

Optimization of the Physical Refining of Sunflower Oil Concerning the Final Contents of *trans* Fatty Acids

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ABSTRACT: The final contents of total and individual *trans* fatty acids of sunflower oil, produced during the deacidification step of physical refining were obtained using a computational simulation program that considered *cis-trans* isomerization reaction features for oleic, linoleic and linolenic acids attached to the glycerol part of triacylglycerols. The impact of process variables such as temperature and liquid flow rate, and of equipment configurations, as liquid height, diameter and number of stages, that influence the retention time of the oil in the equipment, was analyzed using the response surface methodology (RSM). The computational simulation and the RSM results were used in two different

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optimization methods, aiming to minimize final levels of total and individual *trans* fatty acids, while keeping neutral oil loss and final oil acidity at low values. The main goal of this work was to indicate that computational simulation, based on a careful modeling of the reaction system, combined with optimization could be an important tool for indicating better processing conditions in industrial physical refining plants of vegetable oils, concerning *trans* FA formation.

KEY WORDS: *Cis-trans* isomerization, computational simulation, physical refining, response surface methodology, optimization.

1. Introduction

Vegetable oils can be deacidified in a physical manner under the application of high temperatures and low pressures. This process, called physical refining (or steam distillation), aims to vaporize free fatty acids (FFA), thus reducing final oil acidity.¹ The condition of very high temperature (up to 280°C) that improves the separation of FFA from the oil, also eases the occurrence of chemical reactions, such as the *cis-trans* isomerization of unsaturated fatty acids (FA).² *Trans* unsaturated FA are known to have the opposite effect of *cis* unsaturated FA in human body metabolism, i.e., a certain undesirable effect on the level of plasma cholesterol.³ The main portion of *trans* unsaturated FA produced during physical refining/deodorization is the *trans* isomers of polyalkenoic acids.⁴ Schwarz⁴ pointed out that the very low original level of *trans* polyunsaturated fatty acids (PUFA) in crude oils may be increased three to ten times at 230°C. It is of note that one quality parameter for refined edible oil in European countries is that the level of total *trans* FA should be lower than 1.0%.⁵

High temperatures and low pressures also allow the vaporization of an acylglycerol fraction from the oil (mainly partial acylglycerols), known as neutral oil loss (NOL)¹.

The kinetics of the isomerization reaction of oleic (O), linoleic (Li) and linolenic (Ln) acids during physical refining/deodorization processes are available in the literature.^{6,7} According to León Camacho

et al.⁶ and Hénon et al.,⁷ the formation of *trans* unsaturated FA is only influenced by the retention time of the oil in the column and by the processing temperature.

Considering the use of computational simulation for studying deodorization/physical refining of edible oils, Ceriani and Meirelles^{8,9} did an original work. The authors explored industrial and lab-scale continuous deodorizers, in countercurrent and cross-flow configurations, applied in the deodorization and/or physical refining of soybean, wheat germ, palm and coconut oils.

In this work, our first goal was to investigate the applicability of an improved version of this multicomponent stripping column model^{8,9} in the simulation of the continuous deacidification step of the physical refining of sunflower oil, focusing the analysis of the results in terms of the formation of *trans* O, *trans* Li and *trans* Ln acids attached to the glycerol part of triacylglycerols (TAG). The effects of five different factors on the *trans* FA levels, final oil acidity and NOL were investigated using factorial design and the response surface methodology (RSM). Two of these factors (temperature, T , and oil flow rate, (F_{oil})) were related to the processing conditions, while the others (number of stages, N , liquid height, H_{liquid} , and equipment diameter, D) were related to the equipment design. The retention time (t_{rt}) of the oil in the deodorizer was defined as a function of the five factors selected, as shown in Equation 1.

$$t_{rt}[h] = \frac{H_{liquid}[m] \cdot \rho_{oil}(T)[kg/m^3] \cdot \pi/4 \cdot D^2[m^2] \cdot N}{F_{oil}[kg/h]} \quad (1)$$

Besides the successful modeling of the continuous multi-tray deodorizer developed in previous works,^{8,9} in terms of mass and energy balances, equilibrium relationships, Murphree efficiencies, and entrainment, this work included the kinetic of the *cis-trans* isomerization reaction of some unsaturated FA (O, Li, Ln), improving the applicability of the software. To model a more complex reactive system mathematically, using the tools that were available to describe the isomerization reactions in terms of their kinetics,^{6,7} it was necessary to raise some simplifying hypotheses and adopt some shortcuts. We briefly discuss all these required suppositions in Section 2.

The second goal of this article was to combine the developed simulation model with a flexible optimization tool to obtain process parameters which could minimize some desired output variables, such as the level of *trans* fatty acids, final oil acidity and neutral oil loss (NOL). We chose a classical optimization method, named *Scatter Search*, that is known to present good results when the objective function to be optimized depends on time-consuming simulation models, as is the case here. A simplified approach, based on a non-linear optimization using the approximate RSM models (given in Section 3) was also tested, and comparable results were obtained with shorter computational times. In Section 4, both approaches are detailed and the results analyzed.

2. Modeling a Continuous Multitray Cross-Flow Deodorizer with Chemical Reactions

Modeling a continuous deodorizer as a multicomponent reactive stripping column included the description of material and energy balances, and of Murphree efficiencies coupled with vapor-liquid equilibrium relationships for each component in each stage of the column.

In the continuous deodorizer, oil is fed at the top stage while the vapor is fed in all stages of the column, in a way that the flow directions of the phases cross each other in a cross-flow pattern.^{8,9}

The general equations that modeled the continuous multitray cross-flow deodorizer with chemical reactions are described briefly in Appendix I. An iterative procedure (Newton–Raphson) was used for simultaneous convergence of all equations until the true values of $l_{n,i}$ (the component liquid molar flow), $v_{n,i}$ (the component vapor molar flow), and T_n (the stage temperature) were found. Detailed information about the procedures and methods selected for estimating physical properties and other process parameters can be reached referring to our previous articles^{8,9} and in the supporting information. It is noteworthy that the vapor-liquid equilibrium calculation procedure developed by Ceriani and Meirelles¹⁰ for fatty mixtures was capable of distinguishing *cis* and *trans* isomers of fatty compounds in the vapor pressure estimation.

The occurrence of chemical reactions affected the component molar balances with the introduction of the term $R_{n,i}$, the number of moles of compound i that reacted at stage n (see Equation A1). For the *cis-trans* isomerization of TAG, the term $R_{n,i}$ can be defined as the amount, or number of moles, of *cis* TAG consumed or of *trans* TAG produced by the isomerization reaction per hour at stage n . Because the isomerization reaction occurred within the holdup of liquid in each stage, we defined $R_{n,i}$ as a function of the liquid molar holdup (\bar{h}_n , gmol) and of the reaction rate ($r_{n,i}$), as shown below:

$$R_{n,i} \left[\frac{\text{mol } i}{h} \right] = \bar{h}_n [\text{mol}] \cdot r_{n,i} \left[\frac{\text{mol } i}{\text{mol}} \cdot h^{-1} \right] \quad (2)$$

In Equation 2, \bar{h}_n was estimated considering the volume of each stage of the column (v_n , m^3), the oil density (ρ_{oil} , kg/m^3) and the oil molar weight (M_{oil} , $kg/kmol$), according to the relation below:

$$\bar{h}_n = 1000 \cdot \frac{\rho_{oil}}{M_{oil}} \cdot v_{oil} = 1000 \cdot \frac{\rho_{oil}}{M_{oil}} \cdot \frac{H_{liquid} \cdot \pi \cdot D^2}{4} \quad (3)$$

where ρ_{oil} is the oil density calculated using the method of Halvorsen et al. suggested by Ceriani and Meirelles,⁸ H_{liquid} is the height of the pool of liquid at each stage, and D is the column diameter.

Before defining the term $r_{n,i}$ that appears in Equation 2, as a function of the isomerization kinetic constants (k_O , k_{Li} and/or k_{Ln}) given by León Camacho et al.⁶ and Hénon et al.,⁷ one important hypothesis has to be clarified. Considering that the TAG class comprised almost 94% of the oil (see Table 1), we supposed that only TAG reacted in the system, considering that the probability of a *cis* unsaturated TAG isomerize was much higher than a *cis* unsaturated diacylglycerol (DAG), monoacylglycerol (MAG) or FFA.

Table 1. General composition sunflower oil¹

FA (abbreviation)	Mass (%)	
C14:0 (M)	0.06	
C16:0 (P)	5.41	
C16:1 (Po)	0.14	
C18:0 (S)	3.39	
C18:1 <i>cis</i> (O)	26.83	
C18:1 <i>trans</i>	0.00	
C18:2 <i>cis</i> (Li)	62.76	
C18:2 <i>trans</i>	0.00	
C18:3 <i>cis</i> (Ln)	0.09	
C18:3 <i>trans</i>	0.00	
C20:0 (A)	0.26	
C20:1 (G)	0.15	
C22:0 (Be)	0.69	
C24:0 (Lg)	0.22	
Class of compounds	Mass (%)	<i>M</i> (g/gmol)
TAG	93.661	877.00
DAG	3.000	615.90
MAG	2.000	353.95
FFA	1.339	280.23
Molecular weight	819.01	
Iodine Value (IV)	131.99	

In this way, the term $r_{n,i}$ was defined, using the nomenclature of Equation A1, as follows:

$$\text{Consumption of } cisTAG \text{ } i: r_{n,i} \left[\frac{mol \text{ } i}{mol} \cdot h^{-1} \right] = -\frac{l_{n,i}}{L_n} \left[\frac{mol \text{ } i}{mol} \right] \cdot k_{n,i} \left[h^{-1} \right] \quad (4)$$

$$\text{Formation of } transTAG \text{ } j: r_{n,j} \left[\frac{mol \ i}{mol} \cdot h^{-1} \right] = + \frac{I_{n,i}}{L_n} \left[\frac{mol \ i}{mol} \right] \cdot k_{n,i} \left[h^{-1} \right] \quad (5)$$

where $k_{n,i}$ is velocity of the isomerization reaction of the *cis* TAG i , that contains O, Li and/or Ln acids attached to their glycerol part, in the correspondent *trans* TAG j . It assumed a positive value for the formation of *trans* TAG and a negative value for the consumption of *cis* TAG. Observe that both the formation and the consumption equations were based on the concentration of the *cis* TAG (the reacting substance).

The definition of $r_{n,i}$ was based on an elaborated group of hypotheses that are detailed in the next paragraph.

1. In Equations 2 and A1, $R_{n,i}$ and/or $r_{n,i}$ were calculated only for TAG. They were null for all other constituents of the oil, and also for TAG that did not contain any isomers of O, Li and/or Ln acids attached to its glycerol part.
2. The $k_{n,i}$ values in Equations 4 and 5 were calculated for each TAG containing O, Li and/or Ln, as a sum of k_O , k_{Li} and k_{Ln} for each time that these FA appeared in the molecule of the TAG. In this way, supposing a TAG of type JWX, where J, W and X are types of FA, $k_{n,JWX}$ was calculated as follows:
 - 2a. If J = O, but W \neq O or Li or Ln, and X \neq O or Li or Ln, then $k_{n,JWX} = k_O$. In the same way, if J = Li, but W \neq O or Li or Ln, and X \neq O or Li or Ln, then $k_{n,JWX} = k_{Li}$. Also, if J = Ln, but W \neq O or Li or Ln, and X \neq O or Li or Ln, then $k_{n,JWX} = k_{Ln}$;
 - 2b. If J = O, and W = O, but X \neq O or Li or Ln, then $k_{n,JWX} = 2 \cdot k_O$. In the same way, if J = Li, and W = Li, but X \neq O or Li or Ln, then $k_{n,JWX} = 2 \cdot k_{Li}$. Also, if J = Ln, and W = Ln, but X \neq O or Li or Ln, then $k_{n,JWX} = 2 \cdot k_{Ln}$;

2c. If $J = O$, and $W = Li$, but $X \neq O$ or Li or Ln , then $k_{n,JWX} = k_O + k_{Li}$. In the same way, if $J = O$, and $W = Ln$, but $X \neq O$ or Li or Ln , then $k_{n,JWX} = k_O + k_{Ln}$. Also, if $J = Li$, and $W = Ln$, but $X \neq O$ or Li or Ln , then $k_{n,JWX} = k_{Li} + k_{Ln}$;

2d. If $J = O$, $W = O$ and $X = O$, then $k_{n,JWX} = 3 \cdot k_O$. In the same way, if $J = Li$, $W = Li$ and $X = Li$, then $k_{n,JWX} = 3 \cdot k_{Li}$. Also, if $J = Ln$, $W = Ln$ and $X = Ln$, then $k_{n,JWX} = 3 \cdot k_{Ln}$.

3. In our model, it was supposed that a *trans* TAG had only *trans* unsaturated FA. In this way, a *cis* TAG of type $O_{cis}Li_{cis}Ln_{cis}$ would isomerize to its correspondent *trans* TAG $O_{trans}Li_{trans}Ln_{trans}$, not to similar TAG containing simultaneously *cis* and *trans* FA, such as $O_{cis}Li_{trans}Ln_{trans}$, or $O_{cis}Li_{cis}Ln_{trans}$, or $O_{cis}Li_{trans}Ln_{cis}$, as examples.
4. Each *trans* PUFA of type Li_{trans} ($9c,12t$) or Ln_{trans} ($9c,12c, 15t$) were not re-isomerized to Li_{trans} ($9t,12t$) e Ln_{trans} ($9t,12c,15t$), since the concentrations, and consequently, the probability of isomerization of the FA of type Li_{cis} ($9c,12c$) and Ln_{cis} ($9c,12c, 15c$) in the *trans* FA Li_{trans} ($9c,12t$) and Ln_{trans} ($9c,12c, 15t$) were much higher.

Hypothesis number 4 can be justified by the observations of Wolff¹¹ about the isomerization reaction of Li_{cis} ($9c,12c$) and Ln_{cis} ($9c,12c, 15c$) during deodorization. This author detected that the concentrations of Li_{trans} ($9c,12t$) and Ln_{trans} ($9c,12c, 15t$) were always much higher than the concentrations of Li_{trans} ($9t,12t$) e Ln_{trans} ($9t,12c,15t$), respectively, even for long duration times and high temperatures (4 h, 260 °C), which evidenced that the chances to occur a re-isomerization were lower.

To calculate $r_{n,i}$, the reaction rate of component i (always an element of the TAG class) at stage n , it was necessary to use the k values given by León Camacho et al.⁶ for O acid isomerization reaction and by Hénon et al.⁷ for Li and Ln acid isomerization reactions. According to these authors:

$$k_{Li} [h^{-1}] = 10^{-7921.95/T(K) + 12.76} \quad (6)$$

$$k_{Ln}[h^{-1}] = 10^{-6796.63/T(K) + 11.78} \quad (7)$$

$$k_O[h^{-1}] = \frac{1}{x_{O_{cis}}} \cdot 4.92E9 \cdot e^{-1.573E4/T(K)} \quad (8)$$

where $x_{O_{cis}}$ is the molar fraction of *cis* O, defined as the area of the *cis* isomer divided by the sum of the areas of all the isomers of oleic acid.⁶

Equations 6–8 can be replaced directly in Equations 4 and 5 to give the final expressions of $r_{n,i}$. To exemplify the methodology adopted in this work, Equations 9 and 10 show, respectively, the terms $r_{n,i}$ of consumption of a *cis* TAG of type $O_{cis}Li_{cis}Ln_{cis}$ and of formation of the corresponding *trans* TAG of type $O_{trans}Li_{trans}Ln_{trans}$:

$$r_{n,O_{cis}Li_{cis}Ln_{cis}} = -\frac{l_{n,O_{cis}Li_{cis}Ln_{cis}}}{L_n} \cdot \left(\frac{l_{n,O_{cis}Li_{cis}Ln_{cis}} + l_{n,O_{trans}Li_{trans}Ln_{trans}}}{l_{n,O_{cis}Li_{cis}Ln_{cis}}} \cdot k_O + k_{Li} + k_{Ln} \right) \quad (9)$$

$$r_{n,O_{trans}Li_{trans}Ln_{trans}} = \frac{l_{n,O_{cis}Li_{cis}Ln_{cis}}}{L_n} \cdot \left(\frac{l_{n,O_{cis}Li_{cis}Ln_{cis}} + l_{n,O_{trans}Li_{trans}Ln_{trans}}}{l_{n,O_{cis}Li_{cis}Ln_{cis}}} \cdot k_O + k_{Li} + k_{Ln} \right) \quad (10)$$

Note that the term $(l_{n,O_{cis}Li_{cis}Ln_{cis}} + l_{n,O_{trans}Li_{trans}Ln_{trans}})/l_{n,O_{cis}Li_{cis}Ln_{cis}}$, which came before k_O in Equations 9 and 10, was necessary because of the definition of the kinetic constant adopted by Léon Camacho et al.⁶ (see Equation 8).

Sunflower oil was selected for this study due to its important levels of unsaturated FA. According to O'Brien,¹ sunflower oil usually contains from 14.0% to 39.4% of oleic acid, from 48.3% to 74.0% of linoleic acid, and up to 0.2% of linolenic acid. Typically, triunsaturated TAG corresponds to 70.2%.¹ Tables 1 and 2 show the complete composition of sunflower oil considered in this study.

Table 2. Estimated Composition of Sunflower Oil Feed^a

TAG		TAG	
Major TAG	Mass (%)	Major TAG(cont.)	Mass (%)
PPO _{cis}	0.240	Li _{trans} Li _{trans} Li _{trans}	0.000
PPO _{trans}	0.000	Li _{cis} Li _{cis} Ln _{cis}	0.100
PSO _{cis}	0.277	Li _{trans} Li _{trans} Ln _{trans}	0.000
PSO _{trans}	0.000	DAG ^b	
SSO _{cis}	0.102	PP -	0.0129
SSO _{trans}	0.000	O _{cis} M -	0.0015
PPLi _{cis}	0.587	PS -	0.0134
PPLi _{trans}	0.000	PO _{cis} -	0.1172
PSLi _{cis}	0.570	PLi _{cis} -	0.1273
PSLi _{trans}	0.000	SS -	0.0044
O _{cis} PO _{cis}	1.269	O _{cis} S -	0.0664
O _{trans} PO _{trans}	0.000	O _{cis} O _{cis} -	0.3618
SSLi _{cis}	0.173	O _{cis} Li _{cis} -	1.3809
SSLi _{trans}	0.000	Li _{cis} Li _{cis} -	0.8741
O _{cis} SO _{cis}	0.768	Li _{cis} Ln _{cis} -	0.0016
O _{trans} SO _{trans}	0.000	PBe -	0.0033
PBeLi _{cis}	0.203	O _{cis} A -	0.0072
PBeLi _{trans}	0.000	O _{cis} Be -	0.0135
O _{cis} BeO _{cis}	0.232	Li _{cis} Be-	0.0114
O _{trans} BeO _{trans}	0.000	O _{cis} Lg -	0.0031
O _{cis} MLi _{cis}	0.095	MAG ^b	
O _{trans} MLi _{trans}	0.000	M - -	0.0005
O _{cis} PLi _{cis}	5.618	P - -	0.0929
O _{trans} PLi _{trans}	0.000	S - -	0.0298

Table 2. cont.

$O_{cis}SLi_{cis}$	3.271	$O_{cis} - -$	0.7730
$O_{trans}SLi_{trans}$	0.000	$Li_{cis} - -$	1.0897
$O_{cis}O_{cis}O_{cis}$	1.809	$Ln_{cis} - -$	0.0005
$O_{trans}O_{trans}O_{trans}$	0.000	$A - -$	0.0025
$O_{cis}ALi_{cis}$	0.281	$Be - -$	0.0100
$O_{trans}ALi_{trans}$	0.000	$Lg - -$	0.0011
$O_{cis}BeLi_{cis}$	0.593	FFA ^b	
$O_{trans}BeLi_{trans}$	0.000	M	0.0008
$O_{cis}LgLi_{cis}$	0.184	P	0.0724
$O_{trans}LgLi_{trans}$	0.000	Po	0.0018
$Li_{cis}PLi_{cis}$	6.691	S	0.0454
$Li_{trans}PLi_{trans}$	0.000	O_{cis}	0.3593
$O_{cis}O_{cis}Li_{cis}$	16.499	O_{trans}	0.8405
$O_{trans}O_{trans}Li_{trans}$	0.000	Li_{cis}	0.0012
$Li_{cis}BeLi_{cis}$	0.695	Li_{trans}	0.0035
$Li_{trans}BeLi_{trans}$	0.000	Ln_{cis}	0.0020
$O_{cis}Li_{cis}Li_{cis}$	29.818	Ln_{trans}	0.0092
$O_{trans}Li_{trans}Li_{trans}$	0.000	A	0.0029
$Li_{cis}Li_{cis}Ga$	0.163	G	0.0008
$Li_{trans}Li_{trans}Ga$	0.000	Be	0.0724
$Li_{cis}Li_{cis}Li_{cis}$	23.423	Lg	0.0018

^a The sum of the mass fractions of TAG, DAG, MAG and FFA gives 100%. TAG, DAG, MAG and FFA classes summed individually, 93.661%, 3.000%, 2.000%, and 1.339%, respectively.; ^b DAG, MAG and FFA did not isomerize.

The probable TAG composition was estimated from its FA composition, following the statistical procedure of Antoniosi Filho et al.¹² The compositions in DAG and MAG were obtained from the probable TAG composition in the following way: each TAG was split in 1,2- and 1,3- DAG; each

DAG was then split in MAG following the stoichiometric relations of the prior compounds. Both methodologies were used in our previous works^{8,9} in a successful way.

Tasan and Demirci,¹³ quantified the formation of *trans* FA at different steps of the industrial refining process (chemical or physical), and identified a strong increase (from 0.08% ± 0.03% to 2.56% ± 0.25%) in the total *trans* FA content during the deacidification step of the physical refining. The level of *trans* O acid, between the winterized oil (prior step) and the steam distilled oil (last step), increased eleven times (from 0.02% ± 0.01% to 0.22% ± 0.03%), while the level of *trans* Li increased even more (38 times), from 0.06% ± 0.02% to 2.31% ± 0.23%. At the end of the steam deacidification, sunflower oil also had 0.03% ± 0.01% *trans* Ln (the winterized oil had no *trans* Ln acid). The processing conditions at the deacidification step reported by the authors were 265°C for 1h.

To evaluate the formation of *trans* FA during the continuous deacidification step of the physical refining of sunflower oil, we arranged the simulations in a factorial design to get quadratic models for the responses of interest. The complete set comprised 43 simulations (2^5 trials plus a star configuration and one central point).^{14,15} Each trial was simulated using the computational program in MatLab (Mathworks, v.7.1), following the modeling already discussed (see Appendix I).^{8,9} The simulation results were expressed as percentage of *trans* oleic acid (*C18:1trans*, %mass), *trans* linoleic acid (*C18:2trans*, %mass), *trans* linolenic acid (*C18:3trans*, %mass) and *TOTAL trans FA* (%mass). These values were calculated using, respectively, Equation A9, A10, A11, and A12 (see Appendix II). NOL was calculated as the ratio between the amount of acylglycerols (TAG, DAG and MAG) lost in the distillate and the oil feed. The independent variables selected for this study were temperature (T), oil flow rate (F_{oil}), number of stages of the column (N), liquid height of each stage (H_{liquid}), and equipment diameter (D). Surfaces were sketched using the quadratic models for the statistically significant variables. The software Statistica (Statsoft, v. 5.0) was used to analyze the results following the central composite design.

To test the predictive capacity of the statistical models found by this investigation, we calculated the average relative deviations (*ARD*) according to the relation below:

$$ARD (\%) = 100 \cdot \frac{\sum_n \left(\frac{|Y_{simul} - Y_{est}|}{Y_{simul}} \right)_m}{M} \quad (11)$$

where *Y* is the response, *m* is the number of trials, the subscripts *simul* and *est* are related to the values obtained by the simulation program and the estimated ones using the RSM models, respectively.

3. Results and discussion

Table 3 shows all combinations of the factorial design, and the simulation results for the statistical analysis, which allowed to formulate models, as functions of the statistically significant variables. Equations 12 to 15 stand for the percentages of *C18:1 trans* (%), *C18:2 trans* (%), *C18:3 trans* (%) and *TOTAL trans FA* (%). Equations 16 and 17 represent the final oil acidity and NOL, which simulation results were not shown in Table 3. For Equations 12 to 15, all independent variables were statistically significant at 99% of confidence. In the case of Equations 16 and 17, only temperature and the number of stages of the column were significant at 99% of confidence. Looking at Table 3, one can see that the lowest value for the *TOTAL trans FA* concentrations was achieved at simulation number 33 (0.026%) while its highest value, 97 times greater, was found at simulation number 34 (2.522%). Note that both trials had variables *X*₂, *X*₃, *X*₄ and *X*₅ at central point, but *X*₁ was at level $-\alpha$ for trial number 33 and $+\alpha$ for trial number 34. This fact showed the relevance of temperature in the reactive system. Comparing the pairs of values of *TOTAL trans FA* obtained for trials 35-36, 37-38, 39-40 and 41-42, it was possible to note that the concentration of *trans* isomers increased up to 4 times as the levels of variables *X*₂, *X*₃, *X*₄ and *X*₅ were changed from $-\alpha$ to $+\alpha$, which is far from the effect of *X*₁ (97 times).

Table 3. Factorial design of the deodorization of canola oil using RSM^a.

Trial	Coded variables					<i>C18:1 trans</i> (%mass)		<i>C18:2 trans</i> (%mass)		<i>C18:3 trans</i> (%mass)		<i>TOTAL trans</i> <i>FA</i> (%mass)		
	X ₁	X ₂	X ₃	X ₄	X ₅	Simul.	Eq.12	Simul.	Eq.13	Simul.	Eq.14	Simul.	Eq.15	
1	-1	-1	-1	-1	-1	0.015	0.015	0.051	0.051	0.0003	0.0003	0.067	0.067	
2	+1	-1	-1	-1	-1	0.101	0.102	0.348	0.349	0.0014	0.0014	0.451	0.453	
3	-1	+1	-1	-1	-1	0.022	0.023	0.075	0.076	0.0004	0.0004	0.098	0.099	
4	+1	+1	-1	-1	-1	0.149	0.151	0.511	0.517	0.0021	0.0021	0.662	0.670	
5	-1	-1	+1	-1	-1	0.027	0.027	0.090	0.090	0.0005	0.0005	0.117	0.118	
6	+1	-1	+1	-1	-1	0.178	0.179	0.609	0.616	0.0024	0.0025	0.789	0.798	
7	-1	+1	+1	-1	-1	0.039	0.040	0.132	0.134	0.0007	0.0007	0.172	0.174	
Factorial design (32 trials)	8	+1	+1	+1	-1	-1	0.261	0.266	0.894	0.911	0.0035	0.0036	1.158	1.181
	9	-1	-1	-1	+1	-1	0.023	0.023	0.077	0.076	0.0004	0.0004	0.100	0.099
	10	+1	-1	-1	+1	-1	0.152	0.151	0.521	0.517	0.0021	0.0021	0.675	0.671
	11	-1	+1	-1	+1	-1	0.034	0.033	0.113	0.112	0.0006	0.0006	0.147	0.146
	12	+1	+1	-1	+1	-1	0.223	0.223	0.765	0.766	0.0030	0.0030	0.991	0.992
	13	-1	-1	+1	+1	-1	0.040	0.040	0.135	0.134	0.0007	0.0007	0.176	0.175
	14	-1	-1	+1	+1	-1	0.266	0.266	0.912	0.912	0.0036	0.0036	1.182	1.182
	15	+1	+1	+1	+1	-1	0.059	0.059	0.198	0.198	0.0010	0.0010	0.258	0.258
	16	-1	+1	+1	+1	-1	0.391	0.394	1.337	1.350	0.0052	0.0053	1.732	1.749

Table 3. cont.

	17	+1	-1	-1	-1	+1	0.010	0.010	0.035	0.035	0.0002	0.0002	0.046	0.046
	18	-1	-1	-1	-1	+1	0.069	0.069	0.239	0.238	0.0010	0.0010	0.309	0.309
	19	+1	+1	-1	-1	+1	0.015	0.015	0.052	0.052	0.0003	0.0003	0.067	0.067
	20	-1	+1	-1	-1	+1	0.102	0.103	0.351	0.353	0.0014	0.0014	0.454	0.457
	21	+1	-1	+1	-1	+1	0.018	0.018	0.062	0.062	0.0003	0.0003	0.080	0.080
	22	-1	-1	+1	-1	+1	0.122	0.122	0.418	0.420	0.0017	0.0017	0.542	0.544
	23	+1	+1	+1	-1	+1	0.027	0.027	0.091	0.091	0.0005	0.0005	0.118	0.119
	24	-1	+1	+1	-1	+1	0.179	0.181	0.615	0.622	0.0025	0.0025	0.796	0.805
	25	+1	-1	-1	+1	+1	0.016	0.015	0.053	0.052	0.0003	0.0003	0.069	0.067
	26	-1	-1	-1	+1	+1	0.104	0.103	0.358	0.353	0.0015	0.0014	0.463	0.457
	27	-1	+1	-1	+1	+1	0.023	0.023	0.077	0.077	0.0004	0.0004	0.101	0.100
	28	+1	+1	-1	+1	+1	0.153	0.152	0.526	0.522	0.0021	0.0021	0.681	0.676
	29	-1	-1	+1	+1	+1	0.028	0.027	0.092	0.091	0.0005	0.0005	0.120	0.119
	30	+1	-1	+1	+1	+1	0.183	0.181	0.627	0.622	0.0025	0.0025	0.812	0.806
	31	-1	+1	+1	+1	+1	0.041	0.040	0.136	0.135	0.0007	0.0007	0.177	0.176
	32	+1	+1	+1	+1	+1	0.268	0.268	0.920	0.921	0.0036	0.0037	1.192	1.192
Star points	33	$-\alpha$	0	0	0	0	0.006	0.006	0.020	0.020	0.0001	0.0001	0.026	0.026
$\alpha=\pm 2.378$	34	$+\alpha$	0	0	0	0	0.564	0.558	1.952	1.925	0.0064	0.0064	2.522	2.488
(10 trials)	35	0	$-\alpha$	0	0	0	0.037	0.038	0.127	0.130	0.0006	0.0006	0.165	0.169

Table 3. cont.

	36	0	$+\alpha$	0	0	0	0.100	0.097	0.338	0.330	0.0015	0.0015	0.440	0.428	
	37	0	0	$-\alpha$	0	0	0.031	0.031	0.104	0.105	0.0005	0.0005	0.135	0.137	
	38	0	0	$+\alpha$	0	0	0.122	0.119	0.413	0.405	0.0019	0.0018	0.537	0.526	
	39	0	0	0	$-\alpha$	0	0.041	0.039	0.140	0.133	0.0006	0.0006	0.181	0.173	
	40	0	0	0	$+\alpha$	0	0.096	0.100	0.326	0.339	0.0015	0.0015	0.424	0.441	
	41	0	0	0	0	$-\alpha$	0.123	0.120	0.418	0.409	0.0019	0.0018	0.543	0.531	
	42	0	0	0	0	$+\alpha$	0.047	0.048	0.161	0.165	0.0007	0.0008	0.210	0.214	
Central point ^b	43	0	0	0	0	0	0.069	0.068	0.233	0.232	0.0011	0.0011	0.303	0.302	
Real Variables	$-\alpha$ (-2.378)			-1			0			1			$+\alpha$ (+2.378)		
X_1, T (°C)	210			230.3			245			259.7			280		
X_2, H (m)	0.3			0.445			0.55			0.655			0.8		
X_3, D (m)	0.9			1.161			1.35			1.539			1.8		
X_4, N	3			4			5			6			7		
X_5, F_{oil} (kg/h)	2500			3659			4500			5341			6500		
t_{rt} (min) ^c	10.9			23.9			40.1			61.7			96.7		

^a All trials were simulated assuming 3 mmHg, 1% of stripping steam and Murphree efficiencies equal to 50%; ^b There is no trial error evaluation in simulation; ^c Calculated according to Equation 1.

Regarding the degree of isomerization (DI, %), which is usually expressed as a percentage of the ratio of a *trans* isomer content and its corresponding total isomer (*cis* and *trans*) content,⁷ the operating conditions of trial number 34 led to important values: 1.89% for the DI of oleic acid, 3.16% for the DI of linoleic acid, 17.97% for the DI of linolenic acid (the most reactive unsaturated FA) and 2.75% for the DI of the three unsaturated FA together.

Table 4 shows the ANOVA for the six responses studied, at 99.0% of confidence. All of them presented high correlation coefficients and low ARD values (see Equation 11 and Table 3). Additionally, in the F-test (see Table 4), the calculated F values were many times greater than the listed values, showing that the models were reliable. As a practical rule, a model has statistical significance when the calculated F value is at least 3-5 times greater than the listed value.¹⁴

$$\log_{10}[C18 : 1 \text{ trans } (\%, \text{mass})] = -1.1660 + 0.4118 \cdot X_1 - 0.0118 \cdot X_1^2 + 0.0852 \cdot X_2 - 0.0088 \cdot X_2^2 + 0.1232 \cdot X_3 - 0.0090 \cdot X_3^2 + 0.0855 \cdot X_4 - 0.0067 \cdot X_4^2 - 0.0833 \cdot X_5 - 0.0084 \cdot X_5^2 \quad (12)$$

$$\log_{10}[C18 : 2 \text{ trans } (\%, \text{mass})] = -0.6342 + 0.4167 \cdot X_1 - 0.0128 \cdot X_1^2 + 0.0851 \cdot X_2 - 0.0088 \cdot X_2^2 + 0.1231 \cdot X_3 - 0.0090 \cdot X_3^2 + 0.0853 \cdot X_4 - 0.0067 \cdot X_4^2 - 0.0831 \cdot X_5 - 0.0085 \cdot X_5^2 \quad (13)$$

$$\log_{10}[C18 : 3 \text{ trans } (\%, \text{mass})] = -2.9619 + 0.3585 \cdot X_1 - 0.0154 \cdot X_1^2 + 0.0824 \cdot X_2 - 0.0120 \cdot X_2^2 + 0.1207 \cdot X_3 - 0.0107 \cdot X_3^2 + 0.0839 \cdot X_4 - 0.0085 \cdot X_4^2 - 0.0809 \cdot X_5 - 0.0062 \cdot X_5^2 \quad (14)$$

$$\log_{10}[TOTAL \text{ trans FA } (\%, \text{mass})] = -0.5207 + 0.4154 \cdot X_1 - 0.0126 \cdot X_1^2 + 0.0851 \cdot X_2 - 0.0088 \cdot X_2^2 + 0.1231 \cdot X_3 - 0.0090 \cdot X_3^2 + 0.0853 \cdot X_4 - 0.0067 \cdot X_4^2 - 0.0832 \cdot X_5 - 0.0085 \cdot X_5^2 \quad (15)$$

$$\text{Acidity}(\% \text{ oleic acid}) = 0.311 - 0.255 \cdot X_1 + 0.034 \cdot X_1^2 - 0.0111 \cdot X_4 \quad (16)$$

$$NOL(\%) = 0.298 + 0.212 \cdot X_1 + 0.0526 \cdot X_1^2 - 0.0495 \cdot X_4 + 0.0063 \cdot X_4^2 - 0.0233 \cdot X_1 \cdot X_4 \quad (17)$$

It is important to highlight that the models described in Equations 12-17 were not phenomenological, and the dependence expressed in these equations were a consequence of the statistical analysis.

Table 4. Analysis of variance (ANOVA)

Source of variation	<i>C18:1 trans</i> (% mass)				<i>C18:2 trans</i> (% mass)				<i>C18:3 trans</i> (% mass)				<i>TOTAL trans FA</i> (% mass)				Acidity (expressed as % oleic acid)				<i>NOL</i> (%)			
	SS ^a	DF ^b	MS ^c	F _{test} ^d	SS ^a	DF ^b	MS ^c	F _{test} ^d	SS ^a	DF ^b	MS ^c	F _{test} ^d	SS ^a	DF ^b	MS ^c	F _{test} ^d	SS ^a	DF ^b	MS ^c	F _{test} ^e	SS ^a	DF ^b	MS ^c	F _{test} ^f
Regression	8.949	10	0.90	15000	9.122	10	0.91	15167	7.098	10	0.71	7889	9.075	10	0.91	15167	2.269	3	0.756	2520	2.208	5	0.442	4420
Deviation	0.002	32	6E-5		0.002	32	6E-5		0.003	32	9E-5		0.002	32	6E-5		0.012	39	3E-4		0.004	37	1E-4	
Total variation	8.951	42			9.124	42			7.101	42			9.077	42			2.281	42			2.212	42		
R ²	0.9998				0.9998				0.9996				0.9998				0.995				0.998			
<i>ARD</i> (%)	1.069				1.072				1.398				1.069				3.732				3.933			

^a Sum of squares; ^b Degrees of freedom; ^c Mean Squares. ^d $F_{0.99, 10, 32} = 2.94$; ^e $F_{0.99, 3, 39} = 4.31$; ^f $F_{0.99, 5, 37} = 3.51$.

To exemplify this fact, Figure 1 shows the formation of *TOTAL trans* isomers of O, Li and Ln as a function of the retention time within the limits of the factorial design. Note that there are linear dependences between them, despite the fact that the obtained models were of logarithm type.

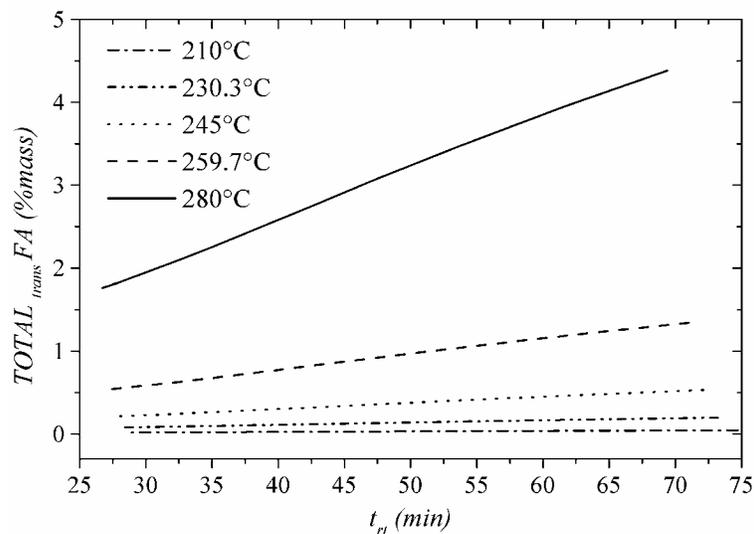
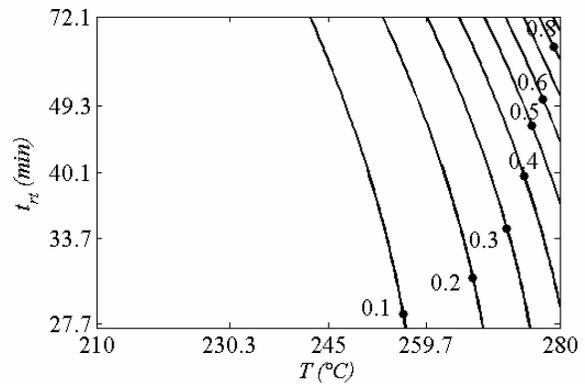
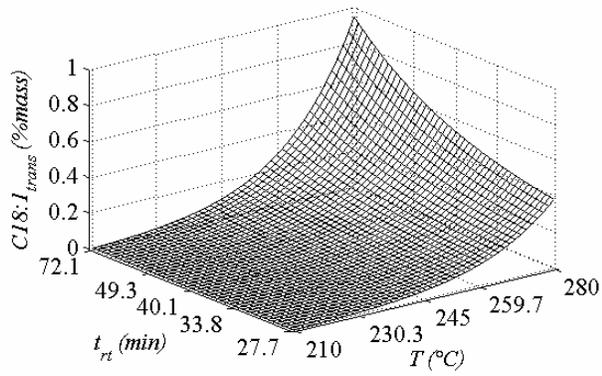
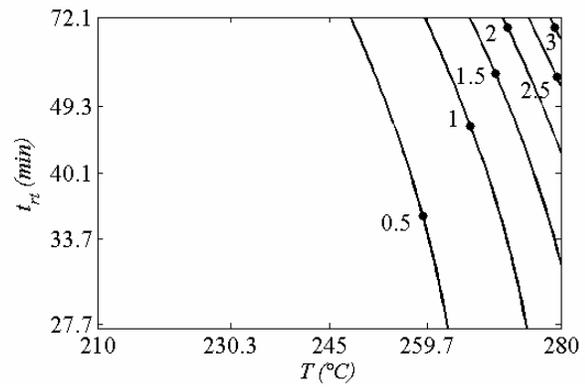
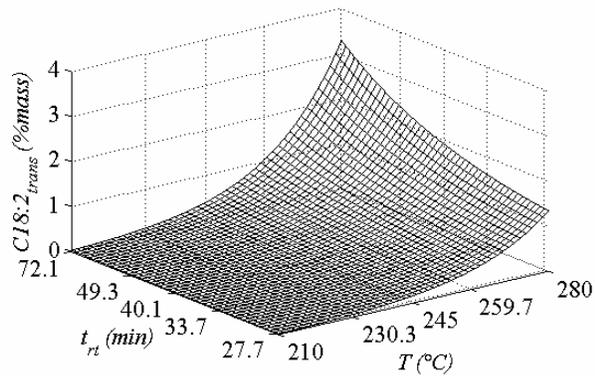


Figure 1. Effect of T ($^{\circ}\text{C}$) and t_{rt} (min) on the formation of *TOTAL trans* isomers of O, Li and Ln. Lines calculated using Equation 15, keeping X_2 , X_3 and X_4 at the central point, while varying X_5 from $-\alpha$ to $+\alpha$, for each value of X_1 .

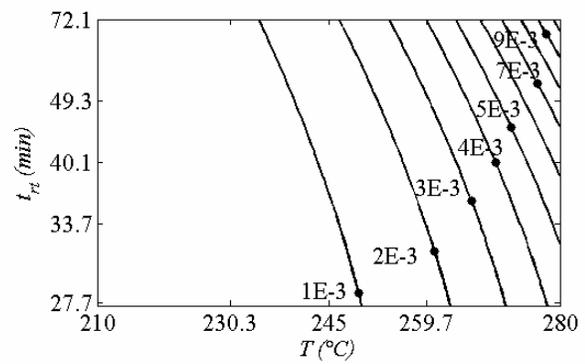
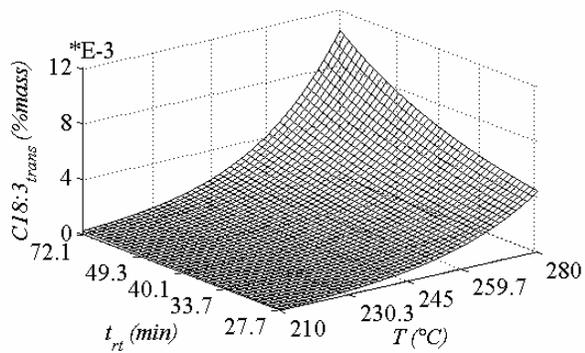
With the models detailed in Equations 12-17, it was possible to plot surfaces that depicted the effects of the independent variables in the responses of interest. Because the responses *C18:1 trans* (%), *C18:2 trans* (%), *C18:3 trans* (%) and *TOTAL trans FA* (%) were all functions of X_1 , X_2 , X_3 , X_4 and X_5 , we chose to illustrate these relations in terms of only two variables: T and t_{rt} (see Figures 2A – 2D). Note that the retention time (t_{rt}) stands for four variables (X_2 , X_3 , X_4 and X_5), as shown in Equation 1. In this way, Figures 2A, 2B, 2C and 2D were plotted supposing X_2 , X_3 , and X_4 at central point (zero value in Equations 12-15), while varying X_1 , and X_5 from $-\alpha$ to $+\alpha$. Other combinations of the independent variables would produce equivalent surfaces.



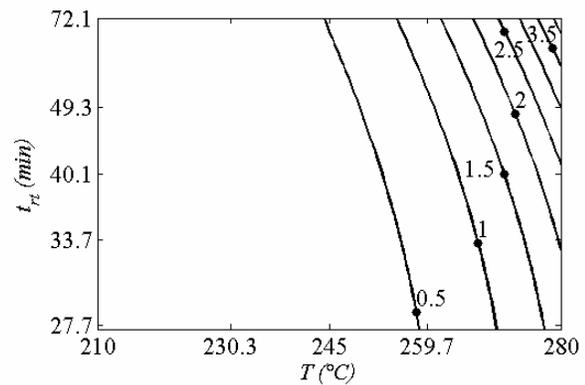
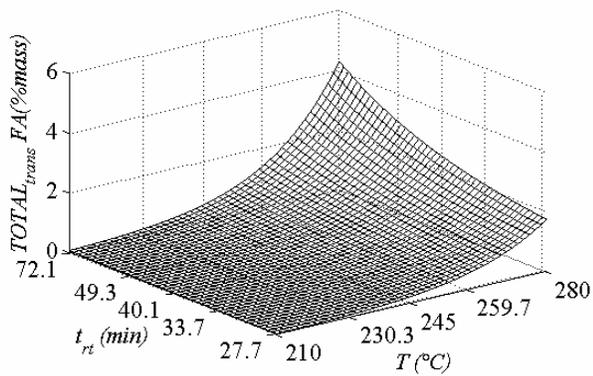
A



B



C



D

Figure 2. Response surfaces and contour curves of (A) *C18:1 trans* (% mass), (B) *C18:2 trans* (% mass), (C) *C18:3 trans* (% mass) and (D) *TOTAL trans FA* (% mass) as a function of T ($^{\circ}\text{C}$) and retention time (t_{rt} , min). X_2 , X_3 and X_4 at the central point in Equations 12-15.

Looking at Figures 2A – 2D, one can see that higher temperatures and retention times led to an increase in the formation of *trans* FA in the deacidified sunflower oil, as expected. In fact, many arrangements of the independent variables could lead to levels of *TOTAL trans FA* higher than 1.0%, which is, nowadays, the maximum value for a quality parameter for refined edible oils in European countries.⁵ In general, the main fraction of the *TOTAL trans FA* was given by the *trans* linoleic acid, followed by the elaidic (or *trans* oleic) acid, and *trans* linolenic acid, as a result of the higher concentration of Li acid in the oil composition (see Table 1).

The contour curves for final oil acidity, expressed as percentage of oleic acid, and NOL (Equations 16 and 17) are shown in Figure 3. Observe that temperatures above 245 $^{\circ}\text{C}$ led to values of final oil acidity lower than 0.3%. According to Carlson,¹⁷ for industrial deodorization, most flavors and odors have usually been eliminated when the FFA content is below 0.03%. This limit region is also shown in Figure 3A. Note that this range of temperature would generate important values of NOL (>0.5%).

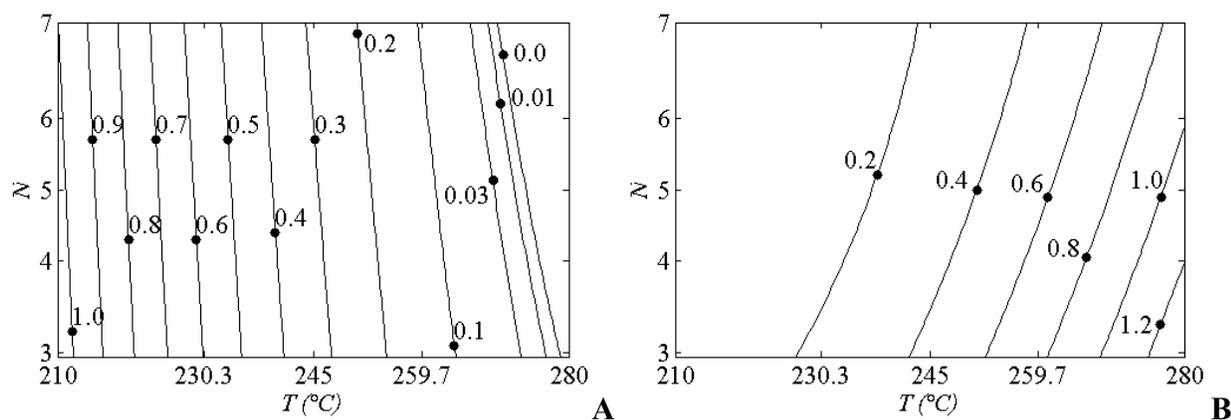


Figure 3. Contour curves of (A) final oil acidity and (B) NOL as a function of temperature (T , $^{\circ}\text{C}$) and the number of stages of the column (N). See Equations 16 and 17.

For further analyses of our methodology we compared the results reported by Tasan and Demirci¹³ for *trans* FA formation during the industrial physical refining of sunflower oil with our results. Unfortunately, the authors informed only the binary T/t_{rt} (265°C/ 1h). None information about the equipment was reported. This gap allowed us to perform calculations with some arbitrariness. At 265°C and 1 h of retention time ($F_{oil} = 4800$ kg/h, $H_{liquid} = 0.8$ m, $D = 1.3$ m and $N = 6$, as a possible configuration for the column), Equations 12-15 gave the following values for *C18:1trans*, *C18:2trans*, *C18:3trans* and *TOTAL trans FA*: 0.36%, 1.23%, 0.004% and 1.60%, respectively. A direct comparison of them with the work of Tasan and Demirci¹³ showed that our value for *C18:1trans* was higher than the value reported by the authors ($0.22 \pm 0.03\%$), and that their values for *C18:2trans*, *C18:3 trans* and *TOTAL trans FA* ($2.31 \pm 0.23\%$, $0.03 \pm 0.01\%$ and $2.56 \pm 0.25\%$, respectively) were higher than ours.

At this point, one should consider the elevate range of the standard deviations (up to 33 % of the measured mean value) reported by Tasan e Demirci¹³ in the experimental analysis of the FA composition of sunflower oil and its *trans* FA contents using the GC analysis procedure. It is worth mentioning that Henon et al.¹⁸ had the same problem, while developing RSM equations for the experimental study of *trans* FA formation during the canola oil deodorization in a batch lab-scale deodorizer.

Taking into account that the initial level of *cis* unsaturated FA affects the formation of *trans* unsaturated FA (a first order reaction), and the uncertainty indicated above, we estimated an additional FA composition for sunflower oil, within the standard deviation limits of the GC analysis reported by Tasan and Demirci,¹³ to perform new simulations. The levels of *C18:1cis* and *C18:2cis* in the oil fed to the equipment were changed, respectively from 26.83% to 26.24%, and from 62.76% to 65.18%. The concentration of *C16:0* were also modified (from 5.41% to 5.58%) to attain 100%. For comparison purposes, see Table 1. The concentration of *C18:3cis* was not modified because its value, 0.09%, was

already at the maximum limit reported by Tasan and Demirci,¹³ taking into account the standard deviation. The main differences in the concentration of the new estimated TAG composition were in six TAG: $O_{cis}O_{cis}O_{cis}$ (from 1.809 to 1.313), $Li_{cis}PLi_{cis}$ (from 6.691 to 7.796%), $O_{cis}O_{cis}Li_{cis}$ (from 16.499 to 10.568), $O_{cis}Li_{cis}Li_{cis}$ (from 29.818 to 28.574), $Li_{cis}Li_{cis}Li_{cis}$ (from 23.423 to 25.794), and $Li_{cis}Li_{cis}Ln_{cis}$ (from 0.100 to 0.106). For comparison purposes, see Table 2.

Simulating the deacidification of this new oil composition at 265°C and 1h of retention time ($F_{oil} = 4800$ kg/h, $H_{liquid} = 0.8$ m, $D = 1.3$ m and $N = 6$, as the configuration of the column), we found 0.30% of $C18:1trans$, 1.33% of $C18:2trans$, 0.005% of $C18:3trans$, and 1.64% of $TOTAL trans FA$. As expected, the concentration of the *trans* isomers changed: $C18:1trans$ decreased (17% lower), $C18:2trans$ increased (8% higher), $C18:3trans$ increased (25% higher), and $TOTAL trans FA$ increased (2.5% higher).

Considering not only these uncertainties, but also deviations in some operational conditions of the equipment, such as temperature and residence time, other two simulations were done. In one simulation, temperature was set as 270 °C and retention time was equal to 66 minutes. The other one had a temperature of 260°C and 54 minutes of retention time. The comparison of these simulation results and the experimental results are shown in Figure 4. As one can see, considering some uncertainties in the processing parameters and in the oil composition, our simulation program were capable of reproducing the experimental values. The best agreement was for the concentration of $C18:1trans$, followed by the concentrations of $TOTAL trans FA$ and $C18:2trans$.

These last simulations were also accomplished for other equipment configurations ($F_{oil} = 3200$ kg/h, $H_{liquid} = 0.8$ m, $D = 1.3$ m and $N = 4$; $F_{oil} = 3785$ kg/h, $H_{liquid} = 0.5$ m, $D = 1.6$ m and $N = 5$; $F_{oil} = 5985$ kg/h, $H_{liquid} = 0.5$ m, $D = 1.7$ m and $N = 7$; $F_{oil} = 2565$ kg/h, $H_{liquid} = 0.5$ m, $D = 1.7$ m and $N = 3$), always keeping the residence time equal to 60 min (1 h). The concentration values of *trans* FA given by the simulation program changed slightly from one simulation to another (up to 2.0%), indicating that one specific equipment configuration did not influence in the isomerization reaction.

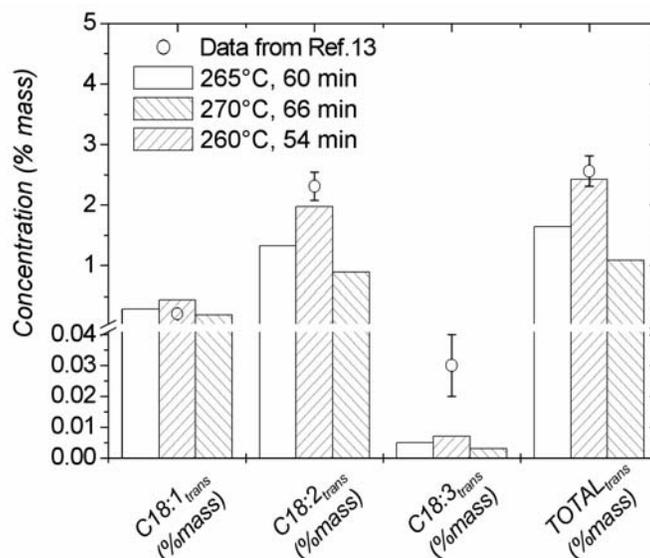


Figure 4. Comparison between the values of *trans* O, *trans* Li, *trans* Ln and *TOTAL trans FA* (% mass) reported by Tasan and Demirci,¹³ and the values obtained from the simulation of the deacidification of sunflower oil with the modified FA composition (26.24% of C18:1, 65.18% of C18:2 and 5.58% of C16:0) in three conditions of temperature and residence time (265°C and 60 min, 270°C and 66 min, and 260°C and 54 min).

In conjunction to our previous works^{8,9} dealing also with the investigation by computational simulation of lab-scale and industrial refining process of edible oils (deodorization and physical refining), this work was an effort to evidence that reliable results could be achieved with a careful modeling of the system under study. Despite the suppositions assumed for some reaction features, the software developed in the present work detailed the real problem acceptably.

4. Optimization

The results presented in Section 3 indicate that the developed models are accurate enough to estimate the main output variables of interest, such as the *TOTAL trans FA*, for a given set of processing parameters. Although the presented discussion is of great utility to understand the effects of processing parameters on the output variables, an automatic optimization tool combining the developed models

could be advantageous in the determination of the *best* set of parameters (or a good approximated solution) for a given optimization measure.

The applicability of such an optimization tool is increased if this tool is flexible enough to test different situations and can be easily modified to include new constraints or different objective functions. This is particularly true in the problem under study, considering that there are several output variables of interest which values depend (non-linearly) on the combination of the input parameters. For this reason, we chose to work with *Scatter Search*¹⁹, an optimization method that can be easily customizable and that has the advantage of being effective for optimization models that rely on time-consuming simulation models.

Scatter Search is an evolutionary optimization method that maintains a pool of solutions and provides unifying principles for joining them (and obtaining new ones) based on generalized path constructions in the Euclidean space²⁰. Each new solution is generated via combinations of the existing solutions and is integrated to the solution pool either if it has a good objective function or if it increases the diversity of the set of existing solutions. The maintenance of the diversity is important to avoid earlier convergence of the algorithm to local optima.

We used an implementation in C that allowed us to customize the objective function²⁰, which was first designed with the goal of minimizing the TOTAL *trans* FA, as seen in the initial objective function:

$$\text{Minimize TOTALtransFA} \tag{18}$$

Since it was desired to maintain the final oil acidity and the NOL at controlled levels, penalty functions were included in Equation 18, to avoid acidity and NOL values superior to 0.3% and 0.5%, respectively. In order to maintain the retention times (t_{rt}) between reasonable limits, a third penalty function was included. Finally, to indicate the fact that we would like the acidity and NOL values to be

as low as possible (even among the values that respect the constraints) two optimization terms on these variables were added. This lead to the following minimization function:

Minimize: $\alpha \cdot \text{TOTALtransFA} + \beta \cdot \text{NOL} + \gamma \cdot \text{acidity} + KK \cdot \text{AcPenal} + MM \cdot \text{NOLPenal} + NN \cdot t_{rt} \text{Penal}$
with :

$$t_{rt} \text{Penal} = \begin{cases} 0, & \text{if } 10 \leq t_{rt}(\text{min}) \leq 100 \\ NN \cdot (10 - t_{rt}), & \text{if } t_{rt}(\text{min}) < 10 \\ NN \cdot (t_{rt} - 100), & \text{if } t_{rt}(\text{min}) > 100 \end{cases} \quad (19)$$

$$\text{AcPenal} = \begin{cases} 0, & \text{if } \text{Acidity} \leq 0.3 \\ KK \cdot (\text{Acidity} - 0.3), & \text{if } \text{Acidity} > 0.3 \end{cases}$$

$$\text{NOLPenal} = \begin{cases} 0, & \text{if } \text{NOL} \leq 0.5 \\ MM \cdot (\text{NOL} - 0.5), & \text{if } \text{NOL} > 0.5 \end{cases}$$

where KK , MM and NN are numbers large enough to discourage constraint violations and α , β and γ are user-defined parameters that indicate the relative importance of optimizing each term. Note that the objective function is sufficiently flexible to include other variables or constraints (in terms of penalty functions).

A second optimization approach was also developed, due to the fact that the RSM method provided an approximation of each desired variable in terms of the input parameters (see Equations 12 to 17). In this case, the presence of an analytical description of the variables led us to use a commercial non-linear optimization software. A sequential quadratic programming (SQP) method, available in MatLab®, was applied. This method allows the explicit definitions of constraints and solves the problem by obtaining, at each iteration, approximations of the Hessian of the Lagrangian function. Therefore, the limits on the retention times, on the NOL and on the acidity were explicitly included in the model, leading to a formulation that minimized:

$$\text{Minimize } \alpha \cdot \text{TOTALtransFA} + \beta \cdot \text{NOL} + \gamma \cdot \text{acidity} \quad (20)$$

subject to the constraints limiting acidity, NOL and retention time, and with the TOTAL *trans* FA, acidity values and NOL given by the approximations of Equations 15 to 17.

Since the non-linear optimization is effected on an approximate function, we found useful to develop a local-search post-optimization method, evaluating each solution with the full simulation procedure and no more by the approximate equations. As a first approach we chose to use an adaptation of the classical Nelder and Mead method²¹, limiting the steps of the algorithm to include the bounds on the decision variables.

4.1 Optimization Results

After preliminary tests, the first observation was that the non-linear optimization on the approximate values of the variables given by Equations 12 to 17, followed by the local-search approach of Nelder and Mead²¹, reached very similar results to those obtained by the *Scatter Search* method. In this way, Equations 12 to 17 were indeed good approximations of the simulation results. The non-linear procedure quickly found a good region in the search space and the impreciseness caused by the approximate functions could be corrected with the local-search algorithm. In other words, the full simulation procedure needed to be evaluated only during the post-optimization phase, contrary to what happened when using the *Scatter Search*, for which the simulation procedure needed to be run for each new tested solution. The fact that the simulation procedure was time-consuming (1 to 3 minutes for each simulation, with a C++ implementation run on a Intel-Centrino 1.73GHz with 1Gb RAM), and that many simulations were needed in order to obtain convergence with the *Scatter Search* method, led us to concentrate on the more economic second approach.

Table 5 shows the results obtained for the parameters $\alpha = 1$, $\beta = 0.1$ and $\gamma = 0.1$. These parameters indicate that priority was given to the minimization of TOTAL *trans* FA, and minor weights were given to the minimization of the NOL and final oil acidity, which were already contemplated in the constraints. The choice of parameters β and γ higher than zero represented the fact that between two solutions with similar TOTAL *trans* FA, that respected all constraints, the one with less acidity and NOL should be chosen.

Table 5. Results for $\alpha=1, \beta=0.1, \gamma=0.1$

Solution						Results		
N	T (°C)	H (m)	D (m)	F_{oil} (kg/h)	t_{rt} (min)	TOTAL <i>trans</i> FA (%)	NOL (%)	Acidity (expressed as % oleic acid)
3	247.68	0.302	1.413	6500.00	10.0	0.090	0.487	0.297
4	245.83	0.474	0.907	5618.27	10.0	0.080	0.363	0.300
5	244.86	0.383	0.900	5594.29	10.0	0.075	0.291	0.300
6	244.22	0.331	0.904	5863.83	10.0	0.072	0.243	0.300
7	243.76	0.300	0.926	6498.00	10.0	0.070	0.208	0.300

In Table 5, five tests were run, one for each possible value of the number of stages. We preferred not to include the number of stages directly in the method, since it was the only integer (discrete) parameter. Note also that the restriction on the acidity levels was active in most of the found solutions (except for $N = 3$). Also important was the inferior bound on the retention time indicating, once more, the importance of this variable in the process, not one specific equipment configuration.

In relation to the limits on the NOL (<0.5%), we observed that the minimization of TOTAL *trans* FA frequently occurred in the direction of lower NOL values during several tests. For this reason, the constraint on the NOL was relaxed.

It is important to notice that results in Table 5 are a mere indication of the usability of our simulation programs. Indeed, the main feature of the method developed here is its flexibility, which enables to test different situations. Note, for instance, that α, β and γ can be used to obtain solutions that fit better one interests. If, for example, one is not satisfied with the NOL values found on Table 5, an increase in parameter β can be used to guide the optimization to other solutions in the search space. Likewise, one can modify the limits on the constraints: this is done in the next example, for a case in which the desired limit on the level of acidity is tighter (< 0.03%). Table 6 shows the new results. As one can see, searching for solutions within this new limit, other area of the search space was explored, leading

mainly to higher temperatures. As expected, the reduction on the acidity levels was obtained on the expense of higher levels of TOTAL *trans* FA (which still remained lower than 1.0%) and NOL. Note that for $N = 3$, no solution respecting the acidity constraint was found. The algorithm then presented the solution with best objective function, taking in consideration the active penalty.

Table 6. Results for $\alpha = 1, \beta = 1, \gamma = 0.1$ with constraints on NOL relaxed.

Solution						Results		
N	T (°C)	H (m)	D (m)	F_{oil} (kg/h)	t_{rt} (min)	TOTAL <i>trans</i> FA (%)	NOL (%)	Acidity (expressed as % oleic acid)
3	280.00	0.420	1.045	4779.95	10.0	0.660	1.360	0.038
4	280.00	0.302	1.226	6307.87	10.0	0.661	1.227	0.025
5	275.09	0.455	0.904	6500.00	10.0	0.495	0.971	0.030
6	273.17	0.300	0.982	6082.33	10.0	0.442	0.836	0.030
7	271.82	0.300	0.926	6307.92	10.0	0.407	0.735	0.030

Other similar tests could be run by modifying the bounds on the input parameters, the characteristics of the considered oil, the relations between coefficients α, β, γ , or any combination of these changes, leading to a method that can be used to explore a wide variety of situations.

5. Conclusion

In general, the results shown in this work were a strong indicative that very important levels of TOTAL *trans* FA could be generated during the deacidification step of physical refining, which, in fact, corroborates with other findings.^{13,18} To minimize *cis-trans* isomerization of unsaturated FA, lower temperatures and shorter heating times should be used. Otherwise, poorer quality refined sunflower oil, in terms of the recommended *trans* FA content, could be produced. A computational simulation model, integrated in a flexible optimization tool, as the one described in this work, could be advantageous for oil producers as a tool to perform previous studies of possible changes in processing conditions of an industrial plant to attend new quality demands, as *trans* FA contents. The relevance of the developed

tools relies on its flexibility in terms of inputs, as different types of oils and the seasonality of crops, bounds levels and relations between coefficients α , β , γ , inclusion of other responses of interest (nutraceutical compounds, as an example), or any combination of these changes.

Nomenclature

ANOVA	Analysis of variance
<i>ARD</i>	Average Relative Deviation
<i>D</i>	Diameter of the deodorizer, in m
DAG	Diacylglycerol(s)
DF	Degrees of freedom in the ANOVA table
DI	Degree of isomerization, in %
<i>f</i>	Component feed flow as liquid, in gmol/h
<i>F</i>	Component feed flow as vapor, in gmol/h
FA	Fatty acid(s)
FFA	Free fatty acid(s)
$F_{k(n,i)}$	Test function
F_{oil}	Oil flow rate, in kg/h
h_f	Liquid feed enthalpy, in J/h
H_f	Vapor feed enthalpy, in J/h
H_{liquid}	Liquid height, in m
h_n	Liquid phase enthalpy at stage n , in J/h
H_n	Vapor phase enthalpy at stage n , in J/h
\hat{h}_n	Liquid molar holdup, in gmols
k_O, k_{Li} and k_{Ln}	Reaction velocity of O, Li and Ln, 1/h
$l_{n,i}$	Component liquid molar flow at stage n , in gmols/h

L_n	Total liquid molar flow at stage n , in gmols/h
Li	Linoleic acid (C18:2)
Ln	Linolenic acid (C18:3)
M_{oil}	Oil molar weight, in kg/kmol
MAG	Monoacylglycerol(s)
mlfFAK	Molar fraction of FA of type K
msfFAK	Mass fraction of FA of type K
MS	Mean Squares in the ANOVA table
MWFA	Molecular weight, g/mol of FA of type K
N	Number of stages in the deodorizer
NMFAK	Number of moles of FA of type K
NMTAG	Number of moles of TAG
O	Oleic acid (C18:1)
PUFA	Polyunsaturated fatty acid(s)
R^2	Correlation coefficient in the ANOVA table
RSM	Response surface methodology
$r_{n,i}$	Reaction rate of component i at stage n , in $\frac{mol\ i}{mol} \cdot h^{-1}$
$R_{n,i}$	Number of moles of component i consumed or produced by the isomerization reaction per hour at stage n , in gmol
SS	Sum of squares in the ANOVA table
T	Temperature, in °C
TAG	Triacylglycerol(s)
t_{rt}	Retention time of the oil in the deodorizer

$v_{n,i}$	Component vapor molar flow at stage n , in gmols/h
V_n	Total vapor molar flow at stage n , in gmols/h
X	Coded variable
$x_{O_{cis}}$	Molar fraction of <i>cis</i> O, defined as the area of the <i>cis</i> isomer divided by

the sum of the areas of all the isomers of oleic acid.⁶

Y	Response of interest, independent variable
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Greek symbols

ρ_{oil}	Oil density, in kg/m ³
v_n	Volume of each stage of the deodorizer, in m ³

Subscripts

<i>est</i>	Related to estimated results using the RSM models
<i>i</i>	Related to component <i>I</i>
<i>n</i>	Related to stage <i>n</i>
<i>oil</i>	Related to oil
<i>simul</i>	Related to simulation results

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Appendix I: Equations for the Continuous Multitray Cross-Flow Deodorizer with Chemical Reactions

For an arbitrary stage n of a stripping column, the related nomenclature can be set as follows.

Subscript n : flow from stage n , $n = 1, 2, \dots, NS$; subscript i : component i , $i = 1, 2, \dots, NC$; H = vapor phase enthalpy (J/h); h = liquid phase enthalpy (J/h); h_f = liquid feed enthalpy (J/h); H_f = vapor feed enthalpy (J/h); V = total vapor flow (mol/h); v = component vapor flow (mol/h); L = total liquid flow (mol/h); l = component liquid flow (mol/h); f = component feed flow as liquid (mol/h); F = component feed flow as vapor (mol/h); R = the number of moles per time of *cis* TAG consumed or the number of moles of *trans* TAG produced by the isomerization reaction (mol/h).

For each stage n , a set of dependent relationships (test functions $F_{k(n,i)}$) must be satisfied.

Component Balances (Total: NS x NC relations)

$$F_{1(n,i)} = l_{n,i} + v_{n,i} + [R_{n,i}]_{if\ i=TAG} - l_{n+1,i} - f_{n,i} - F_{n,i} = 0 \quad (A1)$$

Enthalpy Balances (Total: NS relations)

$$F_{2(n)} = h_n + H_n - h_{n+1} - h_{f,n} - H_{f,n} = 0 \quad (A2)$$

Equilibrium conditions derived from the definitions of the vapor phase Murphree plate efficiency, $\eta_{n,i}$ (Total: NS x NC relations)

$$F_{3(n,i)} = \eta_{n,i} \cdot K_{n,i} \cdot V_n \cdot \frac{l_{n,i}}{L_n} - v_{n,i} + (1 - \eta_{n,i}) \cdot V_n \cdot \frac{F_{n,i}}{\sum_i F_{n,i}} = 0 \quad (A3)$$

The above relationships comprise a vector of test functions

$$\mathbf{F}(\mathbf{x}) = \{\mathbf{F}_1; \mathbf{F}_2; \mathbf{F}_3\} = 0 \quad (A4)$$

which contains NS (2NC + 1) elements, and which may be solved for equally many unknowns

$$\mathbf{x} = \{\mathbf{l}; \mathbf{v}; \mathbf{T}\} \quad (A5)$$

where the vector \mathbf{l} contains all the elements $l_{n,i}$, \mathbf{v} all the elements $v_{n,i}$ and \mathbf{T} all elements T_n .

Once $l_{n,i}$, $v_{n,i}$ and T_n are known, the product compositions, the product flow rates, the concentration, and temperature profiles in the column follow readily. The iterative Newton-Raphson method solves Equation A4 using the prior set of values of the independent variables (Equation A5). A first estimative

is necessary to initiate the calculations. This estimative considers a linear profile for temperature, based on the oil and stripping steam feed temperature in each stage and for the vapor and liquid flows, based on an estimated value for L_n , (total oil feed despising acidity) and for V_n , which is set as the total steam feed plus acidity. The derivatives of test functions (Jacobian matrix) with respect to temperature are found analytically, while those with respect to component flow rates are found numerically.

Appendix II: Calculation of changes in the fa oil composition during steam deacidification

After the final convergence, the simulation program calculated the FA composition of the physically refined sunflower oil and generated the responses of interest for the statistical analysis, which were the percentage of *trans* oleic acid (*C18:1trans*, %mass), *trans* linoleic acid (*C18:2trans*, %mass), *trans* linolenic acid (*C18:3trans*, %mass) and *TOTAL trans FA* (%mass).

Looking at Table 2, one can see that the TAG class were always composed by an arrangement of the FA of type M, P, S, *Ocis*, *Otrans*, *Licis*, *Litrans*, *Lncis*, *Lntrans*, A, G, Be and Lg (for Abbreviations, see Table 1). Therefore, the simulation program calculated the FA composition of the oil in terms of the product composition in the following way:

$$NMFA_K = NMTAG_{JWX} \text{ (if } J = K \text{ or } W = K \text{ or } X = K) + 2 \cdot NMTAG_{JJW} \text{ (if } J = K) + 3 \cdot NMTAG_{JJJ} \text{ (if } J = K) \quad (A6)$$

where $NMFA_K$ is the number of moles of FA of type K and $NMTAG$ is the number of moles of TAG of type JWX , JJW or JJJ , which is equivalent to $l_{n,i}$ (mols of compound i at stage n) in Equation A1.

The molar fraction of FA of type K ($mlfFA_K$) can be calculated from the relation below:

$$mlfFA_K = \frac{NMFA_K}{\sum_{n=1}^{n=nFA} NMFA_n} \quad (A7)$$

where nFA is the number of FA types in the mixture, which is thirteen in our case (M, P, S, *Ocis*, *Otrans*, *Licis*, *Litrans*, *Lncis*, *Lntrans*, A, G, Be and Lg).

And finally the mass fraction of FA of type K ($msfFA_K$) can be obtained as follows:

$$msfFA_K = 100 \cdot \frac{mlfFA_K \cdot MWFA_K}{\sum_{n=1}^{n=nFA} mlfFA_K \cdot MWFA_K} \quad (A8)$$

where $MWFA_K$ is the M.W (g/gmol) of FA of type K .

The responses of interest in the RSM were then:

$$C18 : 1 \text{ trans } (\%mass) = msfFA_{O_{trans}} \quad (A9)$$

$$C18 : 2 \text{ trans } (\%mass) = msfFA_{Li_{trans}} \quad (A10)$$

$$C18 : 3 \text{ trans } (\%mass) = msfFA_{Ln_{trans}} \quad (A11)$$

$$TOTAL \text{ trans } FA (\%mass) = msfFA_{O_{trans}} + msfFA_{Li_{trans}} + msfFA_{Ln_{trans}} \quad (A12)$$

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Fig. 1. Effect of T ($^{\circ}\text{C}$) and t_{rt} (min) on the formation of *TOTAL trans* isomers of O, Li and Ln. Lines calculated using Equation 15, keeping X_2 , X_3 and X_4 at the central point, while varying X_5 from $-\alpha$ to $+\alpha$, for each value of X_1 .

Fig. 2. Response surfaces and contour curves of (A) *C18:1 trans* (% mass), (B) *C18:2 trans* (% mass), (C) *C18:3 trans* (% mass) and (D) *TOTAL trans FA* (% mass) as a function of T ($^{\circ}\text{C}$) and retention time (t_{rt} , min). X_2 , X_3 and X_4 at the central point in Equations 12-15.

Fig. 3. Contour curves of final oil acidity and NOL as a function of temperature (T , $^{\circ}\text{C}$) and the number of stages of the column (N). See Equations 16 and 17.

Fig. 4. Comparison between the values of *trans* O, *trans* Li, *trans* Ln and *TOTAL trans FA* (% mass) reported by Tasan and Demirci,¹³ and the values obtained from the simulation of the deacidification of sunflower oil with the modified FA composition (26.24% of C18:1, 65.18% of C18:2 and 5.58% of C16:0) in three conditions of temperature and residence time (265 $^{\circ}\text{C}$ and 60 min, 266.8 $^{\circ}\text{C}$ and 66 min, and 257.2 $^{\circ}\text{C}$ and 54 min).

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