Effects of deodorization temperature and time on the formation of 3-MCPD, 2-MCPD, and glycidyl esters and physicochemical changes of palm oil

Renan Tivanello [iD], Maisa Capristo, Eduardo Vicente, Roseli Ferrari, Klicia Sampaio, and Adriana Arisseto

Abstract: This study verified the formation profile of esters of 3-monochloropropane–1,2-diol (3-MCPDE), 2-monochloropropane–1,2-diol (2-MCPDE), and glycidol (GE), and evaluated the physicochemical changes (free-fatty acid, acylglycerols, and colour) that occurred during the deodorization of palm oil in different conditions of time (30, 60, 90, and 120 min) and temperature (210, 230, 250, and 270 °C). Levels of 3-MCPD and 2-MCPD esters ranged from 1.91 to 2.70 mg/kg and 0.68 to 1.44 mg/kg, respectively, and were formed at the mildest tested condition (210 °C, 30 min). No correlation was observed between these contaminants and physicochemical changes. GE levels varied from 0.12 to 8.51 mg/kg and showed correlation with color and diacylglycerol content. While the temperature had little influence on the formation of esters of 3-MCPD and 2-MCPD, the content of GE considerably raised above 250 °C.

1. INTRODUCTION

Elucidating the formation of toxic compounds during heat processing of foods is important to reduce risks to human health. Among emerging processing contaminants, the bound forms of chloropropanols, particularly esters of 3-monochloropropane-1,2-diol (3-MCPDE) and 2-monochloropropane-1,3-diol (2-MCPDE), have been intensively studied in the past few years and have been reported in several processed foods and food ingredients (Arisseto, Marcolino, & Vicente, 2014; B. Craft, Chiodini, Garst, & Granvogl, 2013; Svejkovská et al., 2004; Zelinková, Svejkovská, Velíšek, & Doležal, 2006). The formation of glycidyl esters (GE) has similarly attracted worldwide attention (Craft, Chiodini, Garst, & Granvogl, 2013; Hrncirik & van Duijn, 2011).

Refined vegetable oils have been reported with the highest concentrations of these contaminants, especially palm oil. Deodorization is the refining step that favors the formation of these compounds, as demonstrated by many authors (Franke, Strijowski, Fleck, & Pudel, 2009; Hrncirik & van Duijn, 2011; Zelinková et al., 2006). Chlorides and acylglycerols, mainly triacylglycerols (TAG), occur naturally in palm oil and can act as precursors of 3-MCPD esters (Destaillats, Craft, Sandoz, & Nagy, 2012; Ermacora & Hrncirik, 2014; Šmidrkal et al., 2016). High concentrations of diacylglycerols (DAG) and monoacylglycerols (MAG) play an important role in the formation of GE (Ermacora & Hrncirik, 2014).

Toxicological studies have confirmed adverse effects associated with free 3-MCPD, mainly nephrotoxicity (Cho et al., 2008), while glycidol may cause DNA damage and mutation, as demonstrated by positive genotoxicity results in *in vitro* and *in vivo* assays (EFSA, 2016; FAO/WHO, 2017). The International Agency for Research on Cancer (IARC) classifies 3-MCPD in group 2B (possible human carcinogen) and glycidol in group 2A (probable human carcinogen) (IARC, 2012; 2000). The European Food Safety Authority (EFSA) and the Joint FAO/WHO Expert Committee on Food Additives (JECFA) published contrasting opinions on the establishment of a safe intake parameter for 3-MCPD. EFSA established a tolerable daily intake (TDI) of 0.8 μg/kg body weight (bw) in 2016 while JECFA set a provisional maximum tolerable daily intake (PMTDI) of 4 μg/kg bw in 2017 (EFSA, 2016; FAO/WHO, 2017). In 2018, EFSA re-evaluated the available toxicological data and established a TDI for 3-MCPD of 2 μg/kg bw (*EFSA*, 2018).

There are some proposed mechanisms available in the literature to explain the formation of 3-MCPDE and GE in refined oils (Craft & Destaillats, 2014; Destaillats, Craft, Sandoz, et al., 2012; Rahn & Yaylayan, 2011; Zulkurnain et al., 2012), but the knowledge of the exact precursors and conditions involved in the generation of such contaminants are still in need further research. Moreover, data on the formation of 2-MCPDE as well as the physicochemical changes that occur simultaneously to the formation of the contaminants are something that has not been explored so far. Therefore, the focus of this study is to verify the formation profile of 3-MCPDE, 2-MCPDE, and GE in palm oil, as well as its relation with physicochemical changes along the deodorization process conducted under varying conditions of time and temperature.

2. MATERIAL AND METHODS

2.1 Palm oil sample

A company in the region of Limeira–SP (Brazil) provided the bleached palm oil (BPO), which was previously characterized in relation to free-fatty acids (FFA), composition of acylglycerols, color, and concentrations of 3-MCPDE, 2-MCPDE, and GE. The bleaching was carried out at a temperature of 103 °C using 0.8% of natural clay (pH 7.2) from Oil–Dri (Chicago, USA) and addition of 500 mg/kg of citric acid before the process.

2.2 Solvents and reagents

Heptane (purity ≥ 99%) and acetone were acquired from Scharlau Brand (Barcelona, Spain), while methanol was purchased from J. T. Baker (Mexico City, Mexico). Tetrahydrofuran (THF, inhibitor-free, purity ≥99.99%), toluene (purity ≥99.9%), sodium

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bicarbonate, sodium bromide (NaBr, purity ≥99.5%), and phenyl-boronic acid (PBA, purity ≥97%) were acquired from Sigma-Aldrich (St. Louis, MO, USA). Sodium sulfate and sulfuric acid were delivered from Merck (Darmstadt, Germany) and phenolphthalein was obtained from Synth (Diadema, SP, Brazil). A Milli-Q Plus system from Millipore (Bedford, MA, USA) was used to obtain ultrapure water.

2.3 Standards

The standards rac 1,2-bis-palmitoyl-3-chloropropanediol (purity 98%), 1,3-dipalmitoyl-2-chloropropanediol (purity 98%), glycidyl palmitate (purity 98%), glycidyl palmitate-d5 (chemical purity 97% and isotopic purity 97.6%), and rac 1,2-bis-palmitoyl-3-chloropropanediol-d5 (purity 98%) were purchased from Toronto Research Chemicals Inc (Ontario, Canada). Monoglyceride (MAG), diglyceride (DAG), and triglyceride (TAG) standards were purchased from Sigma-Aldrich Co.

2.4 Deodorization process

The deodorization process was performed in a laboratory-scale batch deodorizer which consisted of a flow meter, hoses, adapters, thermometer, condenser, cold trap, vacuum pump, heating mantle, oil sample flask, flow control, and a vacuometer. Four different temperatures (210, 230, 250, and 270 °C) and times (30, 60, 90, and 120 min) were applied to deodorize 100 g of BPO based on the ideal and extrapolated conditions. Deodorization followed the recommendations from *Bailey's Industrial Oil and Fat Products* (De Greyt & Kellens, 2005): a fixed pressure in the range of 1 to 4 mbar and steam injection set around 1%. A nondeodorized sample was used as control (time zero).

2.5 Determination of 3-MCPDE, 2-MCPDE, and GE

The analyses of the contaminants were carried out by the official AOCS method Cd 29a-13 (AOCS, 2013). The method consisted of the conversion of GE to esters of 3-bromopropane-1,2-diol (3-MBPDE) in the presence of acidic sodium bromide solution, followed by acid-catalyzed transesterification and neutralization with sodium bicarbonate. Subsequently, a salting-out of the fatty acid methyl esters in the presence of sodium sulfate and derivatization of 3-MCPD, 2-MCPD, and 3-MBPD released with phenylboronic acid (PBA) were performed. The samples were analyzed by gas chromatography coupled to a MSD 5975C mass spectrometer (Agilent Technologies, model 7890A, New Castle, DE, USA) using an HP1-MS (30 m × 0.25 mm, 1 μm, Agilent Technologies) capillary column. The following ions were monitored: m/z 147, 196, and 198 for 3-MCPD derivative, m/z 150, 201, and 203 for the internal standard 3-MCPD-d5 derivative, m/z 196 and 198 for 2-MCPD derivative, m/z 147 and 240 for 3-MBPD derivative, and m/z 150 and 245 for the internal standard 3-MBPD-d5 derivative.

2.6 Composition of acylglycerols

The analyses were adapted from the official AOCS method Cd 22–91 (AOCS, 2009). High-performance size exclusion chromatography with a refractive index detector (RID) was employed to analyze TAG, DAG, and MAG using a column Jordi Gel DVB 100A (300 × 7.8 mm) and a Jordi Gel DVB 500A (300 × 10 mm) in series. BPO and refined palm oil samples were dissolved in THF, which was used as mobile phase at a flow rate of 0.5 mL/min. Quantification was expressed in percentage.

2.7 Free-fatty acids (FFA)

Free-fatty acids were determined by the official AOCS method Ca 5a-40 (AOCS, 1998) by titration using standard sodium hydroxide and indicator phenolphthalein. FFAs were quantified according to the mass of the sample, the volume of sodium hydroxide, and the molecular weight of the major fatty acid. The results were expressed as % of palmitic acid.

2.8 Color

The color of palm oil before and after deodorization followed the official AOCS method Cc 13e-92 (AOCS, 2017). A Lovibond® colorimeter was used to measure yellow (Y) and red (R) colors from scales ranging from 0 to 70 with a one inch bucket.

2.9 Statistical analyses

Analyses was conducted with IBM SPSS Statistic 25 software (IBM Corporation, New York, USA). Using Shapiro-Wilk's and Levene tests, the ANOVA requirements, including the homogeneity of variances and a normal distribution of residues, were investigated. All dependent variables were interpreted using one-way ANOVA. Welch's correction was used depending on if the requirement of variances homogeneity was met or not. If a significant statistical effect was found, the means were compared using the Tukey multiple-comparison or Dunnett T3 test also depending on if the equality of variances could be assumed or not. The significance level chosen was 0.05.

A possible correlation between the physicochemical parameters and the levels of the contaminants were analyzed. Depending on the statistical distribution of the data and distribution chart, a Pearson or Spearman correlation was performed.

3. RESULTS AND DISCUSSION

In our study, the figures of merit of the analytical method used to determine the contaminants were those reported by Kamikata et al. (2019). The LOD and LOQ were 0.01 and 0.03 mg/kg for 3-MCPDE while for 2-MCPDE and GE these values were 0.02 and 0.08 mg/kg, respectively. Recoveries ranged from 92% to 104%, reproducibility varied from 4% to 9% and repeatability was between 3% and 6%. The linear ranges for 3-MCPDE, 2-MCPDE, and GE were 0.03 to 8.11 mg/kg, 0.08 to 8.26 mg/kg, and 0.08 to 20.34 mg/kg, respectively, with determination coefficients (R^2) of 0.997 for the MCPDEs and 0.993 for GE.

The BPO used in the experiments presented 4.5% of FFA, 88.2% of TAG, and 7.3% of DAG. The content of MAG was lower than the LOQ (<0.3%) and the red (R) and yellow (Y) colors were 20 and 70, respectively. The levels of the contaminants were <0.01 mg/kg for 3-MCPDE and <0.02 mg/kg for 2-MCPDE and GE.

3.1 Formation of 3-MCPDE, 2-MCPDE, and GE

The results for 3-MCPDE analyses are displayed in Table 1. Mean concentrations ranged from 1.91 to 2.70 mg/kg. In the lowest applied temperature and time (210 °C, 30 min), a concentration of 2.15 mg/kg was observed. Nonsignificant differences were noted in all other times (60, 90, and 120 min), demonstrating that the major proportion of 3-MCPDE was already formed under the mildest evaluated condition. At the other temperatures, the levels of 3-MCPDE varied statistically considering different times. Despite the similarity between the values, a statistical difference between 90 and 120 min was found at a thermal condition of 230 °C. At 250 and 270 °C, the main differences were observed between 30 and 60 min.

Table 1–Concentrations of 3-MCPDE (mg/kg) under the applied conditions of time and temperature.

Time (min)	Temperature (°C)			
	210	230	250	270
30	2.15 ± 0.05[a,B]	2.02 ± 0.06[a,b,A,B]	1.91 ± 0.01[a,A]	2.29 ± 0.09[a,C]
60	2.31 ± 0.23[a,A]	2.03 ± 0.07[a,b,B]	2.31 ± 0.12[b,B]	2.57 ± 0.21[b,B]
90	2.07 ± 0.14[a,A]	2.09 ± 0.07[b,A]	2.15 ± 0.04[b,c,A]	2.70 ± 0.06[b,B]
120	1.97 ± 0.24[a,A,B]	1.93 ± 0.08[a,A]	2.35 ± 0.12[c,B]	2.67 ± 0.04[b,C]

[a–c]Within the same column, mean values with different lowercase letters differ statistically ($P < 0.05$).
[A–C]Within the same line, mean values with different capital letters differ statistically ($P < 0.05$). N = 6 (deodorizations were performed in duplicate and analyses in triplicate).

Data previously published in the literature report the low influence of the temperature on 3-MCPDE formation when the deodorization process is carried out between 180 °C and 265 °C during 1 hr (Hrncirik & van Duijn, 2011). Nevertheless, significant variations were noted for each time while taking into account the evaluated temperatures of the present study, and the highest values were verified when the oil was deodorized at 270 °C, regardless of the time applied.

The concentrations of 2-MCPDE are reported in Table 2. The average levels ranged from 0.68 to 1.44 mg/kg. In general, esters of 2-MCPD were half of the contents of 3-MCPDE, which was similarly observed by (Seefelder, Scholz, & Schilter, 2011). Our results show that 2-MCPD esters can also be verified at the mildest tested condition (210 °C, 30 min). Although concentrations of 3-MCPDE are always higher than those of 2-MCPDE, both compounds have similar formation profiles. Nevertheless, there is a slight rise in the content of this contaminant with an increase in temperature, which was not observed for 3-MCPDE. To the best of our knowledge, no study in the literature has emphasized the formation kinetics of 2-MCPDE so far.

Table 3 shows that the mean concentrations of GE varied from 0.12 to 8.51 mg/kg under the tested conditions. The maximum value observed was approximately eightfold higher than the limit established by the European Commission for vegetable oils used as ingredients in food or direct consumption (EU, 2018). At 230 and 250 °C, no statistical difference was observed between 30, 90, and, 120 min of the process. This suggests that at lower temperatures, time has little influence on the formation of the contaminant. An increase in the concentration of GE over time was observed only when a temperature of 270 °C was applied.

On the other hand, the levels of GE always increased with the temperature, except at 210 and 230 °C in 30 min. This result is consistent with the literature, which describes that temperatures up to about 220 °C do not favor the formation of this contaminant in a significant way. Temperatures above 240 °C are necessary to raise the concentrations of these esters (Craft et al., 2013; Destaillats, Craft, Dubois, & Nagy, 2012; Šmidrkal et al., 2011). This confirmed that the formation of GE depends directly on the temperature applied in the deodorization step (Cheng, Liu, & Liu, 2016; Destaillats, Craft, Dubois, et al., 2012; Hrncirik & van Duijn, 2011).

Taking into account that GE is also considered a precursor of 3-MCPDE (Rahn & Yaylayan, 2011), we can suggest that an excess of GE in the system at 250 and 270 °C may contribute to the formation of 3-MCPDE. Under these extreme temperature conditions, the highest values of 3-MCPDE were produced, especially with extended times such as 90 and 120 min. The results support the hypothesis that there is a difference in formation behavior between MCPDE and GE.
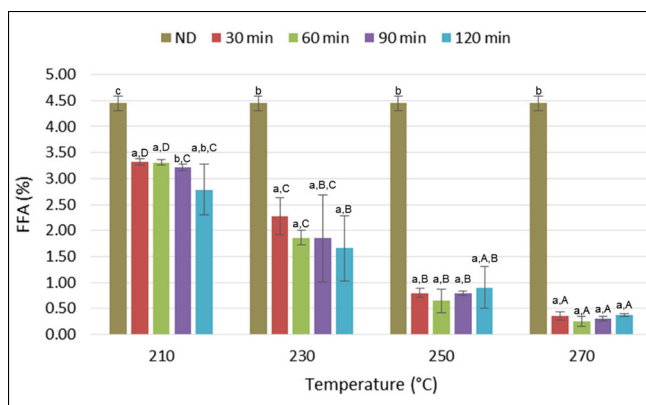
Figure 1–FFA (% of palmitic acid) of palm oil before and after deodorization. A-C Within the same temperature, mean values with different lowercase letters differ statistically ($P < 0.05$). A-D Within the same time, mean values with different capital letters differ statistically ($P < 0.05$). N = 6 (deodorizations were performed in duplicate and analyses in triplicate). ND, nondeodorized.

The results have indicated that using less drastic conditions to deodorize palm oil is not a suitable strategy to mitigate the chlorinated contaminants and alternative methods should be used for their effective reduction. Unlike 3-MCPDE and 2-MCPDE, the levels of GE can be minimized by changing deodorization times and temperatures. At 210 and 230 °C, GE was formed at low concentrations, which were below the limit established by the European regulation for vegetable oil (EU, 2018). However, other quality parameters, such as % of FFA and color, may not be satisfactory under these conditions and should be investigated.

3.2 Physicochemical changes of palm oil during the deodorization

Figure 1 shows the results obtained for FFA of palm oil before and after deodorization, which varied from 0.26% to 4.45%. Except for the treatment performed at 270 °C during 60 min, all values were higher than 0.3%, the maximum limit suggested by the Codex Alimentarius Commission (CAC) (CAC, 2015). The temperature is a very important variable for the acidity decay, as observed for all tested times. The increase of the temperature caused a significant reduction of the FFA content, especially in the first 30 min of the deodorization process. After this time, no significant decrease was observed except for the treatment at 210 °C.

The impact of deodorization on the reduction of acidity is supported by literature in this area. The efficient volatilization of FFA depends not only on the vapor pressure, but also on their

Table 2–Concentrations of 2-MCPDE (mg/kg) under the applied conditions of time and temperature.

Time (min)	Temperature (°C)			
	210	230	250	270
30	0.74 ± 0.15[a,b,A]	0.86 ± 0.05[a,A]	1.03 ± 0.04[a,B]	1.22 ± 0.11[a,C]
60	0.85 ± 0.09[a,b,A]	1.04 ± 0.06[b,B]	1.24 ± 0.07[b,C]	1.41 ± 0.16[b,D]
90	0.68 ± 0.17[a,A]	1.07 ± 0.10[b,B]	1.09 ± 0.03[a,B]	1.44 ± 0.03[b,C]
120	0.93 ± 0.17[b,A]	1.00 ± 0.07[b,A]	1.24 ± 0.05[b,B]	1.43 ± 0.05[b,C]

[a–b] Within the same column, mean values with different lowercase letters differ statistically ($P < 0.05$).
[A–D] Within the same line, mean values with different capital letters differ statistically ($P < 0.05$). N = 6 (deodorizations were performed in duplicate and analyses in triplicate).

Table 3–Concentrations of GE (mg/kg) under the applied conditions of time and temperature.

Time (min)	Temperature (°C)			
	210	230	250	270
30	0.34 ± 0.06[c,A]	0.35 ± 0.04[a,A]	0.95 ± 0.07[a,B]	4.38 ± 0.09[a,C]
60	0.24 ± 0.04[b,A]	0.42 ± 0.04[b,B]	1.60 ± 0.35[b,c,C]	6.36 ± 1.98[a,b,c,D]
90	0.14 ± 0.03[a,A]	0.38 ± 0.14[a,b,B]	1.20 ± 0.22[a,b,c,C]	7.66 ± 0.15[c,D]
120	0.20 ± 0.05[a,b,A]	0.35 ± 0.03[a,B]	1.45 ± 0.43[a,c,C]	8.51 ± 0.24[b,D]

[a–c] Within the same column, mean values with different lowercase letters differ statistically ($P < 0.05$).
[A–D] Within the same line, mean values with different capital letters differ statistically ($P < 0.05$). N = 6 (deodorizations were performed in duplicate and analyses in triplicate).

concentration, the processing pressure and type of flow system in the deodorization step (De Greyt, Kellens, & Huyghebaert, 1999). At the same conditions, other volatile compounds, such as undesirable odors, are volatilized (Ceriani & Meirelles, 2004; Petrauskaitè, Greyt, & Kellens, 2000; Sampaio, Ceriani, Silva, Taham, & Meirelles, 2011). At the high temperatures used to reduce FFA, a decrease of the process efficiency and stability of the final product can also be observed (Ceriani & Meirelles, 2004; De Greyt et al., 1999; Slew & Mohammad, 1989).

A correlation between the final % of FFA and the concentrations of 3-MCPDE, 2-MCPDE, and GE was not observed. However, other authors have reported a correlation between the formation of MCPDE and the initial acidity of the oil (Ramli, Siew, Ibrahim, Kuntom, & Razak, 2015; Šmidrkal et al., 2011).

Figure 2 presents changes in TAG and DAG concentrations during the deodorization. These parameters were evaluated in order to identify possible correlations with the formation of the contaminants. TAG varied from 89.58% to 92.86% while DAG ranged between 6.29% and 7.10%.

No statistical difference in the levels of TAG was observed over time at 250 and 270 °C. For DAG, no statistical difference was verified, except at 210 °C. An inversely proportional variation of those compounds was verified at a temperature higher than 230 °C. This can be explained by the loss of FFA and acylglycerols, especially DAG, by entrainment (Ceriani & Meirelles, 2004; Petrauskaitè et al., 2000). The rise of the temperature from 210 to 270 °C contributed to the increase of TAG and the reduction of DAG until 230 °C. Higher temperatures, such as 250 and 270°C, could contribute to the increase of DAG by the hydrolysis of TAG.

The increase of DAG at high temperatures may have favored the formation of GE, as also observed in several studies (Cheng, Liu, Wang, & Liu, 2017; Cheng et al., 2016; Destaillats, Craft, Sandoz, et al., 2012; Freudenstein, Weking, & Matthäus, 2013). Using the Spearman correlation test, it was found that, at the lower temperatures (210 and 230 °C), the concentrations of DAG and GE had a moderate correlation ($\rho = 0.566$). However, as the temperature rises, the correlation decreases until it is lost under the condition of 270 °C ($\rho = -0.167$). On the other hand, no rela-
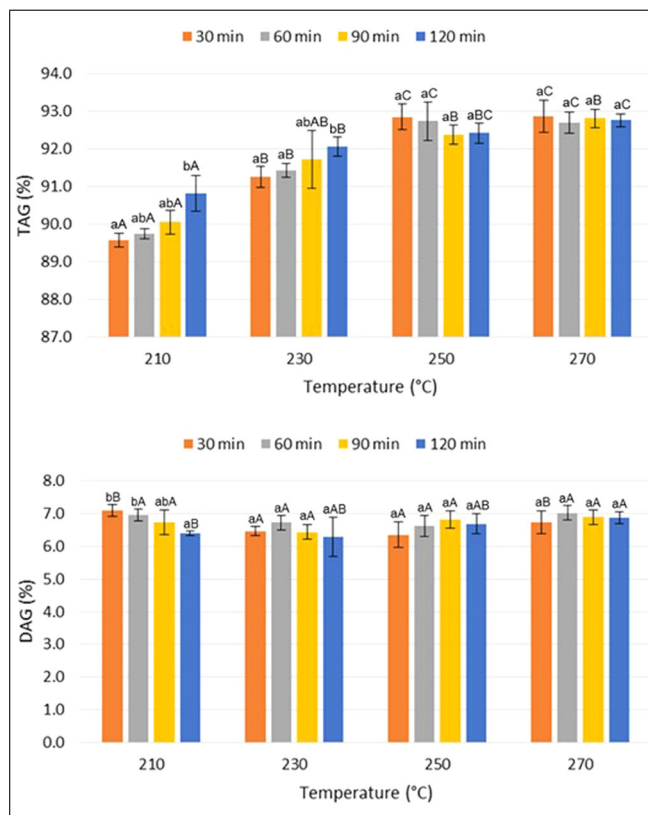
Figure 2–Concentration of TAG (%) and DAG (%) under the applied conditions of time and temperature. A-B Within the same temperature, mean values with different lowercase letters differ statistically ($P < 0.05$). A-C Within the same time, mean values with different capital letters differ statistically ($P < 0.05$). N = 4 (deodorizations were performed in duplicate and analyses in duplicate). ND, nondeodorized.

tionship was found between the concentration of acylglycerols and the formation of 3-MCPDE and 2-MCPDE, according to other authors (Hrncirik & van Duijn, 2011). It is worth mentioning
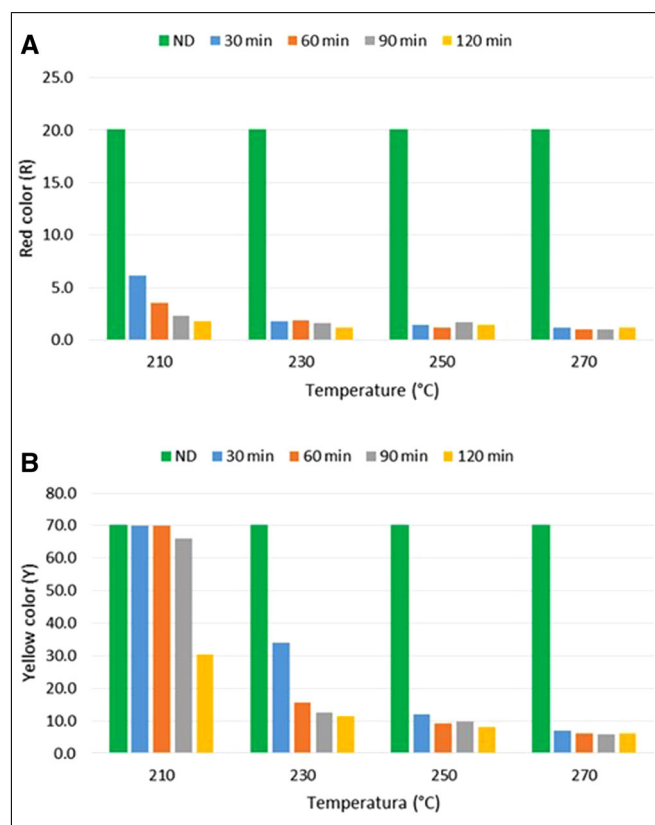
Figure 3–The decay of the red (A) and yellow (B) colors during the deodorization process of palm oil at various conditions. ND, nondeodorized.

that other studies suggest this correlation (Ermacora & Hrncirik, 2014; Freudenstein et al., 2013).

Another relevant parameter for the deodorization of palm oil is color (De Greyt & Kellens, 2005). High temperatures and extended time used in the deodorization step cause a reduction of color in palm oil, which is related to the degradation of carotenoids (De Greyt & Kellens, 2005; De Greyt et al., 1999; Mba, Dumont, & Ngadi, 2015; Sampaio et al., 2013; Slew & Mohammad, 1989; Zulkurnain, Lai, Tan, Abdul Latip, & Tan, 2013).

Figure 3 shows the decay of the parameters red (R) and yellow (Y) over time at the different applied temperatures. There was a constant drop in R only in the process performed at 210 °C. At intermediate temperatures of 230 and 250 °C, there was little variation between values: all below 2.0. The lowest values were observed at 270 °C. Yellow (Y) presented a defined decay profile and varied according to the temperature. As can be seen, the milder thermal condition (210 °C) did not cause a change in the parameter until 90 min. The rise of 20 °C in the process temperature caused a considerable reduction in the Y value with 60 min of deodorization. The increase of the temperature decreased the time needed for the reduction of yellow and red colors, but resulted in an increase of the GE concentrations.

Color reduction presented a negative Spearman correlation of $\rho = -0.827$ and $\rho = -0.932$ with GE for red and yellow, respectively. This correlation is intrinsically linked to the process conditions. The fast reduction of the color using a high temperature would lead to a larger formation of GE and vice versa. No correlation was observed between color and 3-MCPDE and 2-MCPDE.

4. CONCLUSIONS

3-MCPD and 2-MCPD esters were formed at the mildest conditions evaluated in the present study, that is, 210 °C during 30 min. This is sufficient to exhaust the main route for the 3-MCPDE formation and reach concentrations around 2.0 mg/kg. 2-MCPD esters were formed under all tested conditions and have a similar formation profile compared to 3-MCPD esters. On average, the levels of 2-MCPDE were half the concentration of 3-MCPDE, except at 210 °C in which an average of 25% of the concentration of 3-MCPDE was observed. Considering the deodorization parameters of temperature and time currently used in the industry, it is not possible to mitigate the formation of MCPD esters. Differently, GE levels were directly proportional to the temperature used in the deodorization step and the highest concentrations were observed at conditions above 250 °C. The appropriate control of the deodorization step can produce low levels of GE. The results also suggested that GE in excess could act as intermediary compounds in the formation of 3-MCPDE at higher temperatures. No correlation was verified between the final FFA content and the formation of the contaminants. On the other hand, DAG showed moderate and positive Spearman's correlation with GE at milder temperatures, losing this correlation at higher temperatures. The color parameters presented correlation only with GE.

AUTHOR CONTRIBUTIONS

Adriana Arisseto, Eduardo Vicente, Klicia Sampaio, Maisa Capristo, Renan Tivanello, and Roseli Ferrari contributed to the conception and planning of the study. The development of the deodorization system was carried out by Roseli Ferrari and the execution of the experiments by Renan Tivanello and Maisa Capristo. The contaminant analyzes were done by Renan Tivanello with the supervision of Eduardo Vicente. All authors participated in the writing of the manuscript, especially Renan Tivanello with the supervision of Adriana Arisseto.

CONFLICTS OF INTEREST

The authors declare no potential conflict of interest.

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