Simulation of Batch Steam Deacidification of Coconut Oil
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ABSTRACT
A new approach that considers mass and enthalpy balances, equilibrium relationships and heat transfer was tested to simulate a steam deacidification process of coconut oil. These equations had already been used successfully to describe a continuous crosscurrent cascade process in a trayed column. In this work, this approach was adapted to a steam deacidification process in which oil is supplied only at the beginning of the process (batch) while steam is continuously injected into the still, improving the mass transfer of compounds into vapour phase, which is also removed continuously. The equations were partitioned by Naphtali-Sandholm method and then solved by Newton-Raphson method using Matlab software. Group contribution methods were selected to calculate all the physical properties needed in the equilibrium relationships and energy balances. This approach presented good results in relation to the oil final acidity. Oil acidity profile showed an exponential decrease and the temperature presented small variation along the stripping period, which is in accordance with experimental results. In this way, the suggested procedure can be considered as a valuable tool to deeply investigate common processes of the oil and fat industry.

INTRODUCTION
The steam deacidification is the final step in edible oils processing. It can be considered a stripping process which the main objective is to reduce undesirable volatile compounds [1]. Steam deacidification can occur in different ways; continuous, semi-continuous and batch. The latter is suitable for small scale processes and has as advantages the low cost and easy construction [2]. Although batch process is not commonly used in industrial scale, it includes the most important phenomena that occur during the continuous process. For that reason, the batch processing was studied in several works reported in literature [3-5].

In the batch process, oil is supplied only at the process beginning while steam is continuously injected into the oil, improving the mass transfer of compounds into vapour phase, which is also removed continuously. During this process, undesirable removal also occurs, like the loss of triacylglycerols (TAG), diacylglycerols (DAG) and monoacylglycerols (MAG) [2]. Therefore, the process parameters (temperature, retention time, pressure and amount of stripping agent) have to be optimized to ensure final product specification and to avoid neutral oil losses and high costs. In this context, the computational simulation emerges as a tool that allows the process analyses and optimisation without doing experiments and additional costs.

Batch process was already studied using computational simulation as a differential distillation [5]: a tank (still) is charged with feed and then heated, vapour flows overhead, is condensed, and is collected in a receiver. In this study, oil and distillate composition varies with time. The authors considered the process a sequence of numerous and successive vapourisations [5]. This approach was satisfactory to estimate the final oil acidity but presents significant differences when this response is analysed throughout the process [6]. Continuous steam deacidification was also studied by computational simulation presenting good results [7]. Both counter current and cross flow were modelled using mass and enthalpy balance equations and vapour-liquid equilibria (VLE) relations. These equations were adapted in our work to describe a batch steam deacidification.

Thus, the goal of this work was to simulate the batch physical refining of coconut oil, using a realistic approach that considers mass and enthalpy balances, equilibrium relations and heat transfer.

MATERIALS & METHODS
Ceriani & Meirelles described the crossflow steam deacidification process by mass and enthalpy balances and VLE relations [7] for each stage. In this work, the same equations are used to describe the batch steam deacidification as a flash distillation; however time is used instead of stages. Batch process is divided in t times that are considered as a stage of Ceriani & Meirelles column, receiving a certain amount of steam that is removed in the same stage/time (Figure 1).
To simulate deacidification experiments, vapour pressure equations and thermodynamic approach proposed by Ceriani & Meirelles [8] was used to describe Vapour-Liquid Equilibria (VLE) of fatty compounds (Equations 1 and 2).

\[ k_i = \frac{y_i}{x_i} = \frac{y_i \cdot f_i}{P \cdot \phi_i} \]  

(1)

\[ f_i^0 = P_i^{vp} \cdot \phi_i^{sat} \cdot \exp \left( \frac{V_i^L \cdot (P - P_i^{vp})}{R \cdot T} \right) \]  

(2)

where \( k_i \) is the distribution coefficient of \( i \) in both liquid and vapour phases; \( f_i \) is the fugacity of component \( i \) in reference; \( x_i \) and \( y_i \) are molar fractions of component \( i \) in both liquid and vapour phases, respectively; \( P \) is the total pressure; \( R \) is the gas constant; \( T \) is the absolute system temperature; \( P_i^{vp} \) and \( \phi_i^{sat} \) are respectively, vapour pressure and fugacity coefficient of the pure component \( i \); \( \gamma_i \) is the activity coefficient of component \( i \); \( \phi_i \) is the fugacity coefficient of component \( i \); \( V_i^L \) is the liquid molar volume of component \( i \). The exponential term in Equation 2 is called the Poynting factor (POY).

Mass and enthalpy balances (Equations 3 and 4) and equilibrium relations (Equation 5) were adapted from Ceriani & Meirelles [7] to this work.

\[ F_{(t,i)} = l_{t,i} - l_{t-1,i} + \dot{v}_{i,t} - \dot{s}_{i,t} = 0 \]  

(3)

\[ F_{2(t)} = h_t - h_{t-1} + H_{\text{vap}} - H_{\text{t,s}} - UA = 0 \]  

(4)

\[ F_{3(t)} = \dot{v}_{i,t} \cdot k_{i,t} \frac{l_{i,t}}{L} - \dot{v}_{i,t} = 0 \]  

(5)

Where \( l_{t,i} \) and \( l_{t-1,i} \) is total moles of liquid in the still at instant \( t \) and \( t-1 \), respectively; \( \dot{v}_{i,t} \) is the vapour phase formed during the flash in mols/min and \( \dot{s}_{i,t} \) is the vapour injection of component \( i \) in mols/min. Note that, \( \dot{s}_{i,t} \) is equal to the injected steam flow per minute when \( i \) is water and for all the other components, \( \dot{s}_{i,t} \) is equal to zero. \( h_t \) is liquid phase enthalpy in time \( t \); \( H_{\text{vap}} \) is vapour enthalpy of fatty components in time \( t \); \( H_{\text{t,s}} \) is vapour phase enthalpy of steam in time \( t \). \( UA \) is the overall heat transfer coefficient times heat exchange surface area in J/K·min (estimated according to literature [9]). \( k_{i,t} \) is distribution coefficient of component \( i \) in time \( t \).
This approach generates for each time interval \( NC \) mass balances, 1 enthalpy balance and \( NC \) equilibrium relations where \( NC \) is equal to the number of components that constitute the oil. All the equations were partitioned using Naphtali and Sandholm [10] calculation method of multicomponent separation. The equations are related only to times \( t \) and \( t-1 \), so, the Jacobian matrix formed is very sparse and it was solved using the Newton-Raphson method giving as responses \( l_{i,j}, v_{i,j} \) and \( T \). Variations in composition in liquid and vapour phase can be obtained throughout the time using Equations 6 and 7.

\[
x_{i,j} = \frac{l_{i,j}}{\sum_{i=1}^{NC} l_{i,j}}
\]

\[
y_{i,j} = \frac{\dot{v}_{i,j}}{\sum_{i=1}^{NC} \dot{v}_{i,j}}
\]

The vaporisation efficiency was considered equals to one. All equations were compiled using Matlab software. Heat capacities and vapour pressure of fatty compounds were predict using a group contribution methods following previous works [7,8,11]. Necessary input data are retention time, pressure and temperature of the process, percentage of steam and oil composition.

This work used the coconut oil deacidification data obtained by Petrauskaité et al. [3] to run the simulations. The authors have done the experiments in a batch scale equipment containing 250 g of bleached coconut oil. The experiments were conducted for 60 minutes under temperatures and pressures between 190 °C and 230 °C and 1.6 and 3.0 mbar, respectively. Steam percentage varied from 0.6 % to 1.2 %. Since Petrauskaitė et al. [3] have not described the coconut oil composition in terms of partial acylglycerols, this work performed computational simulations considering a coconut oil with one of the compositions used by Ceriani & Meirelles [5] to simulate these experiments: 0.89 % of diacylglycerols (DAG) and 0.27 % of monoacylglycerols (MAG).

**RESULTS & DISCUSSION**

This work simulated the experiments of coconut oil deacidification done by Petrauskaitė et al. [3], using a flash distillation in which VLE is affected by the system pressure, the quantity of oil in still and the quantity of steam injected in a short period of time. In a first step, simulations were done without considering the heat transfer between the equipment and the oil, i.e. \( UA \) equals zero (adiabatic still). Then, the same simulations were done considering \( UA \) equals 29.50 J/K·min [9].

Table 1 presents the results for the final acidity, expressed in lauric acid percentage. Calculated final acidity presents satisfactory values for all process conditions. Note that, all experiments have intermediate response to those obtained in computational simulation. Considering \( UA \) equals zero tends to overestimate acidity responses. In the other hand, considering a \( UA \) equals 29.50 J/K·min tends to slightly underestimate the responses. In this last case, absolute deviations were lower. Thus, it can be noted that is important to add a heat transfer term in enthalpy balance to obtain more realistic results. As expected, our results were closer to experimental results than the ones found by Ceriani & Meirelles [5].

| Table 1. Comparison of Refined final acidity by Petrauskaitė et al. [3] and this work.* |
|---|---|---|---|---|---|---|
| Exp | Temp (°C) | Steam (%) | Pressure (mbar) | Petrauskaitė et al. | \( UA = 0 \) J/K·min | \( UA = 29.5 \) J/K·min |
| 1 | 190 | 0.6 | 1.6 | 0.235 | 0.403 | 0.232 |
| 2 | 210 | 0.8 | 1.6 | 0.070 | 0.135 | 0.058 |
| 3 | 230 | 0.7 | 1.6 | 0.019 | 0.045 | 0.011 |
| 4 | 230 | 0.6 | 2.3 | 0.033 | 0.091 | 0.034 |
| 5 | 230 | 0.6 | 3 | 0.035 | 0.126 | 0.005 |
| 6 | 230 | 1.2 | 3 | 0.017 | 0.058 | 0.016 |

*Experiments numbers correspond exactly to those reported by Petrauskaitė et al.
Figure 2 shows acidity profiles for Experiment 6 (230°C, 3 mbar and 1.2 % steam) considering both UA values. It can be noted that acidity presents a non-linear behaviour: free fatty acids removal is more intense in the first minutes, followed by an slightly decrease in acidity. This behaviour is due to different vapourisation rates calculated throughout the process in our approach. Ceriani & Meirelles [5] obtained a linear decrease of acidity up to 30 minutes as a consequence of the constant vapourisation rate. In fact, experimental acidity profiles shows that acidity removal is not constant with time [12,13]. As expected, acidity values were lower with the inclusion of UA throughout the process, considering that more heat was available in the vaporization process.

![Figure 2. Simulated acidity profile for Exp 6: UA equals 0 (empty square) and UA equals 29.5 J/K·min (full square)](image)

The flash distillation approach proposed in this work can predict satisfactorily neutral oil loss (NOL) results with low absolute deviations values (Table 2). If heat transfer is considered, NOL tends to approximate the experimental values due to the same reason explained above. One probably explanation for this deviation is the entrainment of partial acylglycerols. During experiments, small quantities of neutral oil can be mechanically carried by the steam used improve fatty acids transfer to vapour phase, which was, in fact, reported by Petrauskaitė et al. [3]. This is not considered in our model.

<table>
<thead>
<tr>
<th>Exp</th>
<th>Temp (°C)</th>
<th>Steam (%)</th>
<th>Pressure (mbar)</th>
<th>Petrauskaitė et al.</th>
<th>UA = 0 J/K·min</th>
<th>UA = 29.5 J/K·min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>190</td>
<td>0.6</td>
<td>1.6</td>
<td>0.28</td>
<td>0.12</td>
<td>0.18</td>
</tr>
<tr>
<td>2</td>
<td>210</td>
<td>0.8</td>
<td>1.6</td>
<td>0.57</td>
<td>0.26</td>
<td>0.41</td>
</tr>
<tr>
<td>3</td>
<td>230</td>
<td>0.7</td>
<td>1.6</td>
<td>1.28</td>
<td>0.47</td>
<td>0.85</td>
</tr>
<tr>
<td>4</td>
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<td>0.6</td>
<td>2.3</td>
<td>1.21</td>
<td>0.35</td>
<td>0.60</td>
</tr>
<tr>
<td>5</td>
<td>230</td>
<td>0.6</td>
<td>3</td>
<td>0.89</td>
<td>0.30</td>
<td>0.55</td>
</tr>
<tr>
<td>6</td>
<td>230</td>
<td>1.2</td>
<td>3</td>
<td>0.93</td>
<td>0.43</td>
<td>0.77</td>
</tr>
</tbody>
</table>

*Experiments numbers correspond exactly to those reported by Petrauskaitė et al.

Figure 3 presents NOL profile for Experiment 6 considering both UA values. NOL increases with time: in the first minutes occurs a considerable loss and then it tends to increase linearly. It can be seen that a higher UA value provides higher loss. It is in agreement with acidity results: when the heat transfer is considered the system achieves higher temperatures, and thus, has more energy to volatilize fatty compounds, increasing the acidity removal and oil loss. It was not found in the literature experimental NOL profiles to compare with simulations done in this work.

The last response analysed by this simulations was temperature profiles. Figure 4 presents profiles for Experiments 5 and 6 considering both UA values. It can be noted that when UA equals zero, the oil
temperature decreases due the energy reduction of the system, i.e. the energy to volatile the fatty compounds is removed from the oil resulting in temperature reduction. When $UA$ equals a certain value (different from zero), the necessary energy to volatile fatty compounds is obtained from the heat source and the temperature is maintained quite constant.

![Figure 3](image1.png)

**Figure 3.** Simulated Neutral Oil Loss (NOL) for Exp 6: $UA$ equals 0 (empty square) and $UA$ equals 29.5 J/K·min (full square)

It is also interesting to note in temperature profiles considering the heat transfer that Experiments 5 profile tends to slightly increase while Experiment 6 profile tends to slightly decreases. As these experiments were performed using the same temperature and pressure, the difference is only steam percentage (0.6 % and 1.2 %, for Experiments 5 and 6, respectively). The use of higher amounts of steam entails volatilizing more fatty compounds. As the same $UA$ were used in all experiments, we can note that in Experiment 5, the heat given to the system is bigger than the necessary to volatilize compounds with 0.6 % steam and lower than the necessary to volatilize compounds with 1.2 % steam. In fact, it was observed in experimental works that system temperature tends to decrease during stripping if enough heat is not given to the process [12,13].

![Figure 4](image2.png)

**Figure 4.** Simulated Temperature Profiles for Exp 5 (circles) and Exp 6 (squares): $UA$ equals 0 (empty symbols) and $UA$ equals 29.5 J/K-min (full symbols)
CONCLUSION

In this work, a batch steam deacidification was simulated using a new approach. It presented satisfactory results to describe final acidity and neutral oil loss. This approach was also efficient to describe the process parameters profile. In future works, *cis-trans* isomerisation and hydrolysis reactions and mechanical entrainment may be included. Thus, this computational simulation is a valuable tool to deeply investigate common processes of the vegetable oil industry.

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