

Impacts of Bleaching and Packed Column Steam Refining on Cocoa Butter Properties

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Abstract Natural and alkalized cocoa butters were bleached and subsequently steam refined in a continuous packed column at temperatures ranging between 160 and 220 °C. None of the processes evaluated gave rise to any detectable formation of *trans* fatty acids, interesterification or polymerization. For the pressures and steam injection rates used, packed-column steam refining required a minimum temperature of 170 °C to achieve acceptable taste. Bleaching was highly effective in preventing darkening at high steam-refining temperatures, as well as in removing alkaloids, such as theobromine and caffeine, before steam refining. The impacts on the crystallization properties of cocoa butter were studied using DSC and P-NMR. The more significant changes in crystallization kinetics and equilibrium values can be reliably predicted on the basis of FFA removal from the butter.

Keywords Bleaching · Cocoa butter · Crystallization · Packed column · Steam refining

Introduction

Crude cocoa butter is traditionally produced by hydraulic pressing the nibs of the *Theobroma cacao* tree. Prior to pressing, nibs are often alkalized to promote color development and produce a rich cacao flavor [1]. Obtaining good quality steam-refined cocoa butter (<1.75% free fatty acids (FFA) as oleic acid and free from foreign flavors, molds or rancidity), which is commonly traded as ‘deodorized cocoa butter’, requires very simple refining. Generally, this consists of filtering, followed by a batch or (semi-) continuous steam refining (typically called ‘deodorization’) to remove or reduce undesirable flavor components. However, because of the industry’s demand for different types of cocoa butters (e.g., in terms of color range, degree of neutral flavors, etc) has increased considerably, other and more flexible refining technologies have become necessary [2]. The selected steam refining conditions should also minimize product losses and quality degradation.

The scientific and engineering literature on steam refining mainly originates from equipment manufacturers and predominantly covers the thermodynamic, technological and/or economic aspects of oil steam refining [3–9]. Modifications to this basic technology, such as the use of alternative stripping media or flash conditions [10–13] have found only very limited implementation in the edible oil industry to date. In general, process conditions are chosen to avoid unwanted side-reactions such as interesterification, isomerization, formation of cyclic and *trans* fatty acids [9, 14–16].

Specific to cocoa butter refining, removal of alkaloids, particularly theobromine and caffeine, is important. After removal from the oil, these components can deposit on the surfaces of vapor scrubbers in industrial installations. Over time, these deposits hamper the performance of the

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scrubber. Although bleaching is not commonly applied in cocoa butter refining because of product and natural flavor losses, it is required when cocoa butter is used for white chocolate production. Finally, it is important that the steam-refining process preserves the unique crystallization properties of cocoa butter, since extreme steam refining conditions (combination of time and temperature) could lead to intra-, inter-esterification and even limited *trans* formation. Consequently, such profound changes will have negative repercussions on the crystallization characteristics. Triacylglycerol reactions of this kind have been reported in cocoa butter at steam-refining temperatures of 260 °C [17], while Timms and Stewart [18] have described batch steam refining of cocoa butter at 130–180 °C for 10–30 min, and claim that these conditions do not affect physical properties. To avoid negatively impacting the cocoa butter quality, packed-column technology may offer an alternative-processing route, because it has a higher stripping efficiency and, therefore, residence time at high temperatures can be reduced.

Given the scarcity scientific and engineering data on continuous steam refining of cocoa butter in a packed column and using bleaching pre-treatments, the primary aim of this paper was to provide experimental results obtained with packed column technology as well as to verify and explain the impacts on chemical, sensory and physical properties.

Materials and Methods

Two crude cocoa butters, pressed from normal and alkalized cocoa nibs, were supplied by The Blommer Chocolate Company (East Greenville, PA, USA). All chemicals used were either analytical or HPLC grade.

The FFA contents were analyzed by using titration according to the AOCS Official Method Ca 5a–40 [19] and expressed as % oleic acid (C 18:1). Mono, di- and triacylglycerol distributions of the butters were determined by HPLC, according to AOCS Official Method Ce 5b–89 [19] and using a differential refractometer detector. Minor practical adjustments to the flow rate and mobile phase composition were made in order to improve TAG separation, but all modifications were in compliance with the AOCS Official Method. All equipment (pump, column, autosampler and detector) were supplied by Waters (Zellik, Belgium). Phospholipids contents were determined indirectly from phosphorous contents as described by Carelli et al. [20]. Phosphorous content was analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) according to AOCS Official Method Ca 20–99 [19]. Lovibond color was determined at 70 °C using an automatic Lovibond PFX 880/P instrument mounted with a

heater to avoid solidification of the cocoa butter during the measurement. Total color is expressed as the result of $Y + 10R$.

Theobromine and caffeine contents were determined by reverse-phase HPLC, based on the method described by Neumann [21]. The analysis was carried out using an HP series 1050 chromatograph (Hewlett Packard, Avondale, PA, USA) equipped with a reverse-phase column (OmniSpher 5 C18, 150 mm × 3 mm internal, Varian, St-Katelijne-Waver, Belgium). The mobile phase was prepared by dissolving 1.36 g of KH_2PO_4 in 900 ml distilled water, to which 10% (w/w) H_3PO_4 solution was added until pH 3.5 was obtained. This solution is mixed with 100 ml methanol and delivered at 0.7 ml/min corresponding to a pressure of 125–130 bar. An HP UV-Visible detector set at 272 nm was used for detection. About 0.5 g of crude cocoa butter or 1 g of steam-refined cocoa butter placed in 100 ml of basic water (pH = 8.1) were brought to the boil for 15 min and filtered through a Whatman paper filter No. 1. The filtrate was filtered again through a 0.45- μ m pore HPLC filter. The uncolored and clear filtrate was ready for HPLC injection. Identification and quantification were accomplished with pure standards as reference compounds.

DSC experiments were performed using a DSC Q1000 with a Refrigerated Cooling System (TA Instruments, New Castle, DE, USA). The DSC was calibrated with indium (TA Instruments, New Castle, DE, USA), azobenzene (Sigma–Aldrich, Bornem, Belgium) and undecane (Acros Organics, Geel, Belgium) prior to analyses. Nitrogen was used to purge the system. Cocoa butter (2.5–15.0 mg) was sealed in hermetic aluminum pans (using sample preparation procedure B as described by Foubert et al. [22]) and an empty pan was used as a reference.

The time–temperature program was: holding at 65 °C for 15 min to ensure a completely liquid state, cooling at 8 °C min^{−1} to 20 °C and holding at that temperature for 3–4 h, until crystallization was completed. Crystallization peaks were integrated using a horizontal sigmoid baseline, starting and end points were determined using the calculation algorithm described by Foubert et al. [22]. Between the starting- and end points, the area (the amount of heat released up to that moment) was calculated at 5-min intervals. Integration was performed with the Universal Analysis 2000 software (TA Instruments, New Castle, DE, USA). The algebraic solution of the model described by Foubert et al. [23] written as a function of the induction time was fitted to the data series by non-linear regression using Sigmaplot 2000 software.

Solid fat content profiles were measured according to the AOCS Cd 16–92 method [19] by pulsed Nuclear Magnetic Resonance (P-NMR), following the tempered serial method with a Bruker minispec mq20 (Bruker, Germany).

Before and after the steam refining tests, the sample lot was melted to 40 °C and consecutively tasted and judged by an experienced panel of four persons. Qualitative analysis of flavor was done by attributing the typical undesired flavors of ‘rubbery’, ‘woody’, ‘nutty’, ‘bitter’, ‘roasted’ and/or ‘greeny’ to each sample. Quantitatively, a bland taste was perceived as the optimum; therefore, flavor strength was ranked from ‘strong’ to ‘bland’. Samples were judged as being within specification if three of the four panel members could not attribute any of the undesired flavors to the sample.

Experimental Design

Bleaching Treatment

Prior to steam refining, the alkalized cocoa butter was bleached in a batch reactor according to the following procedure. About 30 kg of butter was heated to 80 °C in a double-jacket reactor and 0.6% (v/w) of a 15% (w/v) citric acid solution was added. After 15 min under vigorous agitation, 1.5% (w/w) of Tonsil Optimum 210 FF (Süd Chemie) was added. The mixture was brought under vacuum and bleaching proceeded for another 30 min. Afterwards, the bleaching earth was separated from the cocoa butter using a plate-and-frame filter mounted with standard filter cloth by pressurizing the reactor with compressed air.

Packed Column Stripping or Steam Refining Trials

Natural, alkalized and bleached alkalized cocoa butters were stripped on pilot-plant packed-column equipment (Scheme 1) under the following conditions: flow rate, 13 kg/h; estimated processing time, approx. 7 min; column

diameter, 7.6 cm; top pressure, 3 mbar; steam, 1%; pressure drop, 0.5–0.75 mbar over 2 m packing with 250 m²/m³ specific surface area; top temperature, 160–220 °C with a 10 °C interval.

Results and Discussion

Main Chemical Properties

Table 1 shows the FA profile and distribution of mono-, di- and tri-acylglycerols of the cocoa butter, before and after steam refining at various temperatures. The steam refining conditions had no effect on the acylglycerols of cocoa butter in terms of saturation, *trans* formation or interestereification. The same tendency (i.e., preservation of the FA profile and TAG-distribution) was also observed for both alkalized and bleached alkalized cocoa butters (Table 2). The content of mono- and di-acylglycerols also remains unaffected by the applied processing conditions (Table 2).

Sensory Properties

The taste panel results are summarized in Table 3. Prior to steam refining, all butters were rejected by the taste panel, and the alkalized butter had the strongest flavor. This particular taste was significantly changed by the bleaching treatment, yet still regarded as unacceptable. The experiments showed that under the pressures and steam injection rates used, all butters required a minimum process temperature of 170 °C in the packed column to be within the required flavor specifications. Although only an absolute appreciation is expressed in Table 3, it is also important to note that blandness of the cocoa butter increased with higher process temperatures. These results showed that

Scheme 1 Continuous packed column lay-out

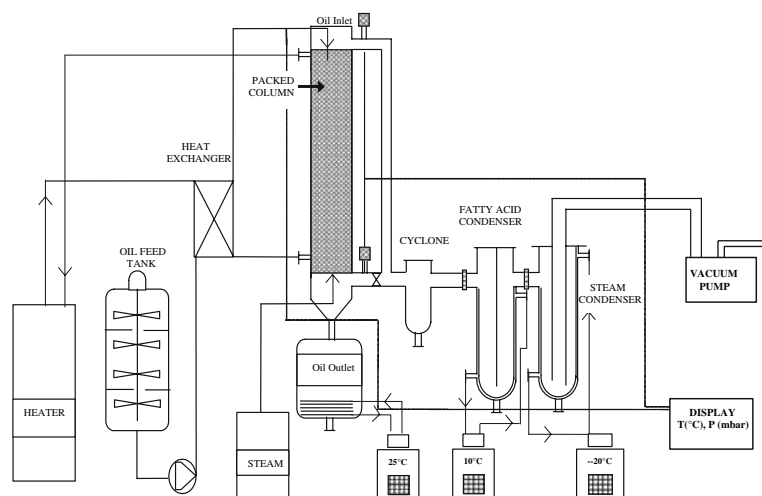


Table 1 Fatty acid profiles and acylglycerol distributions of natural cocoa butters before and after treatment at various temperatures

| Deodorization temperature (°C) | – | 160 | 170 | 190 | 220 |
|--------------------------------|------|------|------|------|------|
| FAP (%w/w) | | | | | |
| C 14:0 | 0.10 | 0.10 | 0.11 | 0.10 | 0.10 |
| C 16:0 | 25.4 | 25.4 | 25.4 | 25.4 | 25.4 |
| C 16:1 | 0.23 | 0.25 | 0.22 | 0.22 | 0.22 |
| C 17:0 | 0.21 | 0.23 | 0.25 | 0.22 | 0.22 |
| C 18:0 | 36.7 | 36.7 | 36.7 | 36.8 | 36.7 |
| C 18:1 | 33.2 | 33.2 | 33.2 | 33.2 | 33.2 |
| C 18:2 | 2.8 | 2.8 | 2.8 | 2.8 | 2.8 |
| C 18:3 | 0.17 | 0.17 | 0.18 | 0.16 | 0.17 |
| C 20:0 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 |
| Distribution (%w/w) | | | | | |
| MAG/DAG | 1.25 | 1.23 | 1.24 | 1.23 | 1.24 |
| PLO | 0.96 | 1.00 | 1.00 | 1.01 | 0.98 |
| PLP | 1.89 | 1.87 | 1.86 | 1.86 | 1.87 |
| OOO | 0.37 | 0.36 | 0.36 | 0.37 | 0.35 |
| POO | 3.18 | 3.07 | 3.08 | 3.06 | 3.08 |
| POP/PLS | 18.4 | 18.2 | 18.2 | 18.2 | 18.3 |
| SOO/SLS | 3.31 | 3.32 | 3.32 | 3.33 | 3.35 |
| POS | 39.3 | 39.2 | 39.3 | 39.2 | 39.2 |
| PPS | 0.33 | 0.29 | 0.30 | 0.31 | 0.29 |
| SOS | 27.1 | 27.2 | 27.2 | 27.2 | 27.2 |
| PSS | 0.63 | 0.55 | 0.59 | 0.58 | 0.53 |
| SOA | 1.59 | 1.65 | 1.60 | 1.62 | 1.56 |
| SSS | 0.33 | 0.36 | 0.32 | 0.35 | 0.34 |
| FFA content (%) | 1.86 | 1.68 | 1.49 | 0.87 | 0.12 |
| Phosphorus (ppm) | 55 | NA | NA | NA | NA |

NA not analyzed

good quality crude cocoa butter can be produced with very mild steam refining conditions.

Color

Figure 1 illustrates the evolution of color of the cocoa butters as function of deodorization temperature in the packed column. The results were quite different for each of the three butters. The natural cocoa butter appears to be slightly ‘heat bleached’ over the complete range of temperatures used, as all the observed color values of the deodorized natural butters remained below the color value for crude natural cocoa butter. However, this heat bleaching effect decreased as process temperature rose. For the alkalized butter, a minor bleaching effect was only observed at 170 °C. At temperatures above 190 °C, the color value significantly increased as function of temperature, greatly exceeding the value of alkalized butter prior to steam refining. Most probably, the cocoa pigments that

were formed during the alkalization of the nibs were responsible for this obvious darkening at higher temperatures. Finally, the bleached alkalized butter showed no sign of darkening during steam refining. Gradual heat bleaching was observed within the temperature range tested, which indicated that the components responsible for the darkening at higher temperatures, such as possibly phospholipids, were indeed removed by the bleaching pre-treatment. However, in this context it must be mentioned that the amounts of phospholipids in natural and alkalized butters were similar, yet the heat darkening and bleaching behavior were different.

Removal of FFA and Alkaloids

An important effect of the steam refining process is the removal of FFA. Together with other volatile components, these molecules are stripped from the oil and then condensed in a scrubber. Of course, substantial FFA-removal is considered as product loss, and thus should be minimized. Figure 2 demonstrates the influence of the process temperature on the residual FFA, theobromine and caffeine contents of the processed butters.

Clearly, the higher the applied deodorization temperature, the lower the FFA-content becomes. For all butters tested, very similar sigmoid shapes of FFA content versus temperature curves indicated that the marginal effect of the process temperature was the largest in the range 180–200 °C, regardless of initial cocoa butter quality. Bleaching pre-treatment only slightly lowered the FFA content in the oil. On the other hand, the bleaching step had far greater impact on the alkaloid content, as the levels of theobromine and caffeine dropped by 90 and 95%, respectively, after bleaching, probably due to the acidic conditions used in this pre-treatment. To achieve a similar reduction by steam refining, a process temperature of 190 or 200 °C was required. Theobromine and caffeine were less efficiently removed from the alkalized butter than from the natural butter. The compositional data of both butters do not adequately explain this difference between the alkalized and natural cocoa butters.

In contrast to the FFA, these alkaloids were completely removed by steam refining around 200 °C. The condensation of co-stripped alkaloids, such as theobromine and caffeine, in the scrubber is another unwanted side effect in industrial cocoa butter refining installations. Although the yield loss as a result of removing these substances is surely negligible, the efficiency of the scrubber and, therefore, of the process is certainly reduced. In this context, our results showed that a bleaching treatment prior to steam refining process offers the advantage of a nearly complete removal

Table 2 Fatty acid profile, and acylglycerol distributions of alkalized cocoa butters before and after treatment at various temperatures

| Deodorization temperature (°C) | Crude | | | | | Bleached | |
|--------------------------------|-------|------|------|------|------|----------|------|
| | – | 160 | 170 | 190 | 220 | 180 | 220 |
| FAP %(w/w) | | | | | | | |
| C 14:0 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| C 16:0 | 25.5 | 25.4 | 25.7 | 25.5 | 25.8 | 25.6 | 25.7 |
| C 16:1 | 0.23 | 0.23 | 0.24 | 0.24 | 0.2 | 0.24 | 0.26 |
| C 17:0 | 0.20 | 0.22 | 0.21 | 0.21 | 0.20 | 0.20 | 0.20 |
| C 18:0 | 36.5 | 36.3 | 36.4 | 36.5 | 36.2 | 36.4 | 36.3 |
| C 18:1 | 33.3 | 33.4 | 33.2 | 33.3 | 33.2 | 33.3 | 33.3 |
| C 18:2 | 2.87 | 2.94 | 2.97 | 2.91 | 2.94 | 2.94 | 2.96 |
| C 18:3 | 0.17 | 0.18 | 0.17 | 0.17 | 0.16 | 0.17 | 0.16 |
| C 20:0 | 1.1 | 1.1 | 1.0 | 1.1 | 1.0 | 1.0 | 1.0 |
| Distribution (%w/w) | | | | | | | |
| MAG/DAG | 1.24 | 1.20 | 1.29 | 1.24 | 1.28 | 1.24 | 1.25 |
| PLO | 0.91 | 0.98 | 0.94 | 0.97 | 0.92 | 0.89 | 0.92 |
| PLP | 1.90 | 1.86 | 1.95 | 1.88 | 1.97 | 1.94 | 1.94 |
| OOO | 0.38 | 0.45 | 0.33 | 0.45 | 0.43 | 0.43 | 0.47 |
| POO | 3.09 | 3.08 | 3.05 | 3.06 | 3.05 | 2.93 | 2.93 |
| POP/PLS | 18.40 | 18.3 | 18.7 | 18.4 | 18.7 | 18.7 | 18.7 |
| SOO/SLS | 3.31 | 3.37 | 3.28 | 3.31 | 3.31 | 3.25 | 3.30 |
| POS | 39.3 | 39.2 | 39.7 | 39.3 | 39.6 | 39.5 | 39.5 |
| PPS | 0.30 | 0.28 | 0.25 | 0.29 | 0.24 | 0.27 | 0.28 |
| SOS | 27.12 | 27.0 | 26.7 | 27.1 | 26.6 | 26.9 | 27.0 |
| PSS | 0.58 | 0.52 | 0.51 | 0.56 | 0.47 | 0.53 | 0.52 |
| SOA | 1.53 | 1.50 | 1.42 | 1.50 | 1.41 | 1.55 | 1.53 |
| SSS | 0.32 | 0.37 | 0.28 | 0.26 | 0.29 | 0.32 | 0.33 |
| FFA content (%) | 1.87 | 1.54 | 1.49 | 1.04 | 0.13 | 1.35 | 0.9 |
| Phosphorus (ppm) | 55 | NA | NA | NA | NA | 9 | NA |

NA not analyzed

Table 3 Results of sensory tests on various cocoa butters before and after treatment

| | Deodorization temperature (°C) | | | | | | | |
|--------------------|--------------------------------|-----|-----|-----|-----|-----|-----|-----|
| | – | 160 | 170 | 180 | 190 | 200 | 210 | 220 |
| Natural | OS | OS | OK | OK | OK | OK | NA | OK |
| Alkalized | OS | OS | OK | OK | OK | OK | OK | OK |
| Bleached alkalized | OS | OS | OK | OK | OK | OK | OK | OK |

OS outside of specifications, NA not analyzed, OK acceptable

of the alkaloids before the cocoa butter enters the packed column.

Physical Properties

In addition to the chemical and sensory aspects, the steam-refining process should also be judged on its impact on the physical properties of the cocoa butter. After all, in most food applications, the use of cocoa butter often relies on its unique physical behavior. It would therefore be

unacceptable for confectionery manufacturers if the steam refining technology and conditions caused the crystallization properties of cocoa butter to deteriorate.

Crystallization Kinetics

The Foubert-model [23] offers the ability to summarize the crystallization kinetics in four parameters:

- t_{ind} [h]: time needed to achieve 1% of crystallization
- K [h⁻¹]: rate constant

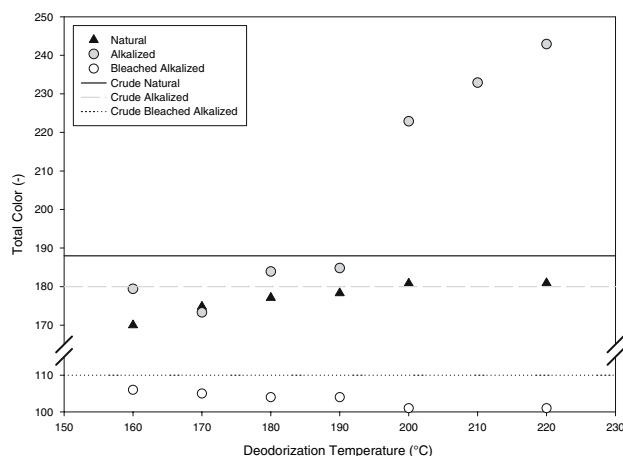


Fig. 1 Total color of cocoa butter as a function of deodorization temperature

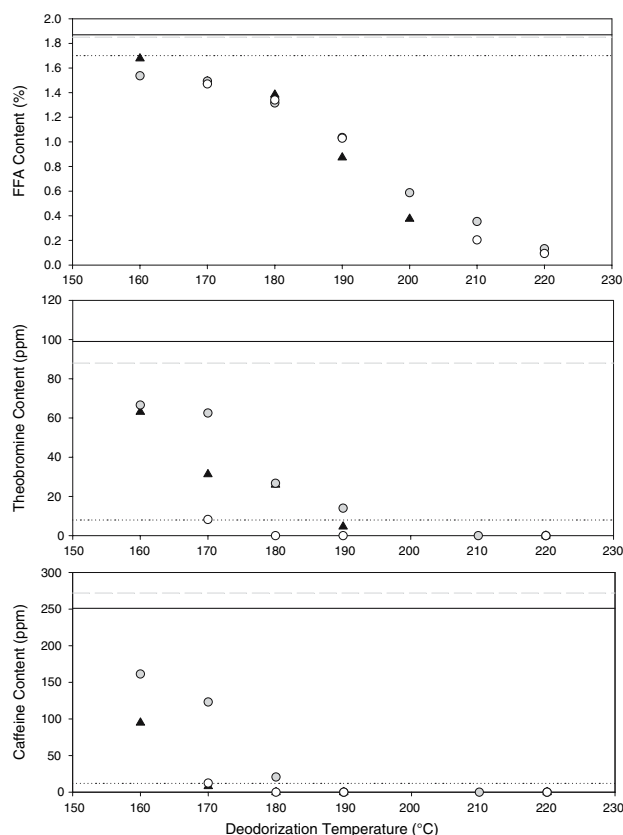


Fig. 2 Level of FFA, theobromine and caffeine as a function of deodorization temperature. See Fig. 1 for the explanation of symbols and lines

- a [J/g]: amount of released heat after reaching equilibrium conditions
- n [–]: order of reverse reaction.

The high resolution of DSC and application of a suitable mathematical model, originally developed for cocoa butter, thus could offer more detailed and fundamental

information on how the crystallization kinetics are actually altered, instead of using the more common Shukoff and Jensen cooling curves [18]. Similar DSC-experiments of isothermal crystallization of cocoa butter at 20 °C in the given time span of 4 h have shown that the cocoa butter does not crystallize in or recrystallize to its more stable β -polymorph, but crystallization occurs in two steps at which α and β' crystals, respectively, are formed [24]. The parameter a gives a proper estimation of the amount of metastable β' -polymorphs formed (direct or through α -mediation) in the experiment. This was verified by checking the melting peak temperatures of the cocoa butter after the crystallization, which ranged between 27 and 28 °C. Such melting peaks indeed suggested the single presence of β' crystals [25]. Hence, the model effectively provides estimated values for β' -formation, the crystallization start, the reaction rate, the order of the reverse reaction, and permits further comparison on these bases.

Figure 3 shows the estimated values of these four parameters for the three studied butters (natural, alkalized and bleached alkalized) as function of the FFA content. The reason to plot the parameters as function of FFA content is because, as previously discussed and shown in Fig. 2, the degree of FFA removal in cocoa butter can be quite reliably estimated as a function of process temperature. Consequently, if the link between FFA removal and the crystallization properties can be quantified, it might serve as a tool to estimate the repercussions of the refining process on the physical properties. The results can then also be compared with the results of Foubert et al. [24], in which the impact of the FFA on cocoa butter kinetics was quantified as a linear regression slope.

In the plots shown in Fig. 3a–d, the outer left data points represent the values obtained for the respective crude butters. To a quite similar degree, the induction time of the natural and alkalized butter is linearly reduced ($R^2 = 0.947$ and $R^2 = 0.976$, respectively) as function of FFA-content (Fig. 3a). An inverse relation was found between the rate constant K and the amount of FFA for the natural ($R^2 = 0.991$) and alkalized butter ($R^2 = 0.962$) (Fig. 3b). This linear relationship within this specific temperature range used, indicated that, for a given cocoa butter, the reduction of induction time and increase of rate constant as a result of a steam refining process could be effectively predicted by the residual amount of FFA. Moreover, these data also suggest that steam refining does not change any factors in the cocoa butter that influence induction time or rate constant, other than FFA. For the bleached alkalized cocoa butter, the relation between FFA removal and the induction time and the rate constant was also quite linear ($R^2 = 0.907$ and $R^2 = 0.999$), but the impact was not as strong as observed for the other two cocoa butters, (the slope of the regression line being far less steep; Fig. 3a, b).

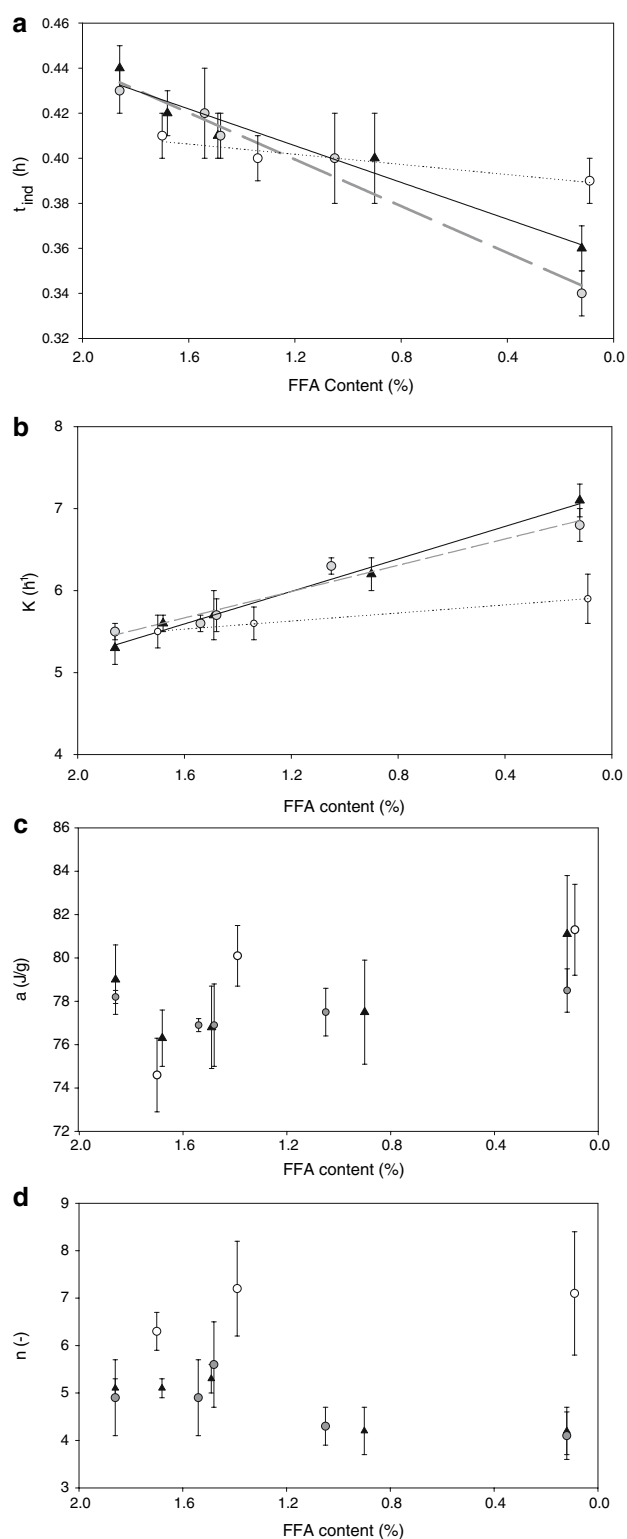


Fig. 3 Crystallization kinetics parameters as a function of FFA-content of cocoa butter. Standard deviations on parameter estimates are indicated. See Fig. 1 for the explanation of symbols, linear regression lines for which $R^2 > 0.9$ are indicated

The linear response of the parameters to the FFA content, however, is not shown for parameters a and n (Fig. 3c, d). Quite consistent for the natural and alkalized butter, the a value dropped after steam refining at low temperatures (180 °C) (Fig. 3c). The drop did not necessarily mean that the deodorized butter crystallizes less, since the parameter a only indicated the amounts of β' -crystallization and α -crystallization were not taken into account. Furthermore, considering only the deodorized butters, the parameter a tended to increase again when more FFA was removed. This result suggests that the removal of FFA positively affects the crystallization of, at least, the β' -polymorph. When the a values were compared with an adapted paired t test, significant differences ($p < 0.05$) appeared to exist between the natural butter processed at 220 °C and the butter processed at 180 °C, and also between the crude alkalized butter and the butter processed at 180 °C. The bleaching pretreatment caused a significant decrease in the a value too, but when the FFA was further removed by steam refining, the value became significantly higher than for the crude and the bleached alkalized butter. So it appeared as if the bleaching process reduced the β' -formation at 20 °C, but steam refining at higher temperatures enhanced this type of crystallization. Once again, this effect might be attributed to a thorough removal of FFA at higher temperatures.

Finally, the parameter n , representing the order of the reverse reaction, remained unaffected if little FFA was removed from the cocoa butter, but dropped slightly once the FFA content was more thoroughly reduced (Fig. 3d). The contrary seemed true for the bleached butter, as the order of the reverse reaction appeared to increase with lower FFA contents. A similar paired t test however did not reveal significant differences between the n values for any butter.

When the above results were compared to values obtained by Foubert et al. [24], the qualitative effect of FFA removal (increase or decrease of the parameter) was quite similar in both studies. However, it must be noted that the respective impacts (regression slope) in the present study were substantially larger, especially when the butters with <1% FFA are taken into account in calculating the linear regression slope. This can be explained by the fact that in the study of Foubert et al. [24] the lowest FFA content was 1.16%, and, therefore, the proposed regression coefficients of Foubert et al. [24] might not necessarily be valid for cocoa butters with <1% FFA.

Solid Fat Profiles

While the previous discussion has dealt with the kinetic aspects of cocoa butter crystallization at a certain tempera-

ture, the following discussion addresses the equilibrium SFC of the cocoa butter as measured in a typical SFC-profile measurement. Figure 4 shows the SFCs of the three butters at 20, 25 and 30 °C. At all temperatures, the increase in solid fat as function of FFA removal was confirmed for each cocoa butter, and this correlation is once more surprisingly linear for the natural and alkalized cocoa butter. The greatest effect of FFA removal (or highest slope) was observed at 30 °C, which is in fact the steepest part of the typical melting curve of cocoa butter. At this temperature, the difference between crude natural cocoa butter and its counterpart processed at 220 °C was more than 5% solid fat, although less than 2% FFA was removed from the cocoa butter. This demonstrated that the lower solid fat values of crude cocoa butter cannot be simply be attributed to the presence of uncrystallized FFA, but that the degree of crystallization of the bulk components, the triacylglycerols, is linearly affected by the FFA content. In this context, it should be mentioned that Jacobsberg and Oh [26] have reported a similar tendency in palm oil, claiming this is due to the formation of a eutectic mixture of TAG and FFA.

The bleached butter, however, showed a non-linear trend, similar to what was observed for its parameter a . An

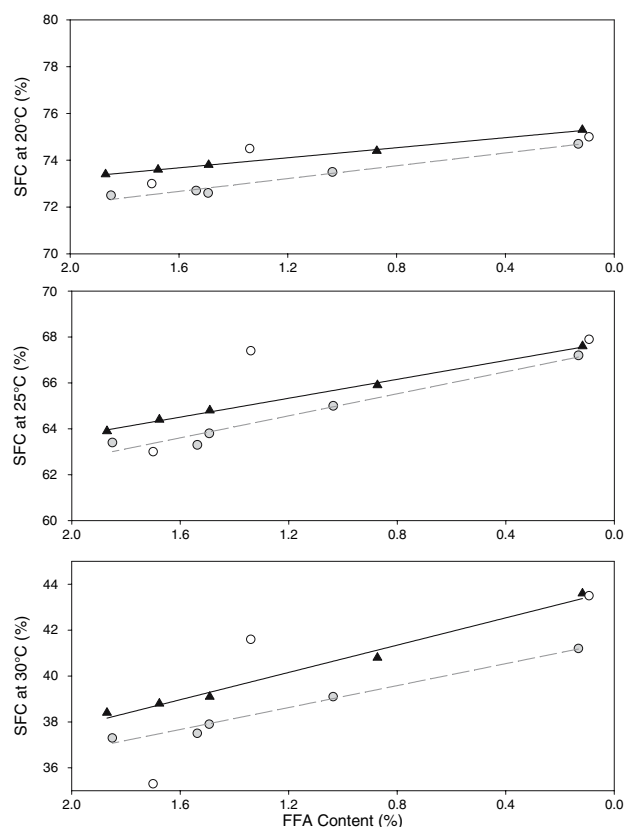


Fig. 4 Equilibrium solid fat content as function of level of FFA of cocoa butter. See Fig. 1 for the explanation of symbols, linear regression lines for which $R^2 > 0.9$ are indicated

explanation could lie in the fact that the bleaching pretreatment also removed over 80% of the phospholipids (phosphorus content dropped from 55 to 9 ppm). Although these minor components are present in concentrations 10–20 times lower than FFA, phospholipids interfere with the nucleation and crystal growth stages of cocoa butter [27]. With these components removed, a 25% reduction in FFA suffices to increase the solid fat significantly as shown in Figs. 3 and 4. In both figures, a further decrease of FFA in cocoa butter did not lead to significantly higher crystallization degrees.

Finally, remarks are needed to clarify the distinction between the steam-refining process technology and actual removal of FFA. Being a main consequence of the process, FFA reduction is demonstrated to be a good indicator for the impact of the steam-refining step on crystallization. However, the objective of this study was not to study the impact of the FFA on the properties of cocoa butter, but to verify the influence of the total process itself. One can wonder what changes are in fact directly related to FFA content, and which are due to other causes. Therefore in one experiment, the alkalized bleached cocoa butter was sent through the column at 200 °C without steam injection, in order to minimize FFA stripping. The taste of this particular sample was found to be stronger than all other samples processed around 200 °C, which indeed indicates the important role of stripping in flavor removal in cocoa butter. However, none of the parameters tested, chemical or physical, was found to be significantly different from the non-steam-refined equivalent, which indicated a negligible impact of the high temperature and passage through the packed column in terms of composition and crystallization properties. Therefore, the observed changes in physical properties, which were highly relevant in the case of cocoa butter, can be largely related to FFA removal. This means that a well-directed steam-refining process can cause cocoa butter to crystallize sooner, faster and develop more solid material at equilibrium conditions. It could, therefore, in some cases, offer an improvement of the physical quality of cocoa butter, next to the actual refining itself.

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