

Comparison of Steam and Nitrogen in the Physical Deacidification of Soybean Oil

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ABSTRACT: Deacidification in physical refining is one of the most sensitive steps in refining edible vegetable oils because of its large impact on the quality of the oil. The removal of volatile compounds such as FFA is accomplished at elevated temperatures and a high vacuum with a stripping gas, usually steam. The aim of this work was to verify, at the laboratory level, the advantages of using an alternative stripping gas, nitrogen, instead of steam. An ideal vapor–liquid equilibrium model (IVLE) was used to compare the stripping capacities of steam and nitrogen and to analyze the effects of various operational parameters (temperature, pressure, amount of stripping gas) on the residual acidity of the oil. There was no clear evidence that nitrogen showed a higher capacity to strip FFA than steam. The IVLE model seemed suitable to describe FFA laboratory distillation by using steam or nitrogen, provided the final residual content of FFA was not too low.

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In the physical refining process, FFA are removed during the deacidification/deodorization process, i.e., vacuum–steam distillation at high temperatures (220–270°C) and low pressures (2–5 mbar) by the addition of live steam (0.5–2 % w/w) as a stripping gas. The total pressure is equal to the sum of the partial vapor pressure of each volatile compound (Raoult's law) and the stripping gas pressure. As a consequence, the deacidification process can work at a higher total pressure with the use of a stripping gas than one without. Eliminating the FFA without a stripping gas would require a higher level of vacuum (0.001–0.1 mbar) for the same result; this is the domain of molecular distillation. From a simple thermodynamic point of view (ideal model), the required amount of stripping gas is proportional to its M.W. Therefore, stripping gases with the lowest possible M.W. are selected.

Steam is generally the most commonly used stripping gas. Although it is not an inert gas and hydrolysis of the oil during deodorization can occur (1), it is usually the most preferred option for economical reasons. However, the use of alternative inert stripping gases has been suggested by several authors (2–5). Among them, the use of nitrogen has been recently proposed as an alternative to steam in deacidification (6–12). The advantages of using nitrogen as a stripping gas

include having a more stable deodorized oil, better distillate quality, and lower neutral oil losses. Nevertheless, most edible oil refiners do not prefer nitrogen since it is a noncondensable and inert gas that requires a significantly larger vacuum unit, thus increasing the investment.

Graciani-Constante and coworkers (7,8) concluded that the use of nitrogen is possible under normal deodorization conditions, although profitability depends on many factors, such as the production and transport (i.e., pipe installation) costs of nitrogen vs. steam, the size of the required vacuum unit, and waste effluent treatment. It will therefore vary from one plant to another. In determining the operating cost of the deacidification process with either steam or nitrogen, one important factor to consider is the stripping efficiency of both gases. On this matter, contradictory observations are reported in the literature.

Some authors (9–11) claim a significantly higher stripping efficiency for nitrogen, meaning that substantially lower amounts of nitrogen are required for a given deacidification process [5–10 times lower than steam, i.e., 22 to 230 standard cubic feet (scf) N₂/ton of oil, or the molar equivalent of 0.05 to 0.5% w/w of steam]. The higher stripping efficiency of nitrogen may be due to an enhanced oil–gas mass-transfer rate because a smaller bubble size may result from gaseous nitrogen having a different viscosity and therefore a different interfacial surface tension. On the other hand, Graciani-Constante and coworkers (7,8) reported that nitrogen consumption in the range of 1–1.5 times the molar amount of steam (1.56–2.34 times on a mass basis) is required to obtain a refined oil with similar residual acidity and organoleptic characteristics. One of the potential explanations for these reported contradictory stripping efficiencies for nitrogen is that the nitrogen dosage was inaccurate. Unlike steam, nitrogen is not easy to dose accurately, and calibrated equipment is required.

In this study, the ideal vapor–liquid equilibrium (ILVE) model was used to compare the stripping efficiency of nitrogen and steam, with special attention being given to accuracy of the nitrogen dosage. The effect of nitrogen stripping on the quality of edible oil (*trans* FA, tocopherol retention, oxidized compounds, stability, and color) is discussed in a separate publication (Decap, P., S. Braipson-Danthine, B. Vanbrabant, W. De Greyt, and C. Deroanne, unpublished data). An evaluation of organoleptic characteristics was not performed because of the authors' lack of experience in this field.

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EXPERIMENTAL PROCEDURES

Material. Neutralized and bleached soybean oil, with an initial acidity of 0.1% (w/w), was obtained from Extraction De Smet (Zaventem, Belgium). Oleic acid (1% w/w) (Mosselman, Ghlin, Belgium) was added before each stripping experiment to study the stripping efficiency of the different gases. The purity of the oleic acid was 83.3%, as determined by GLC. The impurities were also FA (mainly linoleic acid, which has a volatility similar to oleic acid).

Deacidification method. Physical refining experiments were conducted in a laboratory-scale batch deodorizer (Fig. 1). Neutralized and bleached soybean oil (260 g) was blended with oleic acid (2.6 g) to obtain an initial FFA content of 1.1%. The blend was introduced into a glass batch deodorizer (1000-mL fat flask) and placed in a hot-air oven [UT600 heating oven; Heraeus (Kendro), Hanau, Germany], which effectively controlled the temperature of the oil. The oil layer was around 3 cm in the middle of the batch deodorizer flask. The stripping-gas injector was a 5-mm inlet diameter glass pipe with four holes (<1 mm) at the nozzle. It was introduced into the oil flask as illustrated in Figure 1. After degassing at reduced pressure, the oil was heated to the desired process temperature, and the pressure was adjusted to the desired value. Once the oil had

reached the required deodorization temperature (see Table 1), the flow rate of the stripping gas was adjusted to the desired value. The top part of the batch deodorizer was heated (20–35°C above the deodorization temperature) to avoid reflux of the volatile components. The vapor phase leaving the batch deodorizer was collected in a small vessel (because it was only partially condensed, the contents of the distillate could not be measured accurately by GLC analysis). After deodorization, the oil was cooled under vacuum (at operating pressure) to <85°C. The deodorized oil was weighed to allow the calculation of the neutral oil losses and was then stored in an opaque glass vessel under nitrogen atmosphere at –20°C until further analysis.

Steam injection. A burette was filled with 10 mL of water (vacuum degassed for 30 min). The injection of steam was actually controlled by the flow rate of the water *via* a microperistaltic pump (Gilson, Villier le Bel, France), and the water was vaporized in a heating coil. Fluctuations in flow rate and droplet entrainment were prevented by using a heated buffer vessel placed behind the heating coil. The inlet connection to the gas injector was heated at 155–160°C to avoid cooling the injector surface inside the oil flask (to avoid FFA reflux).

Nitrogen injection. The burette and the peristaltic pump were replaced by a system adapted for controlling the nitrogen

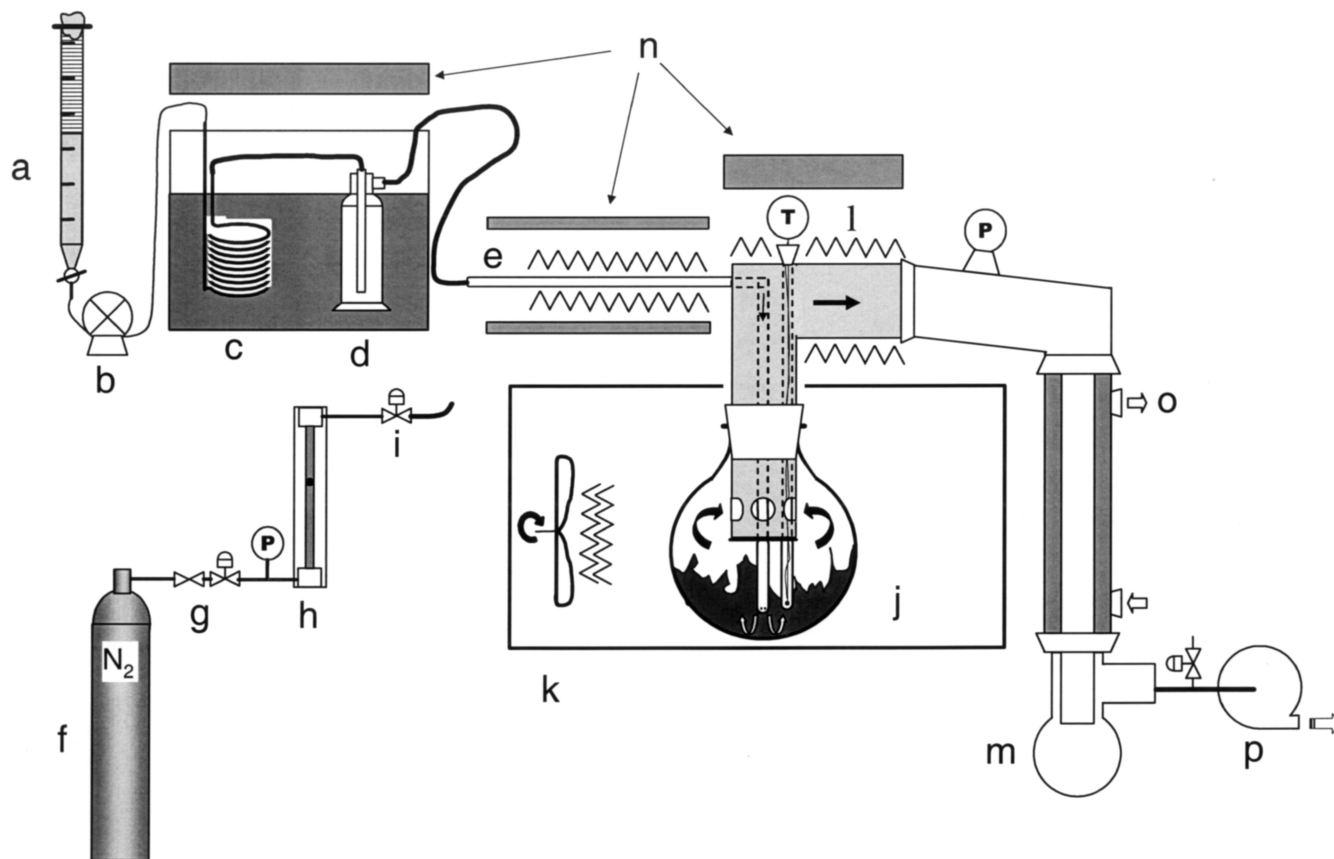


FIG. 1. Experimental setup: a, burette; b, microperistaltic pump; c, heating coil; d, buffer vessel; e, electric heating of inlet connection; f, nitrogen carboy; g, pressure-reducing valve; h, flowmeter; k, hot-air oven; i, microvalve; j, glass batch deodorizer; l, heated gas outlet; m, condenser; n, glass wool heat-insulation; o, cooling fluid; p, vacuum pump; T, thermometer; P, manometer.

TABLE 1
Overview of the Experiments of the Full-Factorial Design

Operating variables	Level		
	Minimum	Central	Maximum
Temperature (°C)	210	230	250
Pressure (mbar)	3	4	5
Amount of gas			
H ₂ O (wt%)	0.5	1.0	1.5
N ₂ (N _L /kg) ^a	6.2	12.4	18.6

^aN_L, liters in normal conditions, at 1 atm and 20°C.

flow rate. A pressure-reducing valve (double effect) ensured good stability of the outlet pressure independent of the fill level of the nitrogen carboy. This pressure was accurately adjusted at 2 bar abs. The nitrogen flow rate was then measured with a calibrated laminar flow meter (Brooks-Brooksmite Purgemeter, Hatfield, PA). The volumetric flow rate of nitrogen or steam was converted into a molar flow rate by using the law of the perfect gas. The nitrogen flow rate was adjusted with a downstream microvalve that depressurized the gas to the operating pressure. As in the case of steam, the connection to the gas injector was heated (155–160°C).

Experimental design. Experiments were carried out using a 2³ full-factorial design with five central points to estimate the reproducibility of the trials. The range of variables was selected according to the typical European operating conditions needed in soft oil physical refining (13) and to the capacity of the laboratory vacuum pump (Table 1). The stripping time was fixed at 1 h in all experiments while equimolar amounts of steam and nitrogen were injected.

Analytical determinations. The FFA content was determined using AOCS Analytical Method Ca 5a-40 (14).

Statistical analysis. The 18 experiments were divided in two groups (steam and nitrogen). Each group included 1 central point experiment (with five repetitions) and 8 experiments corresponding to the extremities of the experimental domain. The effect of the three operating variables (temperature, pressure, amount of gas) and nature of the stripping gas on the

residual FFA was studied by ANOVA, whereas the most influential operating variables (or combination of variables) were determined by Tukey's test (Minitab Inc., State College, PA).

RESULTS AND DISCUSSION

Analysis of results. Experimental results are reported in Table 2. The low SD of the central point bore out the repeatability of the stripping experiments with steam or nitrogen. Statistical analyses revealed very highly significant ($P = 0.95$) influences for temperature, amount of gas, and pressure. These operating variables interacted strongly and in numerous ways to influence the residual FFA. Tukey's test showed predominant effects for temperature and amount of gas. Although, the influence of the stripping gas was not statistically significant, it could have been hidden by interaction effects.

Neutral oil losses were determined by mass balance by measuring the initial and final acidity of the oil and any weight loss. For the central points, neutral oil losses were $1.31 \pm 0.03\%$ (w/w) for steam and $1.25 \pm 0.05\%$ (w/w) for nitrogen.

Discussion. The statistical analyses allowed us to select a physical model that described the distillation phenomena. A classical thermodynamic model, the IVLE model, was used to compare the stripping efficiency of steam and nitrogen. The IVLE model is a simple method used in chemical process modeling (15). This approach is applied to vegetable oil refining (16) and has the merit of replacing the traditional Bailey equation (4), which is inadequate for simulating physical refining (when the initial FFA content is significant, i.e., >2%). The IVLE model was based on two main assumptions: (i) an ideal vapor–liquid FFA/oil equilibrium (Dalton's and Raoult's laws) and (ii) negligible oil losses by entrainment (only 1.3% was carried by the gas in our experiments).

In our experiments, FFA were eliminated only by gas stripping. No spontaneous distillation of FA occurred before the injection of stripping gas, because the initial oleic acid content (1.1% w/w) was too low to produce a partial pressure of oleic acid higher than the total pressure. Indeed, at 250°C,

TABLE 2
Experimental Results and Interpretation: Residual FFA After Stripping Treatment and Overall Oleic Acid-Stripping Efficiency Based on the Ideal Vapor–Liquid Equilibrium Model (E_{IVLE})

Temperature (°C)	Amount of gas ^a	Pressure (mbar)	Residual FFA (oleic acid) (% w/w)		E_{IVLE} (%)	
			Steam	Nitrogen	Steam	Nitrogen
210	0.5	5	0.803	0.860	84	66
210	0.5	3	0.554	0.708	106	69
210	1.5	5	0.452	0.349	81	104
210	1.5	3	0.262	0.186	77	97
230	1.0	4	0.170 ± 0.017	0.178 ± 0.008	81 ± 4	81 ± 2
250	0.5	5	0.262	0.270	70	67
250	0.5	3	0.062	0.121	81	62
250	1.5	5	0.060	0.034	49	59
250	1.5	3	0.040	0.025	34	38

^aIn wt% for steam or the molar equivalent for N₂.

the initial partial pressure of oleic acid was initially around 1.3 mbar (Raoult's law).

The overall FFA gas-stripping efficiency, E_{IVLE} , was defined as the ratio between the actual capacity of the gas to strip FFA from the oil and the theoretical capacity predicted by the IVLE model. The overall FFA gas-stripping efficiency, E_{IVLE} , was calculated from the following IVLE model equation (15) (see the Appendix for a demonstration):

$$E_{IVLE} = \frac{P_{total}}{P_{sat,oleic\ acid}(T)} \times \frac{\left\{ \ln \left(\frac{X_{oleic\ acid}^{initial}}{X_{oleic\ acid}^{final}} \right) + (X_{oleic\ acid}^{initial} - X_{oleic\ acid}^{final}) \right\}}{\frac{MW_{oil}}{MW_{gas}} \times \frac{Q_{gas}}{Q_{oil}} + (X_{oleic\ acid}^{initial} - X_{oleic\ acid}^{final})} \quad [1]$$

where (in SI units) $P_{sat,oleic\ acid}(T)$ is the vapor pressure of the oleic acid at temperature T , derived from Lederer's equation (17); MW is the M.W.; the mean value $MW_{soybean\ oil} = 870$ is based on the FAME profile of the present soybean oil; Q is the weight amount; $X_{oleic\ acid}$ is the molar fraction on a partial basis (i.e., the quantity of moles of oleic acid in oil divided by the quantity of moles of soybean oil); and P_{total} is the mean total pressure at which the mass transfer and phase equilibrium take place in the oil layer.

Stage (18) considered that, for a batch deodorizer without a gas lift pump, the mean total pressure is the head pressure over the oil layer added, with the hydraulic pressure at half the depth of the oil layer. This has a real impact on the total pressure value since each centimeter of oil layer² leads to an additional 0.75 mbar of hydrolytic pressure. In our approach, P_{total} was taken as the operating pressure measured at the top of the batch deodorizer, since the main objective of the study was to compare the stripping efficiency of steam and nitrogen in a relative way.

According to the ILVE model, a mole of any gas should have the same stripping effect. In practice, however, this is not always the case. Moreover, the real stripping efficiency is also affected by physicochemical phenomena and the geometry of the deodorizer. More specifically, the influence on the mass-transfer rate of physicochemical interactions between a gas and the FFA/oil mixture attributable to the nonpolarity of some gases (e.g., nitrogen bubbling effects) are not considered in the ILVE model.

ILVE data for the different stripping experiments with steam and nitrogen are presented in Table 2. There are many reasons why E_{IVLE} was not equal to 100%. As just mentioned, not knowing the actual total pressure at which the exchange and equilibrium have taken place is a source of inaccuracy (18). Second, phase equilibrium could not be reached because the FFA mass transfer was limited by too short a gas-phase residence time or by too small a gas-liquid interfacial area.

Limitations in mass transfer could explain the low E_{IVLE} values (30–40%) observed when the lowest residual FFA was

reached. Another reason for these low results could be the existence of FFA recondensation on cold surfaces inside the oil flask (reflux). Some chemical reactions, such as hydrolysis, could also be possible (1). As mentioned by Stage (19), an infinite activity coefficient of lower than 1 for FFA in the oil is another hypothesis. However, this last suggestion is not in accordance with Sarkadi (20), for whom the nonideality of FFA-oil mixtures resulted in an infinite activity coefficient of around 1.5.

Two values of E_{IVLE} were slightly above 100%; however, more experimental points would have had $E_{IVLE} > 1$ if some hydraulic pressure were taken into account in the calculation of P_{total} . Sarkadi's infinite activity coefficient could be a first hypothesis that justifies an easier stripping of FFA. Second, possible interactions between FFA and other volatiles, such as tocopherols, sterols, glycerides, and odoriferous substances, in the distillation process cannot be excluded. The esterification reaction between FFA and free sterols to form steryl esters, promoted by the temperature, was mentioned previously (21). Another explanation is the presence of palmitic and linoleic acids, which were detected in the collected fraction of the distillate (but not accurately quantified). The presence of palmitic and linoleic acids were not considered in our model, since the major objective of the study was to compare steam and nitrogen in a relative manner. Palmitic and linoleic acids have higher volatility than oleic acid (~1.60 and ~1.15, respectively). The impact of palmitic acid was relatively enhanced when the experimental conditions were moderate (e.g., 210°C, 3 mbar, 0.5%, or 210°C, 5 mbar, 1.5%). In these cases, most of the palmitic acid should have been stripped; however, only a small portion of the oleic acid was stripped (as shown by the high residual acidity).

The nitrogen efficiencies obtained by Graciani-Constante *et al.* (7) on a laboratory and pilot-plant scale varied from 45 to 57%. Their experimental conditions were: soybean oil with initial acidities of 0.4–1% of stearic acid, 220–260°C, 2–3 mbar, and an amount of nitrogen that was the molar equivalent to 0.176–0.565% (w/w) of steam. In a second article, Graciani *et al.* (8) tested the nitrogen deacidification of sunflower oil with an initial acidity of 0.56%. Those conditions were 230–265°C, 3.3–6 mbar, and an amount of nitrogen that was the molar equivalent to 0.5 to 1% (w/w) steam. From data presented in this article, an overall stripping efficiency of 15 to 68% could be calculated using the authors' formula, which is similar to Equation 1.

Graciani and colleagues could have obtained such low efficiencies because the hydrolytic pressure of the oil layer was less negligible in their batch deodorizer (around 50 cm) but was not taken into account. Moreover, in their second study, the sunflower oil contained "natural" acidity, i.e., numerous FFA with distinct volatilities. The vapor pressures of stearic, oleic, linoleic, and palmitic acids at 240°C are, respectively, 24.6, 26.0, 29.7, and 40.4 mbar. Rather than using the vapor pressure of each FFA, the authors used only one "mean" value for FFA vapor pressure (e.g., 37 mbar at 240°C), which seems to have been estimated too high, leading to overly pessimistic efficiencies.

¹The stripping efficiency could vary with the time of the distillation process; the overall efficiency was the mean efficiency over the total process.

²The depth is to be expressed in terms of clear liquid (degassed oil).

In our study, the five central experiments gave the same mean efficiency for the two gases, 81% with a low SD, proving that the process treatments were done in a reproducible way. For the many reasons just mentioned, this value of E_{IVLE} is to be taken not in absolute terms but in a relative way to compare nitrogen and steam. In our laboratory experiments, nitrogen was less capable of stripping FFA than found by Cheng and colleagues (9,10) and Ruiz-Mendes and colleagues (11), who had observed E_{N_2} to be ~5 to 10 times E_{steam} . It could even be concluded in our case that a mole of nitrogen had almost the same stripping capacity as a mole of steam.

The gas flow rate was the only significant operating variable leading to a small difference between the two gases (Fig. 2). At a low vs. high flow rate, a slight distinction appeared between the efficiencies of steam and nitrogen. At a high gas flow rate, steam showed a lower E , possibly caused by the additional FFA generated by hydrolysis (at 230°C, 0.02% of additional FFA is a rough estimation) (1). At a low gas flow rate, nitrogen showed a lower E . The nonpolarity of this gas could have led to a small bubbling effect unfavorable to mass transfer.

The IVLE model seems suitable to roughly describe FFA distillation using both steam and nitrogen. The limitations of this model are shown clearly by the variations in E_{IVLE} , which tripled from 34 to 106% in our experiments. E_{IVLE} values were the most different from 100% when the final residual acidity was very low (extreme experiments at 250°C and 1.5% w/w).

A reliable explanation for the variations in efficiency as a function of operational parameters (pressure, quantity of stripping material, temperature) is beyond our present objective. Such a study demands the use of a more elaborate physical model (mass transfer, activity coefficient, and hydrolysis) and an improved experimental setup (distillate, high-purity material).

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APPENDIX

Demonstration of the Formula (Eq. 1)

(For the notations used in our demonstration, see the end of this Appendix.)

(i) Based on the assumption of the ideality of the liquid mixture between the neutral oil and the volatile solute (FFA), Raoult' law gives:

$$P_{FFA}^{ideal\ equilibrium} = P_{sat, FFA} \cdot x_{FFA} \quad [2]$$

The liquid molar fraction of the volatile solute,

$$x_{FFA} = n_{FFA}^{liq} / n_{total}^{liq} \quad [3]$$

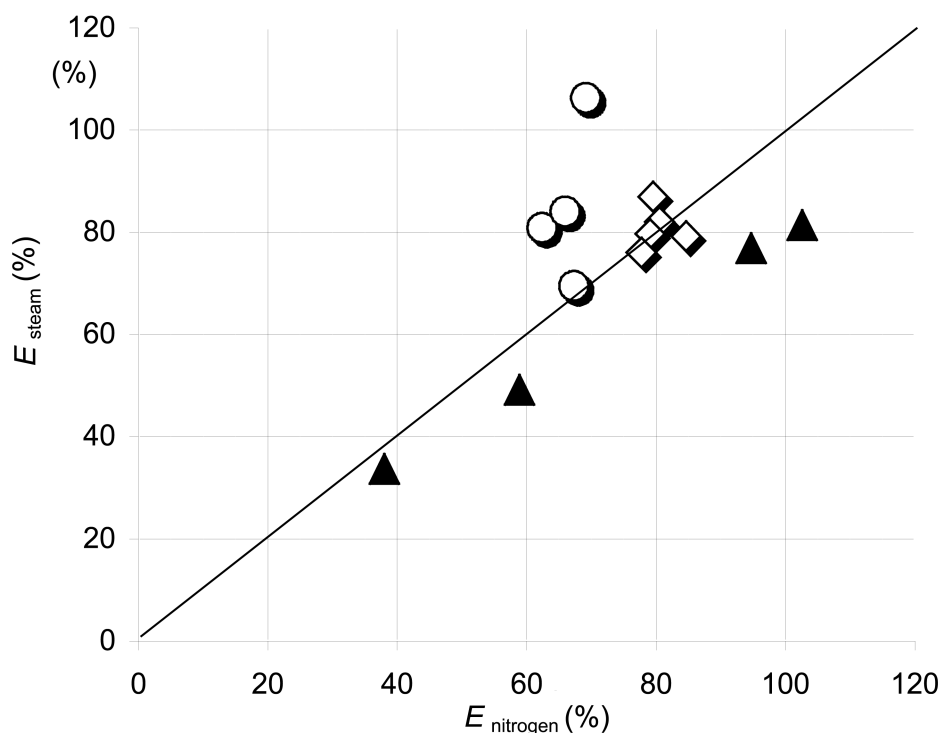


FIG. 2. Steam–nitrogen comparison: overall FFA gas-stripping efficiencies based on the ideal vapor–liquid equilibrium (IVLE) model. (○) Low gas flow rate (0.5%/h); (◇) medium gas flow rate (1.0%/h); (▲) high gas flow rate (1.5%/h).

can be related to the liquid molar fraction of the volatile solute on a partial basis,

$$X_{\text{FFA}} = n^{\text{liq}}_{\text{FFA}} / n^{\text{liq}}_{\text{oil}} \quad [4]$$

Indeed, as

$$n^{\text{liq}}_{\text{total}} = n^{\text{liq}}_{\text{FFA}} + n^{\text{liq}}_{\text{oil}} \quad [5]$$

we can write:

$$x_{\text{FFA}} = n^{\text{liq}}_{\text{FFA}} / n^{\text{liq}}_{\text{total}} = (n^{\text{liq}}_{\text{FFA}} / n^{\text{liq}}_{\text{oil}}) / (n^{\text{liq}}_{\text{FFA}} / n^{\text{liq}}_{\text{oil}} + n^{\text{liq}}_{\text{oil}} / n^{\text{liq}}_{\text{oil}}) \quad [6]$$

Then

$$x_{\text{FFA}} = X_{\text{FFA}} / (X_{\text{FFA}} + 1) \quad [7]$$

The FFA gas-stripping efficiency, E , is defined as the ratio between the FFA *actual* partial pressure and the FFA *ideal equilibrium* partial pressure:

$$E = P_{\text{FFA}} / P^{\text{ideal equilibrium}}_{\text{FFA}} \quad [8]$$

The combination of Equations 2, 7, and 8 gives:

$$P_{\text{FFA}} = E \cdot P_{\text{sat,FFA}} \cdot X_{\text{FFA}} / (X_{\text{FFA}} + 1) \quad [9]$$

(ii) Dalton's law (ideal gas mixture) is applied to the stripping gas (i.e., steam) carrying the volatile compound (i.e., FFA):

$$D_{\text{FFA}} / D_{\text{steam}} = P_{\text{FFA}} / P_{\text{H}_2\text{O}} \quad [10]$$

As the total pressure is the sum of the partial pressures,

$$D_{\text{FFA}} / D_{\text{steam}} = P_{\text{FFA}} / (P_{\text{total}} - P_{\text{FFA}}) = 1 / (P_{\text{total}} / P_{\text{FFA}} - 1) \quad [11]$$

(iii) The FFA mass balance of the exchange between the liquid and gas phases can be written:

$$D_{\text{FFA}} = -dn^{\text{liq}}_{\text{FFA}} / dt \quad [12]$$

If the neutral oil losses are *negligible*,

$$dn^{\text{liq}}_{\text{oil}} / dt = 0 \quad [13]$$

Then

$$dn^{\text{liq}}_{\text{FFA}} = n^{\text{liq}}_{\text{oil}} \cdot dX_{\text{FFA}} \quad [14]$$

$$D_{\text{FFA}} = -n^{\text{liq}}_{\text{oil}} \cdot dX_{\text{FFA}} / dt \quad [15]$$

(iv) The combination of Equations 11 and 15 is

$$(-n^{\text{liq}}_{\text{oil}} \cdot dX_{\text{FFA}} / dt) / D_{\text{steam}} = 1 / (P_{\text{total}} / P_{\text{FFA}} - 1) \quad [16]$$

and

$$D_{\text{steam}} \cdot dt = +n^{\text{liq}}_{\text{oil}} \cdot (1 - P_{\text{total}} / P_{\text{FFA}}) \cdot dX_{\text{FFA}} \quad [17]$$

Then Equation 17 combined with Equation 9 gives:

$$D_{\text{steam}} \cdot dt = n^{\text{liq}}_{\text{oil}} \cdot \left\{ 1 - P_{\text{total}} / \left[E \cdot P_{\text{sat,FFA}} \cdot X_{\text{FFA}} / (X_{\text{FFA}} + 1) \right] \right\} \cdot dX_{\text{FFA}} \quad [18]$$

and

$$D_{\text{steam}} \cdot dt = n^{\text{liq}}_{\text{oil}} \cdot \left\{ 1 - 1/E \cdot P_{\text{total}} / P_{\text{sat,FFA}} \cdot (X_{\text{FFA}} + 1) / X_{\text{FFA}} \right\} \cdot dX_{\text{FFA}} \quad [19]$$

(v) As

$$-\int_0^1 \frac{X+1}{X} \cdot dx = -\int_0^1 \left(1 + \frac{1}{X} \right) \cdot dX = (X_0 - X_1) + \ln \left(\frac{X_0}{X_1} \right) \quad [20]$$

and as

$$\int_0^1 dX = (X_1 - X_0) \quad [21]$$

then the integration of Equation 19, from the initial to the final time of the steam stripping, gives:

$$n^{\text{gas}}_{\text{steam}} = n^{\text{liq}}_{\text{oil}} \cdot \left\{ (X^{\text{final}}_{\text{FFA}} - X^{\text{initial}}_{\text{FFA}}) + 1/E_{\text{IVLE}} \cdot P_{\text{total}} / P_{\text{sat,FFA}} \cdot \left[(X^{\text{initial}}_{\text{FFA}} - X^{\text{final}}_{\text{FFA}}) + \ln(X^{\text{initial}}_{\text{FFA}} / X^{\text{final}}_{\text{FFA}}) \right] \right\} \quad [22]$$

Then

$$n^{\text{gas}}_{\text{steam}} / n^{\text{liq}}_{\text{oil}} + (X^{\text{initial}}_{\text{FFA}} - X^{\text{final}}_{\text{FFA}}) = 1/E_{\text{IVLE}} \cdot P_{\text{total}} / P_{\text{sat,FFA}} \cdot \left[(X^{\text{initial}}_{\text{FFA}} - X^{\text{final}}_{\text{FFA}}) + \ln(X^{\text{initial}}_{\text{FFA}} / X^{\text{final}}_{\text{FFA}}) \right] \quad [23]$$

So the overall FFA gas-stripping efficiency, E_{IVLE} , is calculated from the equation:

$$E_{\text{IVLE}} = P_{\text{total}} / P_{\text{sat,FFA}} \cdot \left[(X^{\text{initial}}_{\text{FFA}} - X^{\text{final}}_{\text{FFA}}) + \ln(X^{\text{initial}}_{\text{FFA}} / X^{\text{final}}_{\text{FFA}}) \right] / \left[n^{\text{gas}}_{\text{steam}} / n^{\text{liq}}_{\text{oil}} + (X^{\text{initial}}_{\text{FFA}} - X^{\text{final}}_{\text{FFA}}) \right] \quad [24]$$

And, as $Q = n \cdot \text{MW}$, finally QED:

$$E_{\text{IVLE}} = \frac{P_{\text{total}}}{P_{\text{sat,FFA}}(T)} \times \frac{\left\{ \ln \left(\frac{X^{\text{initial}}_{\text{FFA}}}{X^{\text{final}}_{\text{FFA}}} \right) + (X^{\text{initial}}_{\text{FFA}} - X^{\text{final}}_{\text{FFA}}) \right\}}{\frac{\text{MW}_{\text{oil}}}{\text{MW}_{\text{gas}}} \times \frac{Q}{Q_{\text{oil}}} + (X^{\text{initial}}_{\text{FFA}} - X^{\text{final}}_{\text{FFA}})} \quad [25]$$

Notations (in SI units)

$P^{\text{ideal equilibrium}}_{\text{FFA}}$: the partial pressure of the volatile solute, FFA, at the gas-liquid interface, at the equilibrium, assuming that the oil-FFA mixture is an ideal solution.

$P_{\text{sat,FFA}}$: the vapor pressure of the pure volatile solute, FFA.

$P_{\text{FFA}}, P_{\text{H}_2\text{O}}$: the actual partial pressure of the volatile solute, FFA, and of the stripping gas, steam, at the gas-liquid interface.

P_{total} : the actual total pressure at the gas–liquid interface.
 $n_{\text{oil}}^{\text{liq}}$, $n_{\text{FFA}}^{\text{liq}}$, $n_{\text{total}}^{\text{liq}}$: number of moles of neutral oil (we can consider neutral oil as TG with mean M.W. based on FAME profile), of volatile solute (FFA) and the total number of moles in the liquid phase.
 x_{FFA} , X_{FFA} : liquid molar fraction of the volatile solute on a total basis and on a partial basis (neutral oil).
 $n_{\text{steam}}^{\text{gas}}$: number of moles of stripping gas injected during the experiment.
 D_{FFA} , D_{steam} : the instantaneous and actual molar flow rates of stripped FFA and stripping gas.
 E : the instantaneous FFA gas-stripping efficiency.
 E_{IVLE} : the overall FFA gas-stripping efficiency.
 MW: molecular weight.
 Q_{oil} , Q_{steam} : the actual mass of neutralized oil and injected stripping gas.

REFERENCES

- Petrauskaitė, V., W.F. De Greyt, and M.J. Kellens, Physical Refining of Coconut Oil: Effect of Crude Oil Quality and Deodorization Conditions on Neutral Oil Loss, *J. Am. Oil Chem. Soc.* 77:581–586 (2000).
- King, W.G., Jr., and A.P. Lee, Improvement in the Purification and Deodorization of Glycerides, British Patent 589,534 (1947).
- Miller, B.D., Method and Apparatus for Removing Gaseous and Readily Vaporizable Materials from Liquids, British Patent 648,310 (1951).
- Bailey, A.E., *Industrial Oil and Fat Products*, Interscience, New York, 1951, p. 771.
- Lozheshnik, V., Y.P. Kudrin, I.D. Plekhno, A.A. Demchenko, G.N. Lozheshnik, and S.V. Maslygina, Method for Refining Fats and Oils, USSR Patent 1,052,535 (1983).
- Huesa-Lope, J., and D. Garcia-Ma Del Carme, A., Process for Deodorizing Oils and Fats, European Patent 0,405,601 (1991).
- Graciani-Constante, E., F. Rodriguez-Berbel, A. Paredor-Torronteras, and J. Huesa-Lope, Deacidification by Distillation Using Nitrogen as Stripper. Possible Application to the Refining of Edible Fats, *Grasas Aceites* 42:286–292 (1991).
- Graciani-Constante, E., J.C. Bada-Gancedo, F. Rodriguez-Berbel, and V. Ruiz-Méndez, Physical Refining of Edible Oils Using Nitrogen as Stripping Gas. Process Optimization., *Ibid.* 45:132–146 (1994).
- Cheng, A.T.Y., J. Ramon-Calvo, and B. Ramon-Rodriguez, Deodorizing Edible Oil and/or Fat with Non-condensable Inert Gas and Recovering a High Quality Fatty Acid Distillate, European Patent 0,513,739 (1992).
- Cheng, A.T.Y., Pulsation Flow to Optimize Nitrogen Consumption, European Patent 0,761,807 (1997).
- Ruiz-Méndez, M.V., G. Márquez-Ruiz, and D. Garcia-Ma Del Carme, Comparative Performance of Steam and Nitrogen as Stripping Gas in Physical Refining of Edible Oils, *J. Am. Oil Chem. Soc.* 73:1641–1645 (1996).
- Ruiz-Méndez, M.V., A. Garrido-Fernández, F.C. Rodriguez-Berbel, and E. Graciani-Constante, Relationships Among the Variables Involved in the Physical Refining of Olive Oil Using Nitrogen as Stripping Gas, *Fett/Lipid* 98:121–125 (1996).
- De Greyt, W., Effect of Physical Refining on Selected Minor Components in Vegetable Oils, Ph.D. Thesis, Universiteit Gent, Belgium, 1998.
- AOCS, *Official Methods and Recommended Practices of the AOCS*, 5th edn., edited by F. Gunstone, AOCS Press, Champaign, 1997, Method Ca 5a-40.
- Vián, A., and J. Ocón, *Elements of Chemical Engineering (Elementos de ingeniería química)*, Colección ciencia y técnica, Ed Aguilar, Madrid, 1963.
- Athanassiadis, A., The Deacidification of Vegetable Oils by Distillation During Deodorization, *Fat Sci. Technol.* 90:522–526 (1988).
- Markley, K.S., *Fatty Acids: Their Chemistry and Chemical Properties*, Interscience, New York, 1947, pp. 161–162.
- Stage, H., The Physical Refining Process, *J. Am. Oil Chem. Soc.* 62:299–308 (1985).
- Stage, H., Optimal Configuration of Large-Scale Technical Plants for Straight Distillation and Fractioning Natural Fatty Acids, *Seifen Öle Fette Wachse* 104:445–453 (1978).
- Sarkadi, S., Laboratory Deodorizer with a Vaporization Efficiency of Unity, *J. Am. Oil Chem. Soc.* 35:472–475 (1958).
- Verleyen, T., Stability of Minor Components During Vegetable Oil Refining, Ph.D. Thesis, Universiteit Gent, Belgium, 2002.

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