Initial oils corresponded to a refined olive oil with and without 2% stearic acid added. Assays were carried out in parallel by using either steam or nitrogen as stripping gas under the conditions described in the table. The results indicated that formation of FFA took place in the four experiments, although to a different extent. Formation of FFA was higher in the assays with stearic acid, as previously reported, because hydrolysis seems to be catalyzed by the FFA originally present (15). As to the differences between the gases, lower values were obtained in the assays with nitrogen. Thermolytic reactions that give rise to FFA have been described when the temperature is higher than 200°C (14), which could account for FFA formation when nitrogen is used. For steam, both thermolytic and hydrolytic reactions could have contributed to FFA formation. However, the increase in fatty acid formation when steam was used could not justify the great differences obtained between both gases in the values of vaporization efficiencies.

The last set of laboratory experiments was carried out with three samples of olive oil, which were physically refined by injecting different amounts of steam and nitrogen. Taking into account the results obtained in the previous experiments, the steam flows selected were below the 2%/h used in the first experiments and above the amount used in the latter assays. For nitrogen, flow was around 0.3%/h, which seems to be closer to that required to reduce FFA to less than 0.1%, under the normal conditions for our discontinuous laboratory system, i.e., temperature, 260°C; pressure, 3 Torr; and operation time, 3 h. Table 4 summarizes the results obtained for quality indices and tocopherol quantitation, and includes the gas flows and efficiencies of FFA vaporization in the last two rows. Overall, the quality indices showed normal values for the final refined olive oils. Higher contents of unsaponifiable matter and α-tocopherol were obtained in experiments with nitrogen as compared to those with steam, which might be due to the lower sparging rate used. This finding might also explain the higher stability obtained in samples 2 and 3. In agreement with the previous assays, the vaporization efficiency was

TABLE 3
Free Fatty Acid Balance (wt% on oil) During Deodorization of a Refined Olive Oil Without and with 2% Added Stearic Acid[a]

Sample	i FFF[b]	f FFA	FFA in distillates	FFA formation[c]
Refined oil				
Steam	0.07	0.06	0.26	0.25
Nitrogen	0.07	0.03	0.21	0.17
Refined oil + stearic acid				
Steam	2.15	0.34	2.97	1.16
Nitrogen	2.15	0.04	2.67	0.56

[a]Operation conditions: oil, 200 g; temperature, 260°C; pressure, 2 Torr.
[b]For abbreviations, see Table 1.
[c][f FFA + FFA in distillates] – i FFA.

TABLE 4
Quality Indices of Olive Oil Physically Refined at Laboratory Scale with Steam or Nitrogen as Stripping Gas[a]

	Sample 1			Sample 2			Sample 3		
	Initial	Steam	Nitrogen	Initial	Steam	Nitrogen	Initial	Steam	Nitrogen
Free fatty acids (% oleic)	3.52	0.04	0.08	1.60	0.04	0.07	1.01	0.07	0.12
Oil stability index (height)	8.3	9.7	9.0	8.1	13.1	15.6	10.5	14.4	20.5
Peroxide value (meq O_2/kg)	30	0.8	0.5	4.9	0.5	0.7	17.6	0.2	0.6
Unsaponifiable matter (%)	0.98	0.78	0.83	1.01	0.91	1.11	0.83	0.58	0.63
α-Tocopherol (mg/kg)	<15	<15	<15	208	122	168	220	140	189
Gas flow (%/h)		1.8	0.5		1.5	0.5		1.2	0.3
Efficiency (%)		14.8	70.0		14.6	57.9		13.2	65.7

[a]Operation conditions: oil, 700 g; pressure, 3 Torr; temperature, 260°C; time, 3 h.

higher when nitrogen was used, and this fact could not be attributed to an excess of steam, as deduced from sample 3, wherein the FFA content was slightly higher after reducing the steam flow. This latter assay supported further that 0.3%/h of nitrogen was not enough to remove FFA to the level required.

Table 5 summarizes the results obtained for quality indices and tocopherol quantitation of the industrial samples. From a technical point of view, the assays with steam as stripping gas were carried out under the conditions normally used in the plant, and the amount of nitrogen established was one-fifth of that for steam. The results obtained in the first experiment with nitrogen indicated that this amount was not sufficient to remove FFA to the required level, below 0.1%. However, an increase of 10% in the nitrogen flow was enough to obtain the required FFA level in the final samples. Thus, the industrial process needed 0.12%/h of nitrogen, whereas the laboratory system required at least 0.3%/h. On the other hand, the vaporization efficiencies of FFA were much higher in the industrial plant than those obtained at laboratory scale.

Regarding the oils obtained, results did not enable distinguishing of the influence of the stripping gas on their quality, not even from the sensorial point of view judged by experts (data not shown). As occurred with the laboratory samples, the main difference between the use of nitrogen and steam depended on the percentages of unsaponifiable matter, higher when nitrogen was used, and attributed to the lower flow of gas injected.

With respect to deodorizer distillates, relevant differences were observed. Table 6 lists the results corresponding to the main groups of compounds quantitated in the distillates by TLC–FID and the values for FFA and unsaponifiable matter obtained by standard methods (9). The compositions of the distillates were within the standard limits in both laboratory assays and the industrial plant (16,17). The rapid method applied to distillate analysis was reliable because results for

TABLE 5
Quality Indices of Olive Oil Physically Refined in a 10-ton Discontinuous Deodorizer with Steam or Nitrogen as Stripping Gas[a]

		Steam		Nitrogen	
	Initial	Assay 1	Assay 2	Assay 1	Assay 2
Free fatty acids (% oleic)	2.06	0.04	0.04	0.12	0.08
Oil stability index (h)	8.1	12.0	9.8	11.0	7.4
Peroxide value (meq O_2/kg)	4.9	1.1	1.7	1.2	1.0
Unsaponifiable matter (%)	1.38	0.94	0.85	1.17	1.13
α-Tocopherol (mg/kg)	94	26	30	29	28
Gas flow (%/h)		0.53	0.53	0.10	0.12
Efficiency (%)		29.5	29.5	175.3	166.9

[a]Operation conditions: temperature, 250°C; pressure, 3 Torr; time, 4.5 h.

TABLE 6
Quantitation of the Main Groups of Compounds (wt%) Present in Deodorized Distillates from Physically Refined Olive Oils

	Lab. sample 1		Lab. sample 2		Lab. sample 3		Industrial sample			
							Steam		Nitrogen	
	Steam	Nitrogen	Steam	Nitrogen	Steam	Nitrogen	1	2	1	2
Hydrocarbons	5.1	1.7	9.6	7.7	10.3	8.2	15.3	14.2	12.2	10.0
Free fatty acids	84.9	90.8	74.1	81.0	71.3	80.2	70.7	63.6	76.0	79.4
Triglycerides	5.2	1.1	11.0	3.1	13.0	2.5	4.1	10.7	1.6	1.0
Sterols	0.8	0.4	0.9	0.5	0.7	0.4	0.6	0.6	0.5	0.3
Free fatty acids[a] (% oleic)	82.8	87.8	73.7	82.1	72.5	80.8	71.6	64.3	79.6	80.4
Unsaponifiable matter[a] (%)	10.7	4.8	13.3	12.8	14.0	10.6	16.8	15.0	12.6	11.7

[a]Values obtained by standard methods.

fatty acid levels were consistent with those obtained by applying the standard method.

Even though distillates were not quantitated, similar amounts of FFA would be expected from the same oil, independent of the gas used. In consequence, the higher proportion of FFA obtained with nitrogen clearly indicated lower total quantities of distillates. Moreover, the low percentages found for hydrocarbons, sterols, and triglycerides demonstrated reduced losses of these components and support the influence of the gas flow on the quantity and composition of distillates.

In summary, results indicate that the use of nitrogen instead of steam would provide not only a higher FFA vaporization efficiency but also a lower loss of the unsaponifiable fraction, a minimal entrainment of triglycerides, and a lower total amount of deodorizer distillates.

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