Simulation of Batch Physical Refining and Deodorization Processes

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ABSTRACT: This work presents an application of a differential distillation model for the simulation of batch physical refining and/or deodorization processes in the vegetable oil industry. The vapor–liquid equilibria of these fat systems are described by group contribution equations for vapor pressures and activity coefficients published elsewhere (Ceriani, R., and A.J.A. Meirelles, Predicting Vapor–Liquid Equilibria of Fatty Systems, *Fluid Phase Equilib. 215*:227–236, 2004; Fredenslund, A., J. Gmehling, and P. Rasmussen, *Vapor–Liquid Equilibria Using UNIFAC*, Elsevier Scientific, Amsterdam, 1977). The full complexity of the oil, expressed as its total composition of TAG, DAG, MAG, and FFA, is considered within the simulation. This approach permitted us to quantify and qualify distillative neutral oil losses during physical refining. Three different models of differential distillation were tested to develop a good representation of the batch process to be applied to the physical refining and/or deodorization of complex mixtures such as vegetable oils. To evaluate the recommended approach, a case study was performed, namely, a batch deodorizer was simulated for coconut oil refining, and the results were compared with those reported in the literature.

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KEY WORDS: Coconut oil, deodorization, differential distillation, edible oils, neutral oil loss, physical refining, vapor–liquid equilibria.

Physical refining and deodorization processes in the oil industry are intended to vaporize odoriferous compounds and FA from the oil. They are based on the large differences in volatility between the oil and the majority of its unwanted substances, and are accomplished by applying high temperatures and low pressures. However, some works in the literature have shown that these conditions also allow the vaporization of an acylglycerol fraction from the oil, known as neutral oil loss (NOL) (1–3). Ordinarily, NOL can be divided into two types: (i) a distillative loss and (ii) a loss due to mechanical carryover (or entrainment), which is usually low, approximately 0.1% (2,4).

The experimental work of Petrauskaitè *et al.* (2) has quantified NOL during the physical refining of coconut oil and confirmed that the distillation of volatile acylglycerolic components (mainly MAG and DAG) is its major cause. Petrauskaitè *et al.* (2) have also highlighted the similarity between the volatilities of long-chain FA and short-chain MAG, indicating the reason for distillative NOL in their study.

Coconut oil is classified as a lauric oil, characterized by a high level of short-chain and saturated FA (5). Its high FFA content (between 1 and 6%) denotes the presence of a considerable amount of MAG and DAG (2). For oils with high acidity, the physical refining method is highly recommended, because it reduces NOL (6).

This work presents an application of a differential distillation model for the simulation of batch physical refining and/or deodorization processes for vegetable oils. The vapor–liquid equilibria (VLE) of these fat systems are described by group contribution equations for vapor pressures (7) and activity coefficients (7,8) published elsewhere. The full complexity of the oil, expressed as its total composition of TAG, DAG, MAG, and FFA, is considered within the simulation in order to quantify and characterize NOL during physical refining. Chemical reactions, vaporization efficiencies, and entrainment are not considered.

Nowadays, simulation results are largely used to design equipment for vapor–liquid contact. Commercial software, such as Aspen Plus®, HYSYS®, and PRO/II® (9), or software developed by research groups (10,11) is usually used, even for complex multicomponent mixtures such as orange essential oil and orange aqueous essence (9). The procedure proposed by Ceriani and Meirelles (7) for calculating vapor pressures and VLE of multicomponent fatty mixtures allows the simulation of different processes within the vegetable oil industry. In the present work, this procedure is used to simulate a batch deodorizer for coconut oil refining.

MODELING A BATCH DEODORIZER

To quantify NOL during physical refining, Petrauskaitè *et al.* (2) performed experiments using a laboratory-scale batch deodorizer initially containing 250 g of bleached coconut oil. The experiments were conducted for 60 min under temperatures and pressures between 190 and 230°C and 1.6 to 3.0 mbar, respectively, and with the addition of 0.6 to 1.2% of sparge steam. Their results showed that partial acylglycerols (MAG and DAG) were the major cause of NOL in lauric oils.

To simulate the experiments carried out by Petrauskaitè *et al.* (2), we applied the vapor pressure equation and the thermody-

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namic approach suggested by Ceriani and Meirelles (7) to predict the VLE of the fatty compounds involved in these experiments. The VLE model is described below (7):

$$y_i \cdot P = \gamma_i \cdot x_i \cdot P_i^{\text{vp}} \cdot \Im_i \qquad [1]$$

where

$$\Im_i = \frac{\phi_i^{\text{sat}}}{\phi_i} \cdot \exp\left[\frac{V_i^L \cdot (P - P_i^{\text{vp}})}{R \cdot T}\right] \qquad [2]$$

where $\Im_i$ is the nonideality factor of the vapor phase; x_i and y_i are molar fractions of component i in the liquid and vapor phases, respectively; P is the total pressure; R is the gas constant, T is the system temperature; P_i^{vp} and ϕ_i^{sat} are, respectively, the vapor pressure and the fugacity coefficient of the pure component; γ_i is the activity coefficient; ϕ_i is the fugacity coefficient; and V_i^L is the liquid molar volume of component i. The exponential term in Equation 2 is called the Poynting factor (POY).

Because of the high temperatures used in deodorizing units, the vapor pressures of some components, such as water and short-chain FA (6:0 to 12:0), are high enough to generate ϕ_i^{sat} values notably different from unity. For this reason, and despite the low pressures prevailing in such units, Equations 1 and 2 are more suitable to describe the VLE observed in this kind of process (7).

In a multicomponent differential distillation process, a tank (still) is charged with feed and then heated. Vapor flows overhead, is condensed, and is collected in a receiver. Since the still composition is changing continuously, this process is inherently dynamic, i.e., it cannot be modeled in steady state. The composition of the material collected in the receiver also varies with time, so the composition of the distillate is an average of all the material collected. It is possible to look at differential distillation as a sequence of numerous and successive vaporizations.

Batch deodorization is similar to multicomponent differential distillation, for which the total and component balances are given by Equations 3 and 4 (12):

$$\frac{dL}{dt} = -V \qquad [3]$$

and

$$\frac{d(L \cdot x_i)}{dt} = -V \cdot y_i \qquad [4]$$

where L is the total moles of liquid in the still, V is the molar vaporization rate in moles/time, and x_i and y_i are the liquid and vapor mole fractions of component i in the liquid and vapor phases, respectively.

Assuming that the liquid and vapor phases are in equilibrium at each instant, i.e., that the still acts as a theoretical stage, the equilibrium relationship can be stated as in Equations 1 and 2. This assumption considers a vaporization efficiency factor equal to unity, which means that the steam becomes totally saturated with the volatiles as it passes through the oil in the still.

For the receiver distillate tank, the total and component balances (12) are

$$\frac{dD}{dt} = V \qquad [5]$$

and

$$\frac{dD_i}{dt} = V \cdot y_i \qquad [6]$$

where D is the total moles of distillate and D_i corresponds to the moles of component i in the tank.

By combining Equations 3–6 with the equilibrium relationship (Eqs. 1 and 2), we have a system that is easily solvable by direct numerical integration (12).

Three different alternatives for simulating batch deodorization (differential distillation) were considered in this work. The simplest one, named Model 1, does not take into account the injection of sparge steam. In this case, the boiling temperature at each instant should be determined by solving Equation 7 (objective function) below: The sum of the partial pressures of the fatty compounds must be equal to the system total pressure,

$$f = P - \sum_{i=1}^{n}[\gamma_i \cdot x_i \cdot P_i^{\text{vp}} \cdot \Im_i] \qquad [7]$$

where n is the total number of fatty compounds.

Model 2 considers the injection of sparge steam, but it assumes that the steam is an inert component that only decreases the system total pressure by its partial pressure in the vapor phase. In this case, steam (water) is believed to be totally immiscible with the oil, and the sum of the fatty component partial pressures, $\Sigma_{i=1}^{n} P_i$, should be equal to the total pressure less the sparge steam partial pressure, P_w. The objective function, f, was appropriately changed, as shown in Equation 8:

$$f = P - \sum_{i=1}^{n}[\gamma_i \cdot x_i \cdot P_i^{\text{vp}} \cdot \Im_i]\left[1 + \frac{\dot{m}_w}{\dot{m}_{\text{vol}}} \cdot \frac{\sum_{i=1}^{n} y_i \cdot M_i}{18}\right] \qquad [8]$$

where n is the total number of fatty compounds, $\dot{m}_w$ and $\dot{m}_{\text{vol}}$ are, respectively, the mass rate of water and volatile fatty compounds in the vapor phase in grams per second (g/s), M_i is the molar weight of each fatty component i, y_i is its molar fraction in the vapor phase, the number 18 refers to the M.W. of water (g/gmol), and $\dot{m}_w / \dot{m}_{\text{vol}}$ gives the ratio of sparge steam to vaporized fatty components used in the batch deodorizer.

Model 3 takes into account the effect of steam upon the liquid (oil) phase. In fact, one should consider that very small amounts of steam (water), which condense and dissolve in the oil, are able to enhance the volatility of the fatty compounds and decrease the necessary boiling temperature. As such, the simulation performed was similar to the operation of an industrial batch deodorizer. Anderson (13) indicates that in a batch deodorizer, the oil is first slowly heated under vacuum conditions until the desired temperature is reached; when this temperature is attained, the injection of sparge steam begins and the process is performed until the required oil acidity (OA) is obtained. For this reason, our process simulation was divided in two parts: (i) *heating* (in the absence of water) and (ii) *stripping* with sparge steam at constant temperature, which was allowed by the presence of water in the liquid phase. The simulation of the first part (heating) was conducted as in Model 1, in which the boiling temperature was determined by Equation 7. When the desired temperature was achieved (the start of stripping), water was included as the $(n + 1)$th component in the liquid phase. Equation 9 below was then solved to determine the water concentration in the liquid at the chosen temperature and pressure conditions:

$$f = P - \sum_{i=1}^{n+1}[\gamma_i \cdot x_i \cdot P_i^{\text{vp}} \cdot \Im_i] \qquad [9]$$

All the models depicted above use an iterative procedure for convergence, as the Newton–Raphson model (14). P_i^{vp}, γ_i, and $\Im_i$ are calculated for each component, including water when suitable, in every iteration.

Model 3 is probably the alternative that better simulates the experiments conducted by Petrauskaitè *et al.* (2). But one should observe that the authors (2) included only the system pressure, the initial oil load and final acidity, the amount and temperature of sparge steam, and the amount and acidity of the distillate; the still (oil) temperature was apparently not measured. The temperature reported in the work is the oven temperature, so the oil temperature during the experiments should probably be a little bit lower than that value to allow heat transfer. As a consequence of the lack of information concerning oil temperature, the value chosen for the second part of the Model 3 simulation was the available oven temperature less 5°C. This difference was justified by supposing that heat transfer occured throughout the 60-min duration of each experiment.

The simulation results were appropriately transformed to mass fraction units and expressed as percentages of NOL, OA, and distillate acidity (DA). Such results were compared with those reported by Petrauskaitè *et al.* (2).

RESULTS AND DISCUSSION

Models 1 to 3 were used to simulate the batch deodorization experiments conducted by Petrauskaitè *et al.* (2). All the property calculations were performed using the procedure of Ceriani and Meirelles (7), with γ_i calculated with UNIFAC r3/4, as suggested by Fornari *et al.* (15). The same FA composition (Table 1) and acidity (3.18%, expressed as the percentage of lauric acid) as those reported by Petrauskaitè *et al.* (2) were used. Since Petrauskaitè *et al.* (2) did not give the partial acylglycerol composition of their samples, three different magnitudes were considered for the simulation: (i) composition 1 (OC1), with a 3% mass concentration of DAG and 1% of MAG (16), (ii) composition 2 (OC2), with a 0.89% mass concentration of DAG and 0.27% of MAG, and (iii) composition 3 (OC3) with no partial acylglycerols (no DAG and MAG). From the data in Table 1, the composition in TAG of the coconut oil (*M*, M.W. of 601.0 g/gmol and iodine value of 9.31) was estimated using the procedure of Antoniosi Filho *et al.* (17), considering 84% of the TAG as trisaturated (18). The estimated TAG composition is shown in Table 2. Even though the partial acylglycerol composition was obtained intuitively from the estimated TAG composition (see Table 2), it is in accordance with the observation of Petrauskaitè *et al.* (2) about the MAG composition of coconut oil (up to 50% of short-chain-length, ranging from C_6 to C_{12}). As a whole, the coconut oil was divided into 72 components, i.e., 9 FA (Table 1), 36 TAG (Table 2), and 27

TABLE 1
FA Composition of Coconut Oils

				Firestone (20)			
		Petrauskaitè *et al.* (2)[a]		More volatile		Less volatile	
FA	Trivial name (abbreviation)	Mass (%)	Mole (%)	Mass (%)	Mole (%)	Mass (%)	Mole (%)
6:0	Caproic (Co)	0.60	1.07	0.60	1.04		
8:0	Caprylic (Cp)	7.29	10.49	9.40	13.17	4.6	6.84
10:0	Capric (C)	5.89	7.10	7.80	9.15	5.5	6.84
12:0	Lauric (L)	46.55	48.24	49.20	49.63	45.1	48.25
14:0	Myristic (M)	18.58	16.89	16.80	14.87	18.5	17.36
16:0	Palmitic (P)	9.49	7.68	7.70	6.07	10.2	8.53
18:0	Stearic (S)	2.70	1.97	2.30	1.63	3.5	2.64
18:1	Oleic (O)	7.00	5.15	5.40	3.86	9.9	7.51
18:2	Linoleic (Li)	1.90	1.41	0.80	0.58	2.1	1.6
18:3	Linolenic (Ln)					0.2	0.15
20:0	Arachidic (A)					0.2	0.14
20:1	Gadoleic (G)					0.2	0.14

[a] FA compositions for oil compositions OC1, OC2, and OC3, where OC1 contains 3% mass concentration of DAG and 1% MAG, OC2 contains 0.89% mass concentration of DAG and 0.27% MAG, and OC3 contains no DAG and no MAG.

TABLE 2
Estimated Composition of Coconut Oil

TAG					DAG			
Group[a]	Major TAG	M^b (g/gmol)	Mass (%)	Mole (%)	Acylglycerol compound	M^b (g/gmol)	Mass (%)	Mole (%)
24:0	CpCpCp	470	0.13	0.18	CoCp-	316	0.23	0.33
26:0	CoCpL	498	0.43	0.57	CpCp-	344	1.15	1.53
28:0	CpCpL	526	1.64	2.05	CpC-	372	1.91	2.36
30:0	CpCL	554	2.99	3.57	CpL-	400	16.11	18.49
32:0	CpLL	582	8.36	9.49	CL-	428	1.2	1.29
34:0	CpLM	610	10.09	10.93	LL-	456	38.61	38.86
36:0	LLL	638	17.39	18.02	LM-	484	16.62	15.76
38:0	LLM	666	15.34	15.23	LP-	512	12.64	11.33
40:0	LLP	694	11.22	10.69	LS-	540	2.29	1.95
42:0	LMP	722	6.41	5.87	MS-	568	0.33	0.26
44:0	LMS	750	2.84	2.50	CpO-	482	1.52	1.44
46:0	LPS	778	1.05	0.89	CO-	510	1.15	1.03
48:0	MPS	806	0.30	0.25	LO-	538	4.01	3.43
50:0	PPS	834	0.07	0.05	MO-	566	1.05	0.85
34:1	CpCpO	608	0.20	0.21	CpLi-	452	0.35	0.36
36:1	CpCO	636	0.41	0.43	CLi-	508	0.28	0.26
38:1	CpLO	664	1.89	1.88	LLi-	536	0.49	0.42
40:1	CLO	692	1.89	1.80	MLi-	564	0.06	0.05
42:1	LLO	720	5.09	4.67	MAG			
44:1	LMO	748	3.44	3.04				
46:1	LPO	776	2.11	1.80	Co--	190	0.11	0.16
48:1	MPO	804	0.93	0.77	Cp--	218	10.30	13.02
50:1	MSO	832	0.27	0.21	C--	246	2.20	2.47
52:1	PSO	860	0.07	0.05	L--	274	64.83	65.19
34:2	CpLiCp	606	0.05	0.05	M--	302	9.27	8.46
36:2	CpCLi	634	0.10	0.11	P--	330	6.79	5.67
38:2	CpLiL	662	0.46	0.46	S--	358	1.44	1.11
40:2	CLiL	690	0.46	0.45	O--	356	4.36	3.38
42:2	LLLi	718	1.26	1.16	Li--	354	0.70	0.54
44:2	LMLi	746	0.96	0.85				
46:2	LPLi	774	0.60	0.51				
48:2	LOO	802	0.79	0.65				
50:2	MOO	830	0.27	0.21				
52:2	POO	858	0.11	0.09				
48:3	LOLi	800	0.28	0.23				
50:3	MOLi	828	0.10	0.08				

[a] Isomer set including different TAG, but all with the same number of FA carbons and double bonds. For example, Group 26:0 means the isomer set of TAG with 26 FA carbons and no double bonds. For abbreviations see Table 1.
[b] *M*, molecular weight (g/gmol).

partial acylglycerols (Table 2). Note that the OA was composed of all FA shown in Table 1. The MAG and DAG considered are listed in Table 2. The concentrations given in Tables 1 and 2 add to 100% within each class of fatty compounds. To calculate the total oil compositions, all three different partial acylglycerol levels should be taken into account.

Using the simulation tools developed in the present work, we simulated the first six experiments reported by Petrauskaitė *et al.* (2). A total of 54 simulations were performed, corresponding to the three different models (Models 1, 2, and 3) and to the three different partial acylglycerol levels in the bleached coconut oil (OC1, OC2, and OC3).

An important concept used to quantify the facility of the compounds in a mixture to be distilled under certain conditions is the relative volatility ($\alpha_{i,j}$), which relates the distribution coefficient, *k*, of one compound or one class of compounds with another less volatile compound or class of compounds. In our simulations, this parameter gives an idea about the range of volatilities of each class of compounds (FFA, MAG, DAG, TAG) considered in relation to the volatility of TAG. It is defined by Equation 10,

$$\alpha_{i,\text{TAG}} = \frac{(y/x)_i}{(y/x)_{\text{TAG}}} \qquad [10]$$

where *i* refers to TAG, DAG, MAG, or FFA classes.

Figure 1 gives the relative volatility ($\alpha_{i,\text{TAG}}$) of the FFA, MAG, and DAG classes for coconut oil (OC2) at 300 Pa. Note that the ($\alpha_{i,\text{TAG}}$) values are inversely proportional to the M.W. of the compound class. The results show that even with a considerable difference between the volatility of FFA and partial acylglycerols, the loss of neutral oil can increase con-

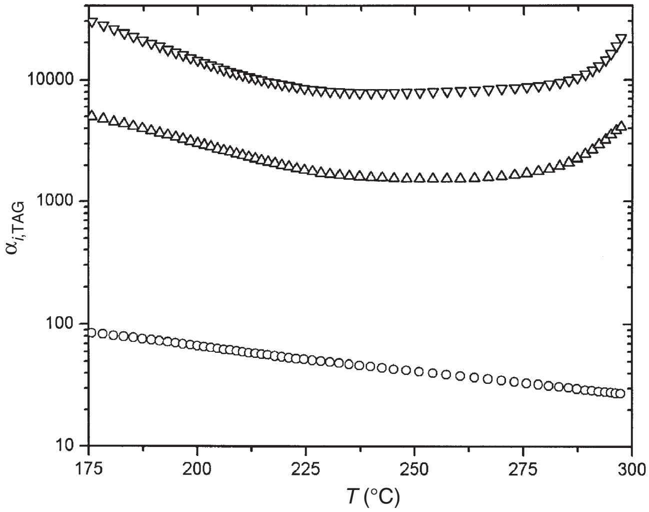

FIG. 1. Relative volatility ($\alpha_{i,\mathrm{TAG}}$) of the FFA, MAG, and DAG classes for coconut oil (OC2) calculated during the Experiment 6 simulation (Model 1). FFA (▽), MAG (△), and DAG (○). OC2, oil composition.

siderably, mainly when the amount of FFA in the still is close to the desired final acidity (in the last 20 min, approximately).

Table 3 shows a comparison of NOL as calculated by Petrauskaitè *et al.* (2) and in this work using Model 3 to illustrate that the oil composition used in their experiments might have a value between OC1 and OC3. Although there is some uncertainty in the partial acylglycerol concentration, its precise value should be not far from our estimations. Our results show that as MAG and DAG concentrations increase (from OC3 to OC1), the NOL also becomes higher, independent of the process conditions selected.

The NOL calculated using Model 3 for OC3, a coconut oil without any partial acylglycerol, is always lower than the experimental results. A possible explanation is that the similar volatility of short-chain MAG and long-chain FA can play no role in this case. Once the crude oil has a larger partial acylglycerol fraction, a portion of these components is evaporated instead of FFA, decreasing the FFA content in the distillate and increasing NOL values.

The literature establishes that the FFA content cannot be reduced indefinitely but reaches a minimum value of 0.005%, due to hydrolysis of the oil caused by the steam (4). The final OA calculated using Model 3 for OC3 (see Table 3) was lower than this limit for the last four experiments (Experiments 3 to 6), whereas the experimental values from Petrauskaitè *et al.* (2) were consistently higher. In fact, our simulations did not consider reactions that might occur during vegetable oil deodorization, such as hydrolysis of acylglycerols, which generates partial acylglycerols and FFA.

As shown in Figure 2A, Model 1 gives higher temperatures compared with the other two models all along the sparging steam period, behavior that occurred for all process conditions and oil compositions studied. It happens that one effect of the sparge steam is to decrease the required partial pressure of volatiles and, as a consequence, the boiling temperature of the mixture. For the heating period, Models 1 and 3 have the same objective function (Eq. 7) and, as a consequence, the same boiling temperatures.

Figures 2B and 2C show the profile per time of two variables studied (DA and OA) for the three models. For the last 20 min of the process, the OA curves for Model 1 became considerably different from the others (Fig. 2C), which can be seen as a consequence of the absence of water effects in the liquid and vapor phases. The same behavior can be observed for the DA curves (Fig. 2B), even though it starts earlier (after 30 min of processing). It is important to highlight the correspondence between the OA and DA curves regarding the component mass balance. For Model 1, as an example, the OA curve is on top of the others, which means that less FFA were withdrawn from the crude oil. On the other hand, the DA curve shows a smaller amount of FFA in the distillate, as expected. However, the experimental points in the two graphs behave in a slightly different way, which is a probable consequence of small errors inherent in experimentation.

The simulation results for Model 3, especially those with oil compositions OC1 and OC2, are more compatible with those reported by Petrauskaitè *et al.* (2). In fact, this model seems better able to reproduce the experimental conditions observed in the operation of batch deodorizers. It should be noted that in all 18 simulations corresponding to Model 3, the calculated water concentration in the oil was consistently less than 0.00003 wt%. Despite this very low level, water has an influence on the VLE so strong that it possibly allows the industrial deodorization process to proceed without a further

TABLE 3
Comparison of Calculated Neutral Oil Loss and Refined Oil Acidity by Petrauskaitè *et al.* (2) and in This Work Using Model 3 as the Simulation Tool[a]

		Refined oil acidity (%)				Neutral oil loss (%)			
			This work				This work		
Experiment no.	P (Pa)	Petrauskaitè *et al.* (2)	OC1	OC2	OC3	Petrauskaitè *et al.* (2)	OC1	OC2	OC3
1	160	0.240	0.670	0.364	0.170	0.28	0.59	0.30	0.10
2	160	0.070	0.466	0.161	0.030	0.57	0.76	0.47	0.34
3	160	0.019	0.165	0.008	0.001	1.28	1.29	1.15	1.13
4	230	0.033	0.266	0.036	0.003	1.21	1.06	0.85	0.81
5	230	0.035	0.295	0.051	0.001	0.89	1.01	0.78	0.73
6	300	0.017	0.280	0.043	0.004	0.93	1.04	0.82	0.77

[a] All simulations have a 60 min duration. The experiment numbers correspond exactly to those reported by Petrauskaitè *et al.*

temperature increase. Note that the literature reports a water concentration in refined coconut oil of 0.09 wt% at room temperature conditions (19). Furthermore, as one can see in Figure 2A, without this water effect on the volatility of the fatty components, the temperature at the final part of the deodorization process would be higher, even higher than the temperature of the heat source used by Petrauskaitè *et al.* (2).

From our simulations, it is also possible to extract important information about the composition of the products throughout the distillation process. We have explored our results to show the usefulness of a simulation program in projecting and evaluating physical refining and deodorization units. Figure 3 illustrates the main FFA and acylglycerol classes found in coconut oil and their behavior under processing conditions (Experiment 6 in Table 3). As shown in Figure 3A, for the first 20 min, short-chain FFA are the key fraction distilled from the oil, and are completely removed after 49 min.

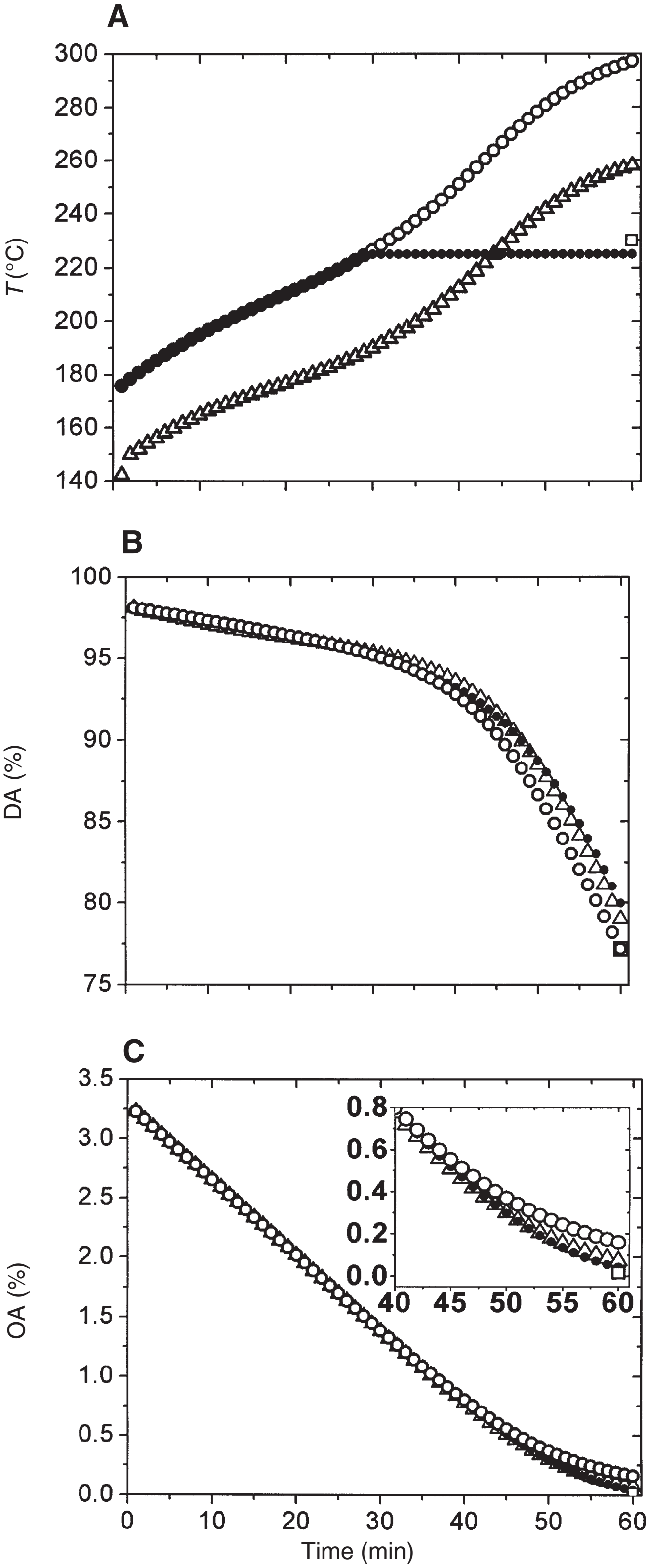

FIG. 2. Variation of the (A) boiling temperatures, (B) FFA content of the distillate (DA), and (C) FFA content of the oil (OA) with time for the physical refining of coconut oil (OC2, 1.16% of partial acylglycerols) for Experiment 6 (see Table 4). Model 1 (○); Model 2 (△), Model 3 (●), and experimental points (□). The experimental temperature shown is the oven temperature. OA, oil acidity; DA, distillate acidity; for other abbreviation see Figure 1.

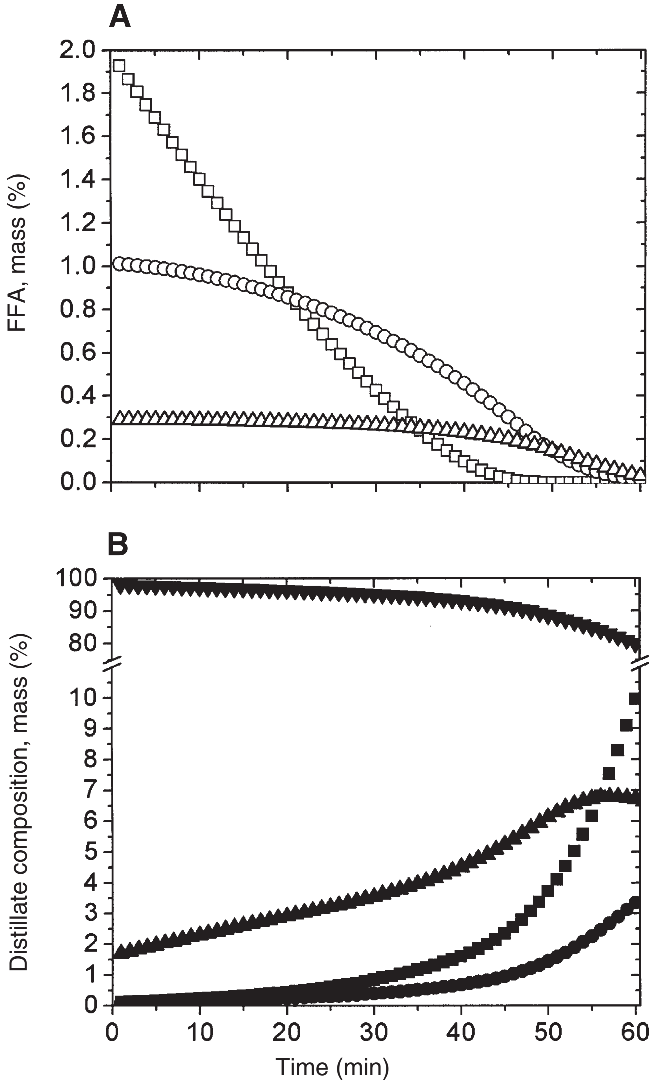

FIG. 3. Main classes of (A) FFA in the oil acidity and (B) acidity and acylglycerols in the distillate for Experiment 6 (see Table 4). (A) 6:0 to 12:0 (□), 14:0 to 18:0 (○), and 18:1 and 18:2 (△); (B) DA (▼), TAG (■), DAG (●), and MAG (▲). For other abbreviation see Figure 2.

At this time, the coconut oil has an OA of 0.337, formed mainly by long-chain and unsaturated FFA, as oleic and linoleic acids. FFA are undoubtedly the main fraction of the distillate (see Fig. 3B). However, it is possible to observe that its acylglycerol portion—and, as a consequence, the NOL—becomes significant in the last 20 min of processing, when it starts to increase exponentially. Note also that after this point, significant amounts of TAG and DAG are distilled, since the MAG concentration in the still is lower than 0.17% (w/w).

We have given special attention to the calculated values of ϕ_i^{sat}, ϕ_i, and POY for all components, including water and short-chain FA, to explain the use of vapor-phase nonidealities, even at the very low pressures found in this work. ϕ_i^{sat} values differentiated considerably from unity ($0.89 < \phi_i^{sat} < 0.96$) for those components, whereas ϕ_i and POY values were close to 1 (>0.978) for all components in the system. This is a consequence of the high values calculated for vapor pressure, along with the high temperatures observed, for water and short-chain FA. Vapor pressure is a parameter that is used in the calculation of ϕ_i^{sat}.

For further analyses of our methodology, we also studied the influence of the FFA concentration itself (initial OA) on NOL, OA, and DA values. Following the composition ranges given by Firestone (20), we estimated two different compositions for coconut oil—one more volatile (MVO), rich in lauric and short-chain FA, and other less volatile (LVO), poor in lauric acid and rich in long-chain FA, as shown in Table 1. Their compositions of TAG, DAG, and MAG were estimated following the same procedure described earlier in this section.

To evaluate the impact of the initial FFA content in the final results, we simulated the deodorization of the more volatile coconut oil, varying its initial acidity from 1 to 6% (expressed as the percentage of oleic acid) while maintaining 1% MAG and 3% DAG and using the conditions in Experiment 3. Model 3 was used as the simulation tool to reach at least 0.03% of final acidity in all cases. As expected, the increase in the initial OA generated higher values for DA and NOL as a consequence of the increased time of processing. The NOL values ranged from 1.60 (1% acidity) to 2.40% (6% acidity). The final acidity (0.03%) was achieved after 31 and 91 min, respectively.

To finalize this work, we studied the influence of the oil composition, expressed in terms of the more and less volatile coconut oils (Table 1). These simulations were conducted to compare NOL, DA, and OA at the same processing conditions stated in the above paragraph. The major differences between the two estimated oils were in their M.W. (574.7 and 631.8 g/gmol for MVO and LVO, respectively), chain lengths, and unsaturation of the fatty compounds (iodine values of 6.03 and 12.83 for MVO and LVO, respectively). Both oils had 1% MAG, 3% DAG, and 2.13 acidity, expressed as lauric acid. As a result, their partial acylglycerols also had different volatilities, having been distilled differently. These results are shown in Figure 4. Note that the OA of the LVO, although composed of long chain-length FFA, was evaporated more easily because its partial acylglycerols were less volatile and, for this reason, there was less competition among them in the vaporization process. As a consequence, the DA was also higher. The total NOL for the MVO was notably higher (2.14%) than the value found for the LVO (1.80%). The processing times were almost equivalent (only 3 min different).

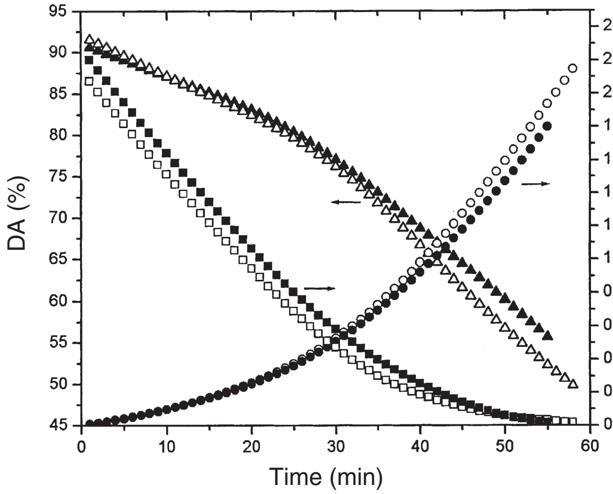

FIG. 4. Variation in DA, NOL, and OA as a function of the FA composition of the coconut oil and its volatility. More-volatile DA (△), OA (○), and NOL (□); less-volatile oil DA (▲), OA (●), and NOL (■). NOL, neutrol oil loss; for other abbreviations see Figure 2.

The concordance of our simulation results with the experimental data from Petrauskaitè *et al.* (2) shows the possibility of applying our methodology to simulate edible oil-refining plants and to evaluate NOL in the presence of MAG and DAG. To scale up our approach and design a real plant, it may be necessary to consider: (i) vaporization efficiency factors in the equilibrium equations, (ii) degradation reactions (as hydrolysis), and (iii) losses due to mechanical entrainment. Nevertheless, our model is a valuable tool for a first estimation of NOL, especially in the presence of considerable amounts of MAG and DAG, as occurs for oils with high acidity.

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