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Temperature Effects on the Deacidification of Mixtures of Sunflower Oil and Oleic Acid

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Abstract Although it is well known that oil temperature is an essential factor for determining the deacidification mass rate and the final free fatty acids content, the influence of the temperature of the gas distillates above the liquid phase in the deodorizer on the oil temperature is much less understood. An extensive study of the effect of the temperature of the oil and of the gas distillates was undertaken in a continuous deodorizer, comparing the results with those obtained using a batch process. Variations in temperature from the temperature obtained without additional heating of the gases to a higher temperature than that of the oil were assayed for the gas distillates at the head of the deodorizer. It was possible to obtain low outlet free fatty acid contents at lower oil temperatures by controlling the overheating of the distillates, even for very high initial free fatty acids content, indicating that this is an essential variable to consider in distillation. However, increasing the temperature of the gas distillates above that of the oil sometimes produces a negative effect in deacidification.

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Introduction

Oil temperature is one of the most important operational parameters in the refining of edible oils, affecting the final free fatty acid content in the refined edible oil, the time required to complete the operation, neutral oil losses, the final quality of the oil [1], the amount of stripping gas required for deodorization [2], and the efficiency, which may be expressed by Vian's [3] formula. Vian's formula was theoretically deduced for distillation operations with a stripping gas. This expression of efficiency includes the vapor pressure of the major component of the distilled fatty acids, which is a function of the liquid phase temperature (see expressions proposed by Schlessinger [4] for the fatty acids).

The expression of efficiency does not include the distillate temperature at the head of the deodorizer. Equal temperatures are assumed for the liquid and vapor inside the deodorizer; however, the temperature may decrease substantially in the distillates from the liquid surface to the deodorized outlet (placed at the head of the deodorizer), and condensation of fatty acids into the liquid phase (known as reflux) may occur. This phenomenon is well known and it is assumed that modern deodorizers do not suffer this problem, as they are well insulated or additional heating is provided to compensate the heat loss caused by the evaporation of the distillates and the surrounding heat transfer. In some classic batch or plate column deodorizers, especially in small plants, the gases exiting the deodorizer generally have lower temperatures than the oil, even when the deodorizer is well insulated. This is partly due to the conductivity of the material in equipment downstream from the deodorizer and to the high vacuum within the system, which affects the mechanisms of heat transfer. Moreover, many deodorizers are not well insulated, because of the well-established criterion that since the gases have to be cooled after exiting, the more they cool due to loss of heat in the head of the deodorizer, less additional energy will be needed to cool the fatty acids in the subsequent condenser. As a consequence, this reflux results in a longer deodorization time and poor efficiency, and reduces the free fatty acid contents of the condensates that are collected in the subsequent condensers.

The importance of the gas temperature distribution inside the deodorizer was first suggested from experimental results in physical refining of soybean oil enriched with stearic acid (4% w/w) using live steam as the stripping gas [5]. In the aforementioned case, the assays were carried out in a 2-L capacity glass batch laboratory deodorizer. More recently, physical refining assays under several operating conditions (two levels for each) in a batch pilot-plant scale stainless-steel deodorizer confirmed the importance of maintaining the same temperature of the gas distillate and the oil [6, 7]. These assays were performed using nitrogen and live steam as stripping gases and showed that the deodorization rate may be doubled (and consequently the time spent for the process reduced considerably) by maintaining the gas distillates at the same temperature as the oil. This result is considered very important for industrial processes due to the economic and quality aspects involved. Additionally, the final free fatty acid content decreased and the efficiency substantially improved.

In the present paper, a more extensive study on the joint effect of the temperature of the oil and of the gas distillates above the liquid phase, i.e., at the head of the deodorizer, was undertaken. Assays were performed in a continuous deodorizer similar in design to that of classical batch technology, though adapted to the continuous process by introducing baffles to increase residence time and contact between oil and stripping gas. The results were compared with those obtained for the batch process [6]. The aim of the present study was to quantify how the temperature of the gas distillate affects distillation and to show how important this parameter is and to what extent a few degrees can affect the deacidification rate.

Materials and Methods

Deodorizer

The pilot-plant scale deodorizer was made of AISI 316 L stainless steel. Basically the same geometry was used for the shell of the deodorizer in both the continuous and batch processes. The deodorizer was a cylindrical vessel (250 × 600 mm) with a hemispherical bottom and a flat top. For the batch process, an inlet tube with a stopcock channeled the incoming nitrogen to the bottom of the deodorizer and the stripping gas was distributed through a perforated stainless-steel ring (120 mm diameter, 0.5 mm hole size). For the continuous process, the deodorizer was internally divided into three zones by three vertical plates to perform three oil passes. Additional internal parts were added so that each zone is always filled from the bottom up. The stripping gas was introduced by means of a perforated horizontal tube (two rows of holes at 45° to the tube axis and oriented towards the bottom) and the flow rate was controlled independently in each of these three zones. The diameter of the holes ranged between 0.5 and 1 mm. There is a drift eliminator at the top of the deodorizer ahead of the gas distillate outlet that recovers the oil droplets. The oil to be deodorized was electrically heated by ceramic brackets installed on the outside surface of the vessel, and the gas distillates were heated by an external heating strip.

The gas distillates were partially condensed and recovered in a horizontal two-pass shell-and-tube heat exchanger cooled with water. 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.

The required vacuum was achieved by connecting the outlet of the vertical heat exchanger to a vacuum pump (model PIL6-11; MPR, San Sebastian, Spain). The entire installation, except for the vacuum pump, was thermally insulated from the surrounding atmosphere by means of 60-mm thick mineral fiberglass.

Deodorization Treatments

Mixtures of refined sunflower seed oil (0.1% w/w free fatty acid, trademark Pulisol, Aceites de Carrión S.A., Toledo) and oleic acid (90% w/w purity provided by Merck, Darmstadt, Germany) were introduced at 5 L h^{-1} flow rate for the continuous process. The free fatty acid content of the refined sunflower oil was increased by adding oleic acid until the desired initial free fatty acid contents for the assays was reached. Nitrogen was injected at 2 bar pressure and at ambient temperature. For the batch process, batches of 13 L with an inlet free fatty acid content of 2.5% w/w composed of the mixture of sunflower seed oil and oleic acid were evaluated at oil temperatures of 245 and 265 °C, the nitrogen flow rate being maintained constant at 30 L h^{-1}.

The oil was introduced into the deodorizer once the desired vacuum was obtained (absolute pressure between 1 and 4 mm Hg). When the oil temperature reached about 90 °C, a low nitrogen flow rate was injected to remove the oil to prevent inappropriate wall temperatures. Injection of the full nitrogen flow rate started when the oil temperature reached 180 °C. On reaching this temperature, the first oil sample was taken and the free fatty acid content was determined. The installation was equipped with a system for taking samples from the deodorizer and from the condenser throughout the refining process without loss of vacuum. Once the desired operating conditions were reached ($t = 0$), samples were taken from the deodorizer and the condenser every 30 min. The trial continued for at least 3 h after reaching steady state in both operating conditions and outlet free fatty acid content. The free fatty acids content of each sample was determined according to standard AOCS methods [8].

The oil temperature was increased from temperatures at which deodorization is very slow to temperatures higher than those usually employed, while avoiding polymerization or damaging the oil. Variations in gas distillate temperature at the head of the deodorizer were assayed, from the temperature obtained without additional heating of gas to higher temperature than that of the oil.

Obtaining low deodorization times and keeping the oil temperature low are very important in industrial processes. The consideration of these variables together means that in practice the maximum initial free fatty acid content for physical refining is 2% w/w; chemical refining being traditionally used for higher acidities. Since the deodorization time decreases considerably when the gas distillates are heated [6], trials were performed to study the free fatty acid content versus time for the continuous process. The results presented correspond to an initial free fatty acids content of 7.3% w/w.

In the experimental trials, we have never pursued the deacidification of oil in accordance with the standards of commercial edible oil refining, but have preferred to work over a broad range of values to be able to draw conclusions regarding the influence of the operating conditions.

Results and Discussion

Tables 1, 2, and 3 summarize the results for different inlet free fatty acid contents for the continuous process. Column 1 identifies the trial wherein: CL indicates the continuous process and low initial free fatty acid content (2.5% w/w); CH indicates the continuous process and high initial free fatty acid content (7.3% w/w); and CO indicates the continuous process wherein equal temperatures of the oil and the gas distillate were achieved and assays were performed over a wider range of initial free fatty acid content. Columns 2–8 show process variables including inlet free fatty acid content (IFFA), temperature of the oil (T_o from 200 to 260 °C), temperature of the gas distillates (T_g with and without additional heating), pressure at the head of the deodorizer (P), nitrogen flow rate V_{N_2} and weight ratio nitrogen/oil (G_{N_2}) or its equivalent weight ratio steam/oil G_{H_2O}. Columns 9–13 show the responses: outlet free fatty acid content (OFFA), removal of free fatty acid (RFFA = IFFA-OFFA), free fatty acid content in the distillates recovered in the condenser (FFAC), saturation temperature (T_{sat}) and difference between the temperature of the gas distillates and the saturation temperature, which will also be called overheating $(T_g - T_{sat})$. The saturation temperature was estimated from the mass flow rate of the volatile components and the pressure at the head of the deodorizer, which allowed the partial pressure of the volatile components in the gases (P_v) to be calculated. Under equilibrium conditions, this partial pressure is identical to the saturation pressure of the volatile components. The saturation temperature, T_{sat} was calculated by applying a relation between the temperature and the vapor pressure, P^o, obtained for oleic acid in the TG-DTA simultaneous analyzer:

$$\log P^o = -\frac{4632.7}{T} + 9.4837; \quad (176 \le T \le 360\,^\circ\mathrm{C}) \tag{1}$$

Tables 1 and 2 show that for assays with the gas distillates temperature obtained without additional heating (CL1,

Table 1 Continuous process trials with 2.5% w/w inlet free fatty acids

Assay	IFFA (% w/w)	T_o (°C)	T_g (°C)	P (mmHg)	V_{N_2} (l/h)	G_{N_2} (% w/w)	G_{H_2O} (% w/w)	OFFA (%w/w)	RFFA (% w/w)	FFAC (% w/w)	T_{sat} (°C)	$T_g - T_{sat}$ (°C)
CL1	2.5	200	133.3	1.8	35.0	1.85	1.19	1.93	0.57	100.56	162.3	-29.0
CL2	2.5	220	169.5	1.6	35.0	1.85	1.19	1.63	0.87	101.99	166.9	2.6
CL3	2.5	240	193.6	2.4	35.0	1.85	1.19	0.70	1.80	98.19	185.0	8.6
CL4	2.5	240	210.0	1.3	35.0	1.85	1.19	0.34	2.16	97.64	175.8	34.2
CL5	2.5	240	240.0	1.5	35.0	1.85	1.19	0.11	2.39	96.19	172.3	67.7
CL6	2.5	240	260.0	2.0	35.0	1.85	1.19	0.27	2.23	91.04	182.9	77.1
CL7	2.5	260	209.9	1.9	35.0	1.85	1.19	0.38	2.12	94.55	176.0	33.9
CL8	2.5	260	280.0	1.2	35.0	1.85	1.19	0.13	2.37	88.15	165.3	114.7

Table 2 Continuous process trials with 7.3% w/w inlet free fatty acids

Assay	IFFA (% w/w)	T_o (°C)	T_g (°C)	P (mmHg)	V_{N_2} (l/h)	G_{N_2} (% w/w)	G_{H_2O} (% w/w)	OFFA (%w/w)	RFFA (% w/w)	FFAC (% w/w)	T_{sat} (°C)	$T_g - T_{sat}$ (°C)
CH1	7.3	200	136.1	1.0	35.0	1.85	1.19	6.49	0.81	97.73	155.3	-19.2
CH2	7.3	220	183.5	1.2	35.0	1.85	1.19	4.64	2.66	99.49	176.5	7.0
CH3	7.3	240	198.0	1.4	35.0	1.85	1.19	1.90	5.40	95.11	191.2	6.8
CH4	7.3	240	210.0	1.3	35.0	1.85	1.19	1.12	6.18	95.95	192.3	17.7
CH5	7.3	240	240.0	1.4	35.0	1.85	1.19	0.64	6.66	93.96	193.0	47.0
CH6	7.3	240	260.0	1.3	35.0	1.85	1.19	0.67	6.63	93.8	192.5	67.5
CH7	7.3	260	207.1	1.4	35.0	1.85	1.19	0.46	6.84	100.64	195.4	11.7
CH8	7.3	260	260.0	1.4	35.0	1.85	1.19	0.33	6.97	98.51	194.3	65.7
CH9	7.3	260	280.0	1.5	35.0	1.85	1.19	0.32	6.98	97.87	195.3	84.7

Table 3 Continuous process trials with very high inlet free fatty acid contents

Assay	IFFA (% w/w)	T_o (°C)	T_g (°C)	P (mmHg)	V_{N_2} (l/h)	G_{N_2} (% w/w)	G_{H_2O} (% w/w)	OFFA (%w/w)	RFFA (% w/w)	FFAC (% w/w)	T_{sat} (°C)	$T_g - T_{sat}$ (°C)
CO1	26.33	240.0	240.0	6.76	35	1.85	1.19	4.69	21.64	99.9	246.5	-6.5
CO2	26.33	240.0	240.0	6.33	90	4.77	3.07	1.96	24.37	99.1	233.2	6.8
CO3	2.89	255.0	255.0	1.55	35	1.85	1.19	0.19	2.70	91.7	180.6	74.4
CO4	7.33	255.0	255.0	1.68	35	1.85	1.19	0.35	6.98	97.2	198.6	56.4
CO5	15.55	255.0	255.0	2.35	90	4.77	3.07	0.12	15.43	97.6	203.6	51.4
CO6	20.36	255.0	255.0	2.09	90	4.77	3.07	0.15	20.21	100.1	204.8	50.2

CL2, CL3, CL7, CH1, CH2, CH3 and CH7), the outlet free fatty acid contents were high and the removals of free fatty acid were low. Moreover, the resulting temperature of the gas distillates was below the saturation temperature for oil (200 °C), the difference being –29 and –19.2 °C; whereas 220, 240 and 260 °C oil temperature, they were above the saturation temperature and the overheating ($T_g - T_{sat}$) was less than 33.9 °C. A condensate free fatty acid content greater than 100% w/w was obtained due to the fact that oleic acid was the reference used when calculating free fatty acid content and there were other fatty acids with higher molecular weights in the gas distillates.

Trials performed for 240 and 260°C oil temperatures and variations in the temperature of the gas distillates by additional heating (CL4, CL5, CL6, CL8, CH4, CH5, CH6, CH8 and CH9) show that both the outlet free fatty acid content and the removal of free fatty acids increase substantially in comparison to trials without heating the gas distillates. The saturation temperature and overheating also increase under these conditions, the latter being more than 34.2 °C. For trials performed at intermediate temperatures of the gas distillates (assays CL4 and CH4), the removal of free fatty acids were also intermediate, thus suggesting the dependence of overheating and the removal of free fatty acids.

The oil temperature effects may be partiallly substituted advantageously by overheating the gas distillates, as can be observed by comparing the results for each inlet free fatty acid content and oil temperature (240 and 260 °C). Thus, for 2.5% w/w inlet free fatty acids content and for assay CL7 (oil temperature of 260 °C and overheating by 33.9 °C), the outlet free fatty acid content was 0.38% w/w, which was less than for CL3 (oil temperature of 240 °C and overheating 8.6 °C), but similar to 0.34% w/w obtained for CL4 (oil temperature of 240 °C and overheating by 34.2 °C). The same occurred for trials with 7.3% w/w inlet free fatty acids content. For the CH7 trial (260°C oil temperature and 11.7 °C overheating), the outlet free fatty acid content was 0.46% w/w, which was less than the 1.9% w/w obtained for CH3 (240 °C oil temperature and 6.8 °C overheating). This result was slightly better than the 0.64% w/w obtained for CH5 (240 °C oil temperature and 47.0 °C overheating).

Increasing overheating represents a better option for saving energy (the specific heat is lower for the gas distillates than for oil) and presumably a better quality of the deodorized oil (less thermal degradation as a result of lower oil temperature). However, excessive overheating produces negative effects at 240 °C oil temperature (CL6 and CH6 compared with CL5 and CH5, respectively).

Nevertheless, substantial overheating produced a positive effect at 260 °C oil temperature (CL8 and CH9 compared with CL7 and CH8, respectively). The free fatty acid contents of the distillates recovered in the condenser tended to decrease with more overheating. For all oil temperatures, the worst result occurred when the gas distillates were heated above the oil temperature. Even so, the values obtained in all the trials were very high, indicating that the neutral oil losses were very low.

Trials CO1 to CO6 show the results for physical refining of oils with very high initial free fatty acid content (from 2.89 to 26.33% w/w). For the highest initial free fatty acid (26.33% w/w), the removal of free fatty acid content was very substantial, increasing with the stripping gas flow rate, as can be seen by comparing CO1 and CO2. Oil with an initial free fatty acid content of 15.55% w/w was satisfactorily refined at 255 °C oil temperature and 3.07% w/w steam/oil weight ratio in trial CO5. The inlet free fatty acid content was increased to 20.36% w/w in the trial CO6, the refining operation conditions being the same as those for CO5. There was only 0.3% w/w increment in the outlet free fatty acid content, from 0.12 to 0.15% w/w, overheating being 10.9 and 10.2 °C respectively. Hence, the increase in oil temperature in conjunction with appropriate overheating enabled physical refining of oils with very high free fatty acid content.

Table 4 Batch process trials with 2.5% w/w inlet free fatty acids

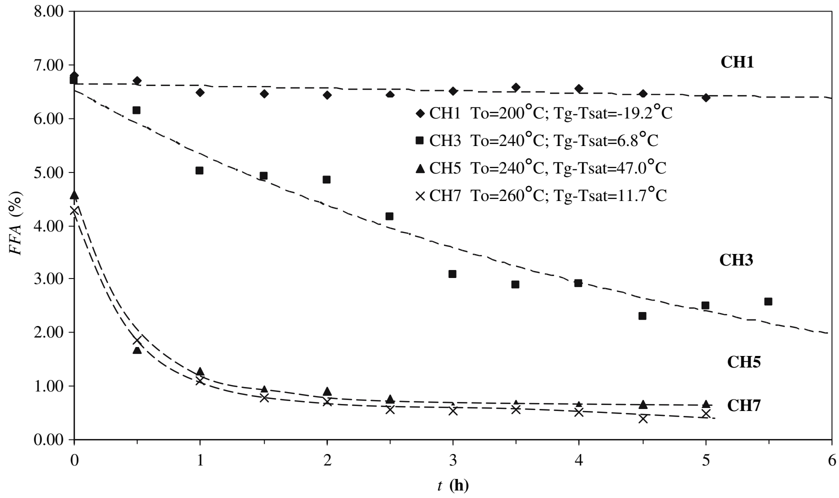
Assay	T_o (°C)	T_g (°C)	OFFA (% w/w)	RFFA (% w/w)	FFAC (% w/w)
D1	245	172	0.47	2.03	92.6
D2	245	245	0.30	2.20	92.1
D3	265	203	0.45	2.05	91.8
D4	265	265	0.09	2.41	85.1

Table 4 presents the results obtained for the batch process, which are similar to those obtained for the continuous process. The saturation temperature was not introduced, as the process was non-steady state and the vapor distillate mass flow rate was not constant. The gas distillate temperature is also time dependent in experiments without heating the gas distillates (D1 and D3), so the value used for T_g corresponded to the maximum value reached during distillation. The outlet free fatty acid content decreased considerably when additional heating was introduced and consequently greater overheating of the gas distillates was obtained (trials D2 and D4), the effect being greater at 265 °C oil temperature. The free fatty acid content of the distillates recovered in the condenser tended to decrease as the oil temperature or the temperature of the gas distillates increased, although the values were always very high.

Heating the gases above the oil in the deodorizer does not incur a high energy cost, because the specific heat of the gas distillate is very low and the nitrogen flow rate is relatively small. Therefore, the temperature of these gases may be raised with very little energy consumption in well-insulated equipment. This heating allows physical refining at lower oil temperatures, as has been shown in the batch process [6]. This reduces the losses of sterols and tocopherols and the formation of trans fatty acids. On the other hand, if the oil temperature was not reduced and the gas distillate heated, the flow rate of stripping gas could be reduced, thus diminishing drag of neutral oil. Moreover, the heating of the gas distillates to the same temperature as that of the oil indicates that neither additional losses of sterols nor changes in the formation of trans fatty acids, as has been also verified in a previous study of deodorization in a batch process [7].

Figure 1 shows the change of free fatty acid content versus time for IFFA = 7.3% w/w. It can be noted how the oil temperature and overheating of the gas distillates affect

Fig. 1 Change of the free fatty acids content in the continuous process (IFFA = 7.3% w/w)



the time needed to reach a specific free fatty acid content. The deacidification rate was low for 200 °C oil temperature and –19.2 °C overheating, whereas the process improved substantially when the oil was heated to 240 °C and the resulting overheating without heating the gases was 6.8 °C (trials CH1 and CH3). For 240 °C oil temperature, if the gas distillate was heated to the same temperature as the oil, 47.0 °C overheating was produced (trial CH5) and distillation improved, the process being as rapid as if the oil were heated to 260 °C without heating the gases and the resulting overheating were 11.7 °C (trial CH7).

It was possible to obtain low outlet free fatty acid content at lower oil temperatures by controlling the temperature of the gas distillate, giving energy savings and an oil with less thermal degradation. Even for very high inlet free fatty acid content, it was possible to achieve low outlet free fatty acid content, which could fulfill the required standards for final free fatty acid content. In this case, however, oil temperature should be increased and appropriate heating should be applied.

In physical refining, we recommend operating at two different temperatures, adjusting the stripping gas flow rate and overheating in each stage; the first at lower temperature to remove most of the fatty alcohols that produce washes and the second at higher temperature in order to adjust the required outlet acidity. This criterion of working at two temperatures together with the work on the kinetics of the decomposition of total aliphatic waxes in olive oil during deodorization [9] led to our research group applying for a patent [10]. The patent defines a procedure that allows the substitution of classical winterization by reforming the deodorizer in order to be able to work at two different internal temperatures.

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