Deacidification by distillation using nitrogen as stripper. Possible application to the refining of edible fats.

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RESUMEN

Desacidificación por destilación mediante arrastre con nitrógeno. Posible aplicación a la refinación de grasas comestibles.

En los últimos años se está investigando la posibilidad de sustituir por nitrógeno el vapor de agua directo utilizado en la desodorización o la destilación neutralizante de aceites y grasas. Dicha posibilidad es factible, sin embargo implica un mayor costo debido al mayor precio del nitrógeno, y una necesidad de adecuar la tecnología para mantener la presión en cabeza del desodorizador (al no condensar el nitrógeno). Estos inconvenientes deben ser solventados por una mejor calidad de los aceites, de los condensados y por una disminución de la contaminación.

Los ensayos realizados indican que la "eficacia" calculada en cada una de las operaciones realizadas está dentro de los valores teóricos; y que los aceites refinados físicamente, mediante el paso de 1 a 1,5 veces la cantidad teórica de nitrógeno, tienen calificaciones de bueno y muy bueno dadas por un experto. Los condensados obtenidos han sido de buena calidad.

PALABRAS-CLAVE: Desodorización – Grasa comestible – Nitrógeno.

SUMMARY

Deacidification by distillation using nitrogen as stripper. Possible application to the refining of edible fats.

The possibility of substituting direct steam by nitrogen as stripper in the deodorizing or neutralizing distillation of oils and fats has been the subject of research in recent years. Although this is a practical possibility, it implies a greater cost due to the higher price of nitrogen, and the need to adapt the technology in order to maintain the deodorizer head pressure (as nitrogen does not condensate). These disadvantages would be compensated by a better quality of the oils and condensates, and a decrease in pollution.

The tests carried out indicate that the efficiency calculated in each of the operations is within the theoretical values, and that using from 1 to 1.5 times the theoretical amount of nitrogen, the refined oils are graded physically as good and very good by an expert. The condensates obtained have been of good quality.

KEY-WORDS: Deodorizing – Edible fat – Nitrogen.

1. INTRODUCTION

The possibility of substituting direct steam by nitrogen as stripper in the operations of deodorization or neutralizing distillation in the fat- and oil-refining industries has been the subject of research in the Instituto de la Grasa y sus Derivados, C.S.I.C. during recent years. Theoretically such a possibility is feasible, as A.E. Bailey stated in 1951: "Any other inert gas, such as hydrogen or nitrogen, would serve equally well if it were as cheap as steam and if it could be condensed and thus easily removed from the deodorizer system". (1). However, in practice, the refining oil industry has only used steam until the present days.

Changing the steam by nitrogen in this type of operation involves several problems (2) and some possible advantages. Among the former stands out the increase in the cost of refining due to the higher price of the new stripper gas. At present, the changes introduced into the technology of gas production from air has meant that it is possible to supply industrial nitrogen with specifications appropriate for its use in the foodstuff industry, with sufficiently low amounts of oxygen not to alter the oils and fats by oxidation during deodorization, and at prices competitive with steam, under certain conditions (3) (4). Another important disadvantage is that the majority of the refining industries use technological systems for obtaining a vacuum and to eliminate the distillates from the oils, which in many cases are neither adequate to maintain the necessary working pressure in the deodorizer head nor to eliminate the uncondensables formed by the non-condensed distillates from the oils and by the nitrogen. It has been shown that the absolute pressure reached in the deodorizer head installed in the pilot plant used rises above 30 - 40 torr on using nitrogen in place of steam when working with the existing vacuum production system (steam injectors followed by barometric condensers).

Among the possible advantages, it is hoped, they are a better conditioning of the refined fats for their

conservation, as they are removed under nitrogen protection, and, by means of an appropriate system of volatiles recovery, the elimination (as much as possible) of the pollution inherent in this type of operation due to dumping of the wastewaters from the barometric condensers into the public sewers and the release of the uncondensables into the atmosphere.

Taking these considerations into account, research was begun, with the help of the two collaborating companies, to demonstrate the advantages that this possible change in refining technology might contribute at the present. While under way, and with the initial results showing that this substitution was headed in the right direction (provided that certain circumstances were met) (3) (4), it was found necessary to modify the installations of the pilot plant, as detailed in the Experimental Part.

This work studies the possibility of using nitrogen in physical refining, measuring the efficiency of distillation of the fatty acids under three different conditions of temperature and using for its calculation the classic theory which describes the phenomenon (5):

$$E = \frac{p}{P_e \ (A+B_1-B_2)} \ (B_1-B_2+I \ \ln \frac{B_1}{B_2})$$

where: E = efficiency of the operation of distillation with gas stripping; A = moles of stripper gas; B_1 and B_2 = moles of distilled component (fatty acids: stearic) in the oil before and after the operation; I = moles of oil; p = absolute pressure in the deodorizer head; and P_e = vapour pressure of the distilled components (fatty acids: stearic).

2. EXPERIMENTAL PART

Oils used

A chemically refined soybean oil was used for the neutralizing distillation tests, and two bleached edible vegetable fats for the physical refining tests.

Deodorizer

The deodorizer was discontinuous. The temperature of the oil under process could be measured to an accuracy of 0.1°C at temperatures lower than 195°C and of 1°C above that. The absolute oil pressure in the head was measured to an accuracy of 1 to 2 tenths for pressures between 1 and 10 torr. The stripper gas was introduced into the centre by means of a nozzle.

Modifications in the refining plant

Given the impossibility of carrying out the programmed tests with the existing technolgy of the plant, a refrigeration system (CRYOCOND) was installed to condense the distillates, and a vacuum system (a ROOTS pump, capable of evacuating 500 m^3/h, followed by a HUCKEPACK pump, model 433, capable of evacuating 250m^3/h) supplied by BUSCH IBERICA S.A.. With this installation, an absolute pressure of 1.1 torr was obtained in the deodorizer head in the absence of stripper gas. In the presence of stripper gas, pressures compatible with the operations to be carried out were obtained. The stripper gases, together with the distillates from the oil, were passed alternately through each of the two cooling towers forming the refrigeration setup. Once one tower was saturated, and while the other was being used, the first was cleaned by melting the products retained inside it. In the case of nitrogen being the stripper gas, only the distillates of the oil were retained -a small fraction with respect to the useful volume of the tower- but it is necessary that both act alternately, as it has been shown that after a certain working period, there are losses in efficiency in their refrigerating power (see Results and Discussion).

After the initial tests, it was found necessary to carry out a further modification in the plant: the installation of a filter capable of retaining the particles of solid stearic acid carried over mechanically by the nitrogen. This filter was installed before the pumps.

Experiments carried out in neutralizing distillation

Following the preliminary tests, the five experiments detailed below were carried out:

1.– The refined soybean oil was introduced into the deodorizer and its heating begun under vacuum. When the temperature reached 150°C, pure stearic acid was added and the passing of nitrogen, as stripper gas, was begun under the experimental conditions (Table I). Heating was continued up to the working temperature, which was kept stable by successive additions of heat. After a certain time at the working temperature, the assay was begun, taking accurate samples at the times shown. In all cases, the segregated oil samples were cooled to room temperature under vacuum before being exposed to air. Once the experiment was finished, the oil was cooled to 130 - 135°C before ceasing the passing of nitrogen, and then cooling was continued under vacuum to room temperature.

Note: The oil heating and cooling operations were all carried out in the same way, except for the differences peculiar to each experiment, which are specified below.

2 and 3 - During heating before reaching 240°C, and in the oil cooling process, the nitrogen flow was from 100 to 150 l/h in standard conditions. The experiments were performed under the conditions shown in Table I.

Table I

Experimental data and results obtained in the experiments.

Experiment		Neutralizing distillation					Physical refining	
Oil		Acidified refined soybean					Decoloured vegetable fat 1	fat 2
Kg treated		175,0	168,0	160,0	161,5	152,7	150 - 155	150 - 155
°C of working (mean)		220,4	238,4	238,4	257,6	257,6	260	260
Head pressure (Torr, mean)		3,1	2,6	2,2	2,6	2,6	3 - 3,5	2
Vapour pressure s.a. (Torr, mean)		7,5	15,7	15,7	32,0	32,0	19,5	20,1
Nitrogen flow (l/h, s.c.)		539,0	368,2	368,2	373,5	373,5	400	400
Acidity (% oleic acid)	initial	1,044	0,514	0,383	0,821	0,449	0,30	0,15
	final	0,706	0,383	0,276	0,449	0,257	0,05	0,02
Time of operation (hours)		2,28	1,00	0,97	0,95	0,98	4,7	4,9
Alpha tocopherol	initial	33	33	31	29	24		
	final	33	31	29	24	25		
Gamma tocopherol	initial	103	95	94	95	97		
	final	99	94	100	97	102		
Delta tocopherol	initial	125	115	101	88	78		
	final	120	101	96	78	66		
Saturated in beta	initial	1,2	1,4	1,5	1,4	1,8		
	final	1,2	1,5	1,8	1,8	2,1		
Efficiency		0,571	0,539	0,508	0,503	0,451	A	B

A = The oil had a good flavour according to the expert.

B = The oil had an excellent flavour according to the expert.

4 and 5 - The pre-heating and cooling conditions of the oil were similar to the above. The working temperature was 260°C (Table I).

Experiments carried out in physical refining

Two physical refining assays were made at 260°C using two decolourized edible vegetable fats under similar conditions to those used in the neutralizing distillations. The experiments were begun when the fats reached 150°C with the passing of nitrogen as stripper gas, and finished when the oil acidity was lower than 0.05% and the fats had cooled (Table I).

Measurement of oil acidity

This was according to Standard UNE 55011, with samples of 20 g of oil and in triplicate.

Measurements of oil tocopherols and saturated f. a. in beta

These were according to Standards UNE 55073 and 55079.

3. RESULTS AND DISCUSSION

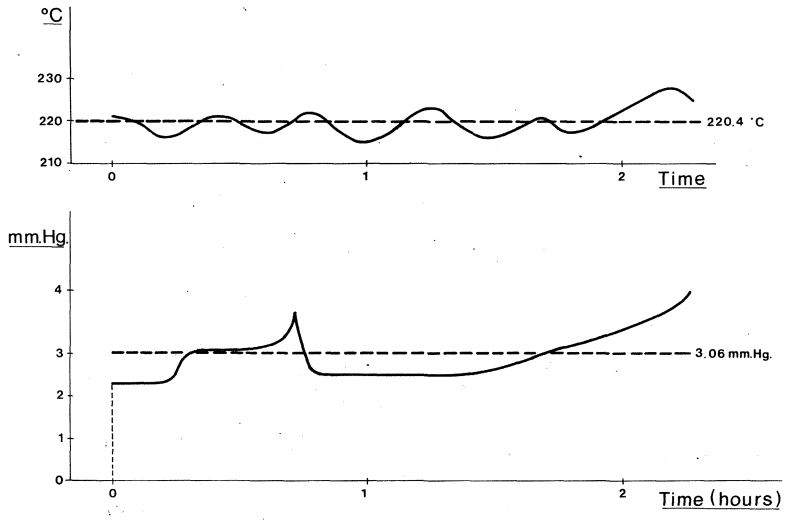
The results obtained in all the tests carried out are shown in Table I.

Preliminary tests were carried out to check the good working of the refining plant after the successive modifications made to it for the new working conditions. The last preliminary test carried out showed the need to include a filter when, under the working conditions in the modified plant, a neutralizing distillation was carried out with nitrogen as stripper gas on a high melting-point fat with free fatty acids.

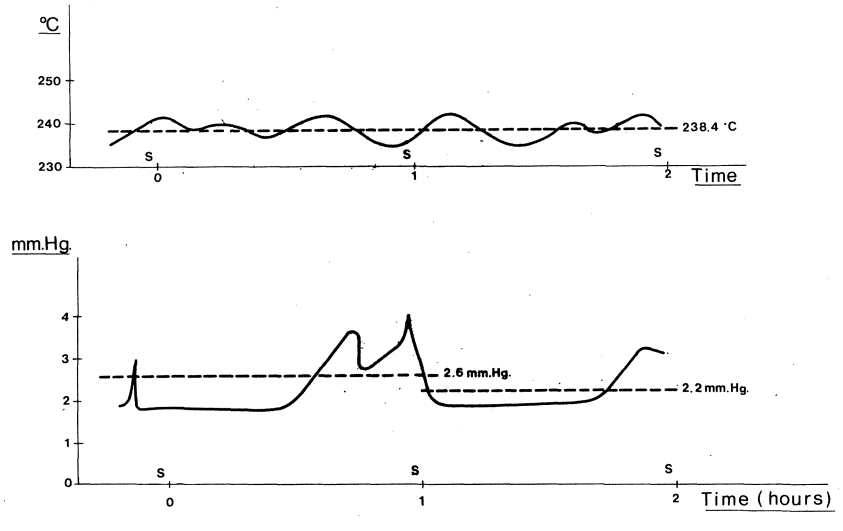
The experiments of neutralizing distillation were carried out in order to be able to determine the quantity of nitrogen necessary as stripper gas in physical refining operations "a priori" and without needing to take successive samples. By these means, the variables influencing the process, and their possible interrelationships, were studied.

Graphs I, II and III show the variations in temperature of the oil and of the absolute pressure in the deodorizing head throughout each neutralizing distillation experiment. The different experimental values were obtained by measurements carried out at short intervals of time from 1 to 3 minutes according to their increments of variations. Table I shows these values. To obtain the vapour pressures of stearic acid throughout the different processes, the following method was used: the value was calculated interpolating for that variable, in accordance with the oil temperature at each moment, in the function log vapour pressure of stearic acid-environmental temperature (6) (7), and represented as a function of time. For the interpolation, it was

supposed that the function was linear in the interval, around the value of the working temperature. Mean values of the vapour pressure of stearic acid were thus obtained by integration from the graph which were more accurate than by direct interpolation of the mean temperature of each assay.



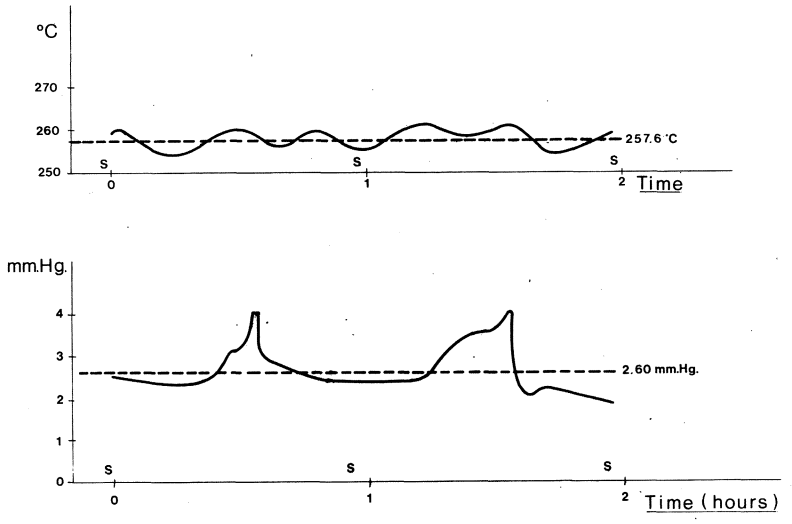
Graph I
Oil temperature and deodorizer head pressure ranges in the first assay. Sample – S.



Graph II
Oil temperature and deodorizer head pressure ranges in the second and third assays. Sample – S.

The results obtained calculating the efficiency in each of the five neutralizing distillations carried out (Table I) do not differ from those values considered normal for this type of operation (between 0.5 and 0.7) (5).

From Graphs I, II and III it is deduced that the system of condensation of the distillates could have a great influence on the overall efficiency of the operation by way of the absolute pressure in the deodorizer head. In these experiments the absolute



Graph III
Oil temperature and deodorizer head pressure ranges in the fourth and fifth assays. Sample – S.

amount of condensates (the great majority of these being formed by solid crystalline stearic acid, crystallized as fine needles in monoclinic form) is small compared with the useful volume of the refrigeration towers. However, the deodorizer head pressure (close to 2 torr) -stable during the initial working period of each tower- increases markedly (3 - 4 torr) after a certain working period, a condition under which it remains for a shorter period of time than before, after which it rises continuously. It is thought that after this certain working period of the tower, depending on the conditions of the operation under consideration, a layer of condensates is formed on the cold surface, causing a change in the heat transmission between the stripper gas -carrying the distillates- and the cold surface. This causes an increase in the mean temperature of the gas, and hence an increase in the absolute pressure of the system. When the thickness of the condensate layer increases greatly, the increase in working pressures is rapid.

For these reasons, it is thought that the system of recovery of the distillates from oils must maintain the temperature gradient of the stripper gas (nitrogen, distillate and air from leaks in the system) stable to prevent oscillations in the working pressure in the deodorizer head.

The stearic acid recovered in the parts posterior to the refrigeration tower (a part of the condensate in these is carried over mechanically by the nitrogen) has an excellent appearance (Figure 1). This leads to the possibility of recovering the condensates for industrial use, given their good quality.

The oils studied show that the content in saturated fatty acids in position beta of their triacylglycerols

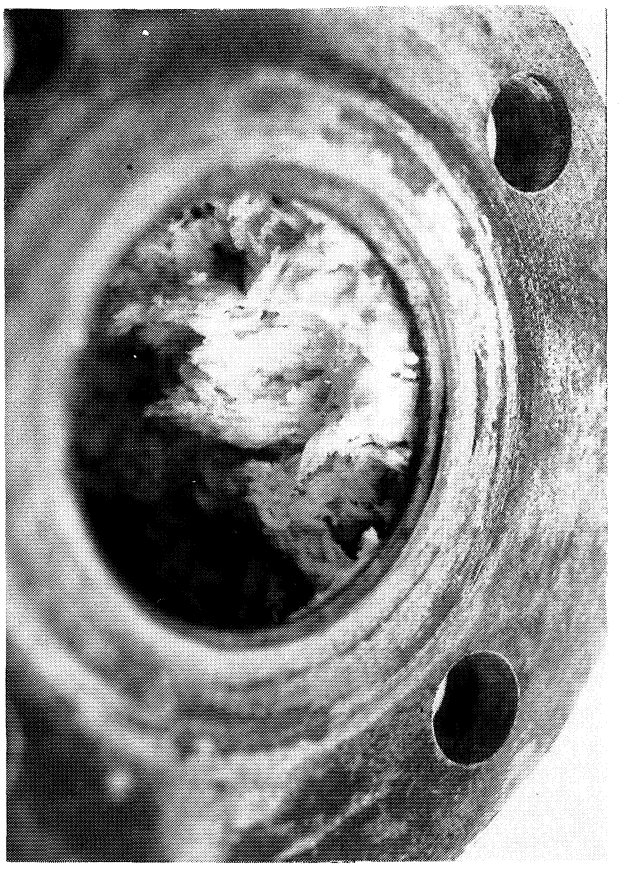


Figure 1
Stearic acid recovered in the neutralizing distillations, after the refrigeration system used to condense the distillates.
(16:0 = 13.5%; 18:0 = 60.1%; 18:1 = 13.1%; 18:2 = 6.9%; others = 6.4%)

increases after undergoing neutralizing distillation with nitrogen stripping at 240 and 260°C. This alteration is not detected in the oils when working at 220°C. At the same time, the tocopherol content decreases markedly when working at 260°C and practically not at all when working al 220°C (Table I).

In the two physical refinings carried out, the amounts of nitrogen passed are of the order of 88% and 136% respectively of those supposedly necessary in accordance with the efficiency of the plant (calculated in the preliminary operations), and the real conditions of the operation (amount of deodorized fat, working temperature, stripper gas flow, deodorizer head pressure) and duration (from the moment when the fats reach 150°C until they return to that temperature) (Table II). This Table also includes kilos of steam per ton of oil equivalent (mol to mol) to the quantities of nitrogen passed. These data could be useful for calculating the quantity of nitrogen which must be used in this type of physical refining operation.

Table II

Quantity of real or theoretical nitrogen: its relationship.

Physical refining	Total nitrogen passed (l in s.c.)	Theoretical nitrogen to be passed (E = 0,514) l in s.c.	% nitrogen passed (real/theoretical)	Oil quality according to the expert	Kilos steam per ton oil equivalent to nitrogen P.R.
1st	1.880	2.144	88	Good	9,7
2nd	1.960	1.440	136	Excellent	10,2

Using pumps of this nature to produce the vacuum in the deodorizers implies that all the distillates from the oils must be condensed, since, given their fat-soluble nature, the non-distillates remain dissolved in the mineral oil of the pumps, and because of their high volatility, raise the vapour pressure, and thus the absolute pressure of the system, without decreasing the capacity of elimination of the stripper gas. This makes more frequent oil changes necessary. The system of recovery of the distillates is considered very important. It should be capable of obtaining good quality condensates, and if possible, fractioned into the most characteristic components for their revaluation.

4. CONCLUSIONS

1.– It is possible to carry out the neutralizing distillation of edible oils and fats using stripping with nitrogen and in conditions similar to those commonly used with steam as stripper.

2.– The values obtained calculating the efficiency of the neutralizing distillations carried out in the Refining Pilot Plant of the Instituto de la Grasa y sus Derivados, C.S.I.C. are within those predicted for these operations in the different theoretical works.

3.– It is considered essential that the vacuum system is appropriate for the elimination of nitrogen, which does not condense as does steam, and it seems advisable to install appropriate systems for the recovery of distillates so that these are obtained with high quality.

If these conditions are met, a great part of the pollution produced by this type of industry can be eliminated, and the by products revalued.

4.– It is possible to use neutralizing distillation by stripping with nitrogen in physical refining, obtaining refined oils with adequate conditions of acidity and flavour.

This organoleptic quality increases if the quantity of nitrogen consumed in the operation is greater than that theoretically necessary according to the real working conditions and the efficiency of the plant. From the tests carried out, it is thought that this consumption may oscillate between 1 and 1.5 times the theoretical. A greater number of experiments in physical refining should be made to fully confirm these suppositions.

5– At this moment, and given the correct conditions, neutralizing distillation by stripping with nitrogen seems to be an appropriate technique for the physical refining of edible fats.

A deeper study is necessary on the quality of the oils and fats obtained, with respect to their conservation, nutritive properties, flavour, and non-alteration of major and minor components, etc.

6– According to the data of the works quoted (4) (5), the profitability of this process, which in part depends on the installations existing in the factory, may be appropriate under certain working conditions and nitrogen supply.

COLLABORATION

The following have collaborated in the present work:

The companies: Carburos Metálicos S. A.

Busch Ibérica S. A.

D. Enrique Pinto García, staff member of the Structural Unit "Procesos Industriales y Medio Ambiente" (Industrial Processes and the Environment) of the Instituto de la Grasa y sus Derivados, C.S.I.C., in the installations of the modifications, perfecting and working, of the Refining Pilot Plant.

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