



The effect of extrusion on the physical and chemical properties of alkalized cocoa

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ABSTRACT

Traditional alkalization, essential for darkening color, modifying flavor and increasing cocoa powder solubility, is a discontinuous time-consuming technique that employs considerable energy. We herein propose extrusion as a promising alternative to improve and increase the sustainability of the traditional process. The aims of this work were twofold: on the one hand, to characterise the effects of extrusion on alkalised cocoa physico-chemical features; on the other hand, to determine if alkalized powders possess similar characteristics to those obtained by conventional treatment. The results showed that alkali was the main variable to increase pH and to diminish color. Compared to commercial samples, the developed cocoas had darker colors than, and similar sensory properties to, their reference commercial cocoas. These findings confirm that extrusion is suitable for producing high sensory acceptable alkalized products quickly, sustainably and continuously.

1. Introduction

Alkalization, also called “Dutching”, is a treatment initially conceived in the 19th century by van Houten to increase cocoa powder solubility. However, its effects on cocoa color and taste made its application also interesting for darkening and reducing the bitterness and astringency of powders (Quelal-Vásquez, Lerma-García, Pérez-Esteve, Talens, & Barat, 2020). Technically, alkalization consists of treating cocoa in combination with an alkali solution in a closed, heated and pressurized vessel (Olam, 2017).

As a process, alkalization has three main industrial drawbacks: it is performed in batches at the same time that, due to a process length up to 2 h, it implies considerable energy and time consumption (Valverde García, Perez Esteve, & Barat Baviera, 2020). For these reasons, looking for a fast, continuous and less energy-consuming alternative method is a key point for the cocoa industry to improve and make alkalization a more sustainable step, and it is here where extrusion appears as a promising alternative.

The advantages of extrusion are that it is a versatile and continuous technique that combines mixing, cooking, kneading, shearing, shaping and forming, and can be employed with different kinds of ingredients and under diverse operating conditions. Extrusion also enables higher productivity and lower processing costs than other methods.

Regarding to physico-chemical properties changes experimented by

extruded materials, this process has been reported to modify the texture, color, flavor and microbiological content of different materials due to several kinds of modifications, such as: hydration, gelation and shearing of starches; denaturalization or reorientation of proteins; melting of fats (Singh, Gamlath, & Wakeling, 2007). Of these modifications, changes in texture are the most relevant for the cocoa industry.

Extrusion also increases protein digestibility by inactivating anti-nutritional factors and by exposing new sites to enzymatic digestion though denaturalization (Fellows, 2000; Zhang, Liu, Ying, Sanguansri, & Augustin, 2017). Finally from a microbiological point of view, low water content and heat applied during extrusion make most extruded-cooked products bacteria-free. Moreover, some studies point out that *Bacillus stearothermophilus* spores are significantly reduce in number after applying high temperatures during extrusion (Nikmaram, Kamani, & Ghalavand, 2015).

Bearing in mind the general technological advantages of extrusion, and the fact that cocoa is a granular or powdered material, extrusion could serve as an extraordinary continuous, sustainable and fast alternative for modifying natural cocoa properties through alkalization.

In a previous work (Valverde, Behrends, Pérez-Esteve, Kuhnert, & Barat, 2020) we demonstrated that the total phenol content and antioxidant capacity of extruded samples were statistically above of those of the commercial ones, making this process suitable to avoid a reduction of the very well appreciated cocoa functional properties. However, for a

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Table 1

Water content, temperature and alkali concentration for constructing the surface response.

Point	X ₁ (%)	X ₂ (°C)	X ₃ (%)
1	20	150	6
2	31.4	105	3.5
3	25	105	6.7
4	30	75	1
5	25	105	3.5
6	25	105	3.5
7	30	75	6
8	25	105	0.3
9	20	75	1
10	30	150	1
11	25	162.9	3.5
12	20	75	6
13	18.5	105	3.5
14	25	75	3.5
15	20	150	1
16	30	150	6

technology to be considered a viable alternative to its reference one (in this case alkalization in pressurized vessels), it is not enough to demonstrate its capacity to provide a product with higher functional properties. In addition, it must be able to provide products with physicochemical and sensory properties similar to those obtained with the conventional methodology.

In this context, the objective of this work as twofold. On the one hand to evaluate the effect of different processing variables (water content, alkali type and concentration, temperature) on the physico-chemical properties of alkalinized powders. On the other hand, to study if the physico-chemical and sensory properties of the produced cocoas could be comparable to those of commercial samples prepared by the traditional alkalization method.

2. Material and methods

2.1. Materials

The cocoa employed for the extrusion experiments was a natural powder from the Ivory Coast. The commercial samples used as the control standard cocoas were all provided by Olam Food Ingredients SL (Cheste, Spain), and were: three natural, one dark natural, three light, two medium and two strongly alkalinized cocoas. Sodium hydroxide and potassium carbonate were supplied by Scharlau (Barcelona, Spain).

2.2. Cocoa extrusion

Before extrusion, each cocoa powder was properly mixed with the corresponding amounts of water and alkali in a Blixer (Robot Coupe, Mataró, Spain).

Mixtures were then placed inside a single-screw extruder 19/25 from Brabender (Duisburg, Germany) equipped with a screw barrel with the following characteristics: 1.9 cm diameter, a 25:1 length to diameter ratio, regular lights (1:1) and no mixing elements. Extruder conditions were selected to prevent the cocoa from getting stuck and/or burning inside the extruder according to the results obtained in previous works: die size (4 mm), extrusion speed (120 rpm), screw dimensions (1:1) and feeding speed (10 rpm). Using these conditions, residence time was about 5 min. The temperatures in the different extruder modules were 37 °C in module 1, 65 °C in module 2, 60 °C or 100 °C in module 3, depending on the assay temperature and the corresponding temperature in module 4.

Once extruded, samples were dried overnight at 100 °C and turned into a powder in a coffee milling machine.

2.3. Experimental design

A response surface methodology was followed to define the combination of conditions to be applied, and to evaluate the relations between the process variables (water content (X₁), temperature (X₂) and alkali concentration (X₃)) and the response parameters (pH, color and moisture). Statistical modelling and analyses were carried out by the design assistant of the experiments of Statgraphics Centurion (Manugistics Inc., Rockville, MD, USA). The selected experimental ranges of the three independent parameters were those found to be the most widely used ones in different alkalization patents (Chalin, 1974; Ellis, 1992; Kopp, Hennen, Seyller, & Brandstetter, 2009; Terink & Brandon, 1981; Wiant, Lynch, & LeFreniere, 1989; Wissgott, 1985). The design selected for the surface response modelling was an orthogonal central composite design 2³ + star with two replicates of the central point (n = 16). The experimental conditions for the analysis are shown in Table 1.

After the data analysis, the behavior of each response variable (pH, color and moisture) in relation to the evaluated independent parameters was fitted in a quadratic polynomial model as shown in Eq. (1).

$$y = a_0 + \sum_{i=1}^3 a_i X_i + \sum_{i=1}^3 a_{ii} X_{ii} + \sum_{i \neq j=1}^3 a_{ij} X_i X_j \quad (1)$$

where “y” represents the response variable (pH, color or moisture), “a₀” is the constant, “a_i”, “a_{ii}” and “a_{ij}” are the linear coefficients and their interactions, and “X_i” and “X_j” are the experimental data for each variable.

The previous surface response methodology was carried out separately for the two alkali agents herein employed: NaOH and K₂CO₃. For all the models, the R² statistical values were obtained to evaluate their suitability.

2.4. Physico-chemical and sensory analyses

2.4.1. Moisture

The moisture content of samples was calculated according to AOAC Procedure 931.04, (AOAC, 2019). For this purpose, 3 g of cocoa were weighed (M0) and dried for 4 h at 102 ± 2 °C (M1). Moisture content was determined as the percentage of mass lost after drying ((M0-M1/M0)*100).

2.4.2. pH and color determinations

The extractable pH and color of the produced and commercial samples were determined following the methods described in the deZaan Cocoa Manual (OLAM, 2017). For extractable pH determinations, a suspension of 2.5 g of cocoa powder was prepared in 12.5 mL of distilled water at 80 °C and stirred. Once powder was dispersed, another 12.5 mL quantity of water at room temperature was added and the suspension was allowed to cool to room temperature. Data collection was carried out in triplicate using a Crisonbasic 20+ pH meter (Barcelona, Spain).

pH was used to classify samples into different categories according to Miller's scale (Miller et al., 2008). Those cocoas with a pH between 5 and 6 were considered natural cocoas, those with a pH between 6 and 7.2 were taken as lightly alkalinized, between 7.2 and 7.6 were moderately alkalinized, and those over 7.6 were strongly alkalinized.

For the determination of the intrinsic color (cocoa dispersed in water), 5 g of the cocoa powder sample were suspended in 15 mL of distilled water at 60 °C and stirred for 1 min. The mixture was cooled down until room temperature and then placed in a methacrylate cuvette. A CM-3600d (Konica Minolta, Azuchi Machi, Japan) spectrophotometer working in the reflectance mode with the specular component exclude (SCE) was used to measure the color of the different cocoa powder samples. Data were converted in the CIE-Lab color space (D65 illuminant and 10° viewing angle). All the samples were read in triplicate.

Table 2
Regression coefficients of the quadratic equations for pH, color and moisture in the samples treated with K₂CO₃ and NaOH. Significance: *** = 0.01 < p-value < 0.05, ** = 0.001 < p-value < 0.01, * = 0.05 < p-value < 0.1, **** = p-value < 0.001.

Regression coefficients	L*			C*			h*			pH			Moisture loss		
	K ₂ CO ₃	NaOH	F. value	K ₂ CO ₃	NaOH	F. value	K ₂ CO ₃	NaOH	F. value	K ₂ CO ₃	NaOH	F. value	K ₂ CO ₃	NaOH	F. value
X ₀	45.22	41.69	0.52	36.81	34.11	0.08	97.02	112.31	0.45	-0.68	1.15	0.57	-0.85	-25.90	12.84
X ₁	-1.71	-1.14	0.83	-1.99	-0.24	0.08	-2.95	-1.41	0.45	0.48	0.13	0.57	0.22*	3.43**	0.22*
X ₂	-0.08	-0.09	3.78	0.05	-0.12	0.87	-0.14	-0.44	1.93	0.02	0.05	0.35	0.11**	-0.28***	20.93
X ₃	-1.52**	-4.42**	66.61	-4.47*	-5.00**	57.31	-3.63*	-12.44*	65.43	0.65*	1.31***	73.53	-3.27	3.41	0.82
X ₁ ²	0.02	0.01	0.35	0.03	-0.01	0.12	0.03	-0.02	0.1	-0.01	0.01	0.01	0.02	-0.04	0.07
X ₁ X ₂	0.01*	0.01	1.74	0.01	0.01	1.08	0.01	0.02	3.54	-0.01*	-0.01	2.03	-0.01	-0.01	0.89
X ₁ X ₃	0.03	0.06	2.84	0.03	0.11	4.29	0.07	0.33*	7.04	-0.01	-0.02	2.81	0.17	1.68	0.10
X ₂ ²	-0.01	-0.01	0.35	-0.01	-0.01	0.05	-0.01	-0.01	0.06	0.02	0.01	0.08	0.01	0.01**	0.97
X ₂ X ₃	0.01	0.43	5.12	0.01	0.01	3.04	0.01	0.02	1.5	-0.01	-0.01*	7.09	-0.01	-0.01	0
X ₃ ²	-0.04	0.17	0.54	-0.14	-0.10	0.57	-0.12	-0.30	1.02	0.01	-0.02	0.35	-0.21	0.42	0.43
R ²	0.86	0.93	0.92	0.82	0.92	0.82	0.85	0.93	0.92	0.85	0.93	0.92	0.92	0.98	0.92

Significance level (α): * (0.01 < p-value < 0.05), ** (0.001 < p-value < 0.01), *** (p-value < 0.001).

To calculate the total color difference (ΔE), the formula reported by Rodríguez, Pérez, and Guzmán (2009) was used (Eq. (2)).

$$\Delta E = \sqrt{\Delta L^*{}^2 + \Delta a^*{}^2 + \Delta b^*{}^2} \quad (2)$$

where ΔL* is the difference in luminosity between an untreated sample and a treated one, Δa* is the difference in red/green, and Δb* is the difference in yellow/blue coordinates. The ΔE for the extruded samples was calculated using the values of the untreated cocoas, while the ΔE for the commercial ones was calculated with the mean value of the natural references.

2.4.3. Sensory analyses

Sensory analyses were performed according to UNE-ISO 6658:2019 by a trained panel made up of nine people. Seven different markers were analyzed: cocoa and chocolate taste, acidity, astringency, alkalinity, body and bitterness. They were scored from 1 to 5, where 0 represented no taste and 5 denoted a very intense taste. For this selection, only those samples with pH values and color coordinates that fell within the range described by standard commercial samples were included. Of the 32 samples, a selection of cocoas comprising 2–4 samples from each category was made for this study.

In order to taste fresh samples that have not undergone any storage process, samples for this second part of the study were again prepared using the experimental conditions described in Table 1 for each of the selected products and characterized following the methodology described in sections 2.4.1 and 2.4.2.

3. Results and discussion

This work presents extrusion as a fast, sustainable and continuous technique to replace traditional alkalization. However, this is rendered useless if the proposed alternative does not produce similar products to commercial ones. To verify if the method was able to produce the necessary changes and how they were made, this work was divided into two parts: the first one focused on analysing the impact of the different extrusion conditions on the physico-chemical properties of cocoa; the second one centred on comparing the produced products with traditionally obtained ones.

3.1. Effect of extrusion variables on cocoa physico-chemical characteristics

3.1.1. Model fitting

In this work, two independent experiments were run according to the alkali used in the treatment (K₂CO₃ and NaOH) to model changes in pH, color and moisture in relation to water content, temperature and alkali concentration. Table 2 shows the coefficients for each response variable that fitted the experimental data in the corresponding quadratic equation. It also indicates their statistical significance.

An analysis of variance (ANOVA) of the models showed that the resulting equations exhibited regression coefficients (R²) above 0.8 in all the response parameters, which meant that the proposed models explained more than 80% of the variability of the different response parameters.

In addition, the significance of the coefficients and the impact of the different variables were evaluated to identify which affected the various response parameters. Among the significant coefficients, the highest F-value indicated which variable most affected a given parameter. Bearing in mind this criterion, and as seen in Table 2, alkali concentration was the main parameter that affected the pH and color of samples (p-value < 0.05), while it was temperature, followed by the water content added to cocoa, for moisture.

3.1.2. Effect of extrusion variables on pH

pH is an important characteristic in the cocoa industry because it is

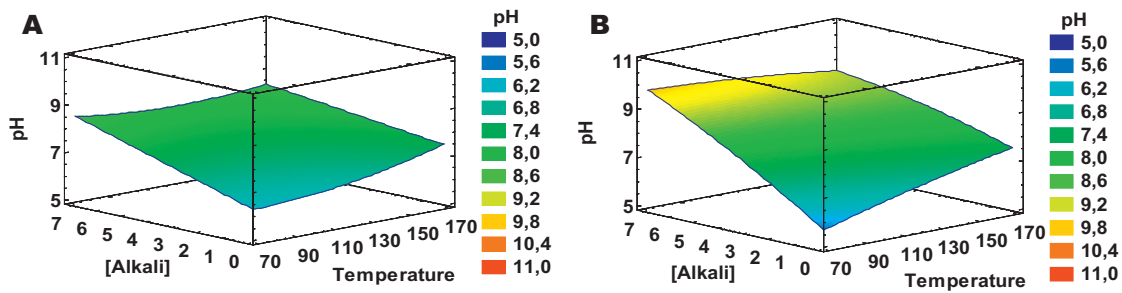


Fig. 1. Surface responses of the effect of temperature and alkali concentration on pH. (A) Surface responses of the samples treated with K₂CO₃; (B) surface responses of the samples treated with NaOH, with an initial 20% water content.

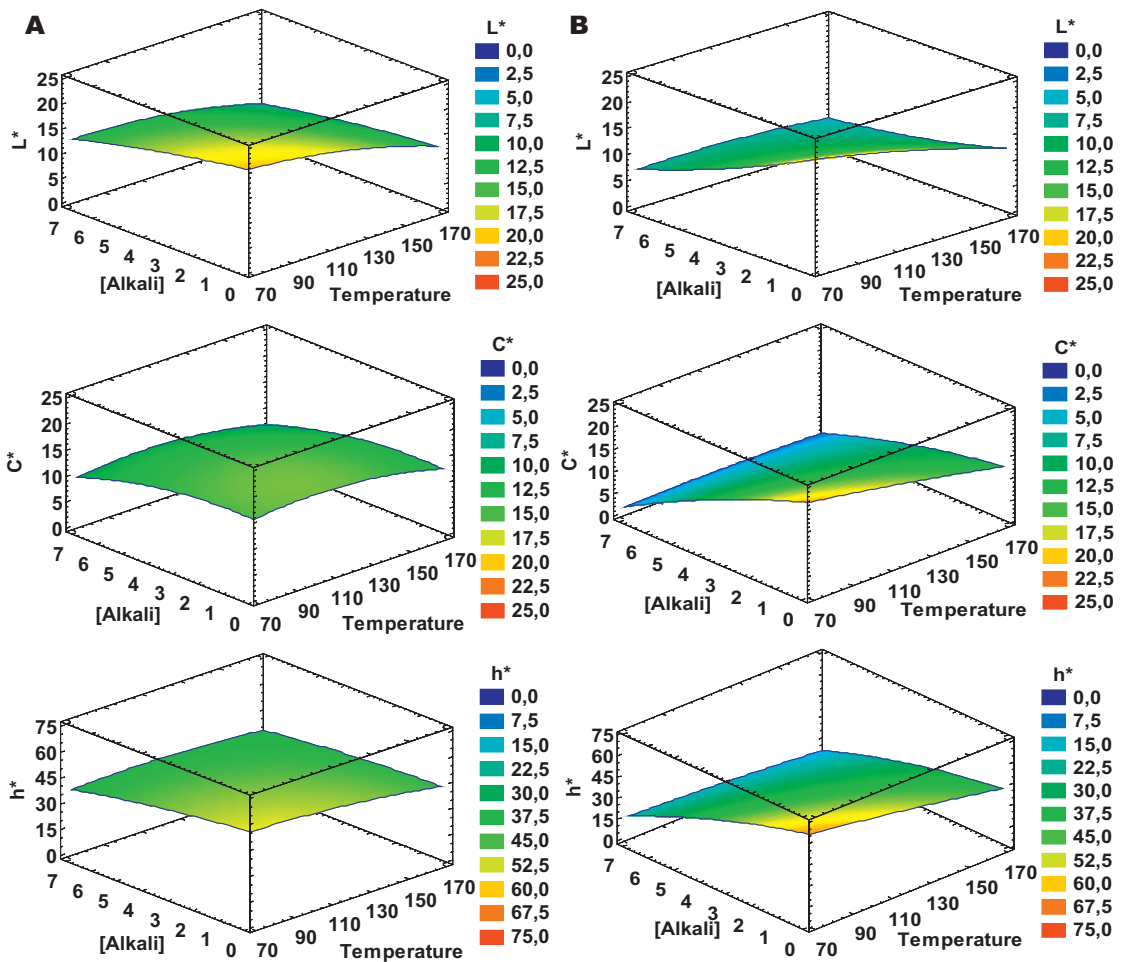


Fig. 2. Surface responses of the effect of temperature, water content and alkali concentration on color components. (A) Surface responses of the samples treated with K₂CO₃ and (B) surface responses of the samples treated with NaOH, with an initial water content of 20%.

used to classify cocoa into different categories (Miller et al., 2008). pH also conditions sample color because it increases the enzyme activity of polyphenol oxidase (Misnawi, Jamilah, & Nazamid, 2003; Rodríguez et al., 2009) and enhances several chemical reactions that darken cocoa (Germann, Stark, & Hofmann, 2019a, 2019b).

Fig. 1 shows the effects of temperature and K₂CO₃ and NaOH concentrations on pH.

As seen in Fig. 1, the pH of the produced cocoas ranged from 5 to 10, which meant that powders of different alkalinization degrees can be produced with both alkali types. Indeed the type and concentration of alkali proved to be determining factors for this characteristic. As seen,

the higher the alkali concentration, the higher the final pH of the alkalinized powder. Regarding type, as expected pH increased more with NaOH than with K₂CO₃ due to the higher alkalinity of NaOH.

In addition to alkali type and concentration, the combinations of water content and temperature for K₂CO₃, and alkali concentration and temperature for NaOH, had a negative impact on increases in pH (p-value < 0.05). For example, when the K₂CO₃ concentration was 6% and temperature was 160 °C, pH changed from 8 to 6.5 because water content rose from 20% to 30%. With NaOH, when the alkali concentration was 6% and water content was 30%, pH changed from 8.9 to 7.9 as temperature increased from 75 °C to 160 °C.

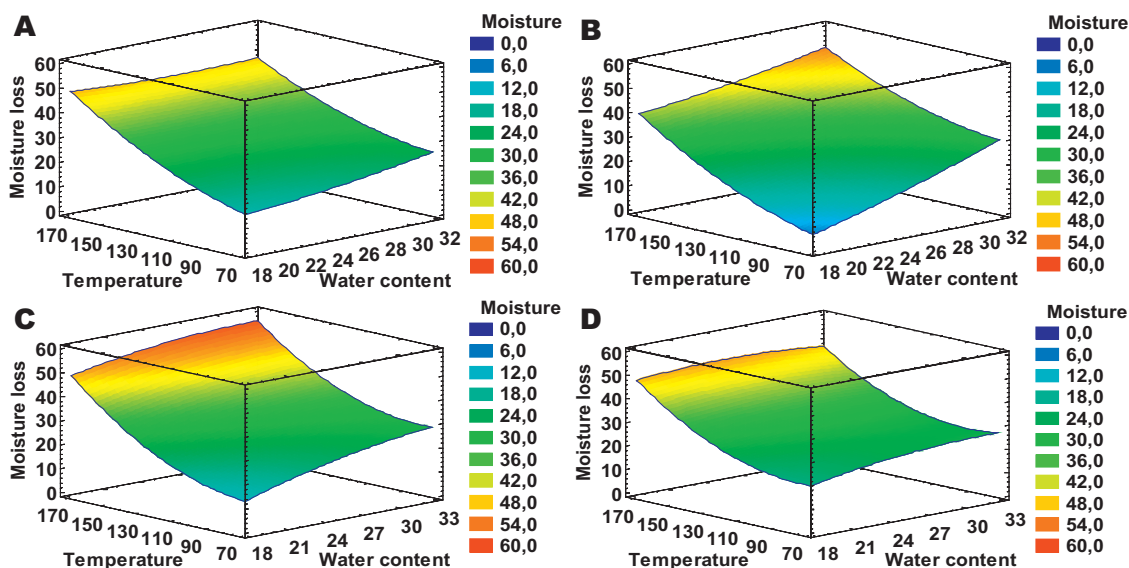


Fig. 3. Surface responses showing the effect of water content, temperature, type and concentration of alkali on moisture loss (%) during the extrusion treatment. (A) The samples treated with 0.28% K₂CO₃, (B) the samples treated with 6% K₂CO₃, (C) the samples treated with 0.28% NaOH and (D) the samples treated with 6% NaOH.

3.1.3. Effect of extrusion treatment variables on color

In this section, the effects of the extrusion variables on the color of the extruded cocoa powders were evaluated. Fig. 2 shows the effects of K₂CO₃ and NaOH concentrations and temperature on color.

In color terms, the extrusion treatment without alkali generally increased the darkening (L*), saturation (C*) and redness (h*) of the untreated cocoa. For example, in the samples treated with 20% water content, 0% alkali and at 70 °C, L*, C* and h* were 20, 20 and 52, and were 25, 25 and 54 in the untreated cocoa, both respectively. This meant that the extrusion treatment was able to darken cocoa when alkali was lacking.

When an alkali was included, samples were darker, redder and less saturated as the alkali concentration increased, which made cocoa color change from the light brown of the untreated powder to dark brown. In addition to alkali concentration, which in statistical terms was one of the variables with the strongest impact on color, alkali type was also

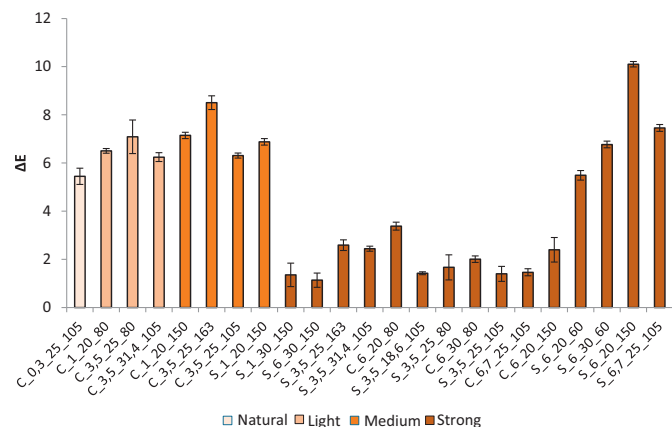


Fig. 4. Total color difference (ΔE) of the extruded selected samples compared to their reference cocoas. Samples are divided to four groups: light orange (natural), orange (light), dark orange (medium) and brown (strong). The developed samples are coded in this order: the alkali employed (K₂CO₃ (C) or NaOH (S)), the proportion of alkali (%), the proportion of water (%) and temperature (°C). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

relevant. According to the obtained results (Fig. 1), and in agreement with other authors like Rodríguez et al. (2009), NaOH was the alkali that darkened the samples the most.

In addition to alkali, L* in the samples treated with K₂CO₃ was affected by the water content and temperature combination. Raising water content at high temperatures increased L*, while raising water content led to lower L* values at low temperatures. By way of example, with the cocoas treated with 6% of K₂CO₃ at 160 °C, L* increased from 9.6 to 14.6 when water content rose from 20% to 30%, while at 75 °C and with 6% alkali, L* lowered from 14.2 to 13.4 as water content increased.

With NaOH, apart from the effect of alkali, h* was affected by the water content and alkali concentration combination. Increasing the water content in the cocoas with high NaOH concentrations reduced h* less, while the same increase at low alkali concentrations more markedly reduced this parameter. For example, in the samples treated with 6% NaOH at 80 °C, h* went from 24.9 to 31.1 when water content increased from 20% to 30%. In the cocoas treated with 1% NaOH at 80 °C, h* went from 56.5 to 46.4 as water content increased by the same order.

Furthermore when comparing Figs. 1 and 2, we observed an inverse relation between pH and color. When pH rose with treatment, color consequently reduced, and vice versa. Between the two employed alkali agents, lower pH and color values were obtained when NaOH was used compared to K₂CO₃. This highlights the importance of alkali selection during cocoa color development.

3.1.4. Effect of extrusion treatment variables on moisture loss

Moisture content in products like cocoa powders, which are nutritionally rich and need to be stored for medium and long time periods, is a negative feature that must be reduced to maintain the product's nutritional and microbiological qualities. It is generally considered that cocoa powder moisture must be lower than 5% to assure good conservation during its shelf life. To reach this content, in the traditional alkalization system performed in a pressurized vessel, the material is first treated, and then separately dried, to reduce moisture content to less than 5% (Olam, 2017).

Due to the aforementioned advantages and to evaluate changes in moisture in the extruded cocoas, the effects of temperature, water content, type and alkali concentration were studied in relation to moisture loss at the end of the extrusion process (Fig. 3).

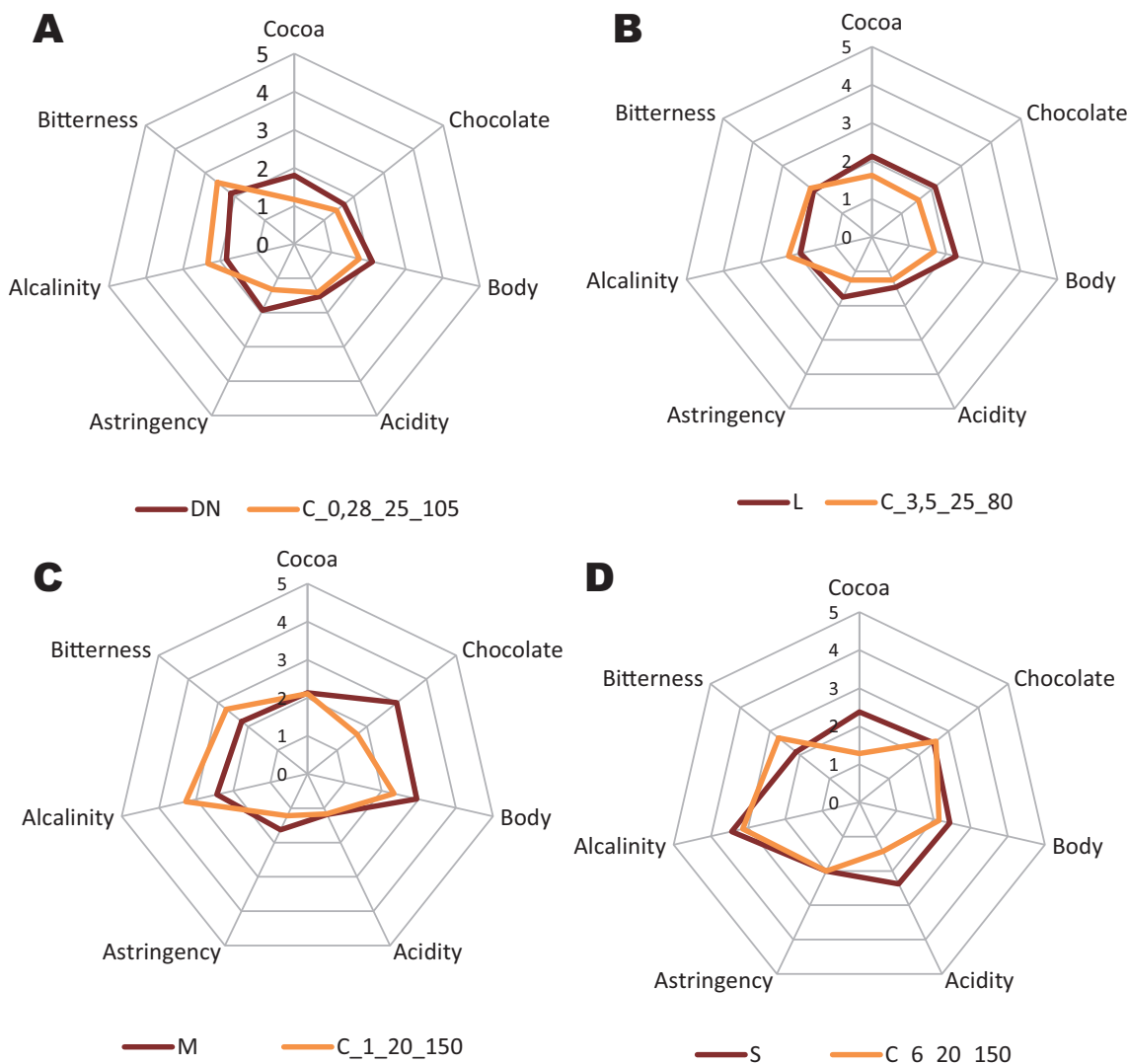


Fig. 5. Comparison made between the extruded and commercial powders for seven sensory-evaluated characteristics. Samples are grouped according to their alkalization level as: (A) natural, (B) lightly, (C) moderately, (D) strongly alkalized.

Water content and temperature, but more specially temperature, increased moisture loss up to 50%. For example, moisture loss was approximately 45% for the 160 °C, 30% water content and 6% alkali conditions. This revealed that, although further drying was still necessary, the proposed method was able to significantly lower water content, which consequently reduced the costs and duration of the drying step compared to the commercial alkalization treatment.

3.2. Comparison to commercial samples

3.2.1. Color comparison

An essential part of designing and applying a new method as an alternative to another is to evaluate its suitability to be that replacement. In this work, apart from studying the effects that the different extrusion variables had on cocoa physico-chemical features, the powders produced by extrusion were compared to traditionally prepared commercial standards.

Of the 32 extruded cocoas, 19 samples were selected because their pH, L*, C* and h* values met the commercial color specifications or had even lower color values than the commercially specified ones. Fig. 4 shows the total color differences of all the selected extruded cocoas, classified by their pH values.

ΔE gives a general idea of how similar two samples are, but does not

indicate if samples are darker or lighter. In our case, ΔE was used to obtain an overview of the similarity of the produced and commercial samples.

As observed in Fig. 4, all the selected extruded cocoas belonging to the natural, light and moderate alkalized groups had a ΔE above 2. This meant that the color of these samples could be detected by the human eye as being different from that of commercial cocoas (Lee & Coates, 1999). Some of the strong alkalized cocoas had ΔE values below 2, which meant that they were not differentiable from their commercial reference. Others had ΔE values of 10, which implies that cocoas clearly differed from their commercial references.

When the color components (L*, C* and h*) of all the selected extruded samples were analyzed, all the cocoas, except for the strong alkalized ones, had lower L* and C* values. This meant that they were darker and less saturated than commercial cocoas, with h* meeting commercial color specifications.

With the strong alkalized cocoas, most samples obtained L*, C* and h* values that met commercial specifications, although two of the samples alkalized with NaOH had lower L*, C* and h* values, which meant that they were darker in color, redder and less saturated. By way of example, L* of 6, C* of 3.4 and h* of 14.4 were obtained for cocoa S_6_20_150. The specifications of the strong alkalized cocoas were 8–13 (L*), 6–15 (C*) and 28–45 (h*).

Most cocoas had lower L*, C* or h* values which, if necessary, could be adjusted by modifying the treatment conditions for having similar colors to commercial cocoas. Indeed the built response surfaces are a useful tool for adjusting alkali concentration, water content and temperature according to, for example, a desired final color.

In addition to being able to darken cocoa, extrusion proved effective in cutting the time and energy use of traditional alkalization. Extrusion needs 92% less time than traditional alkalization and does not involve heating the tank's content before treating it, which speeds up the process and cuts the treatment's energy use. Extrusion also reduces the time and energy use of the cocoa production chain by significantly lowering the moisture content of samples. Therefore, extrusion was generally shown as a more sustainable technique than conventional treatments.

3.2.2. Sensory evaluation of the selected samples

After the physico-chemical characterization, different processing conditions were selected to prepare the cocoas that would be sensory-evaluated by a trained panel formed by nine people. Before sensory analysis, samples were characterized according to their pH and color. Since differences between values belonging to the first and the second batch were not significant, the reproducibility of the process was confirmed.

Fig. 5 shows the spider graphs used to compare the extruded and commercial cocoas.

As we can see, the commercial and extruder cocoas were similar. For dark natural cocoas (Fig. 5A), which were heat-treated without alkali, the sensory patterns only differed in terms of cocoa taste intensity and astringency.

When cocoas were alkalinized (Fig. 5B, C and D), their behavior was also similar. At the lightly alkalinized levels, the commercial and extruded samples did not differ for any evaluated marker. At the medium alkalinized level, chocolate taste was less intense. At the strongly alkalinized level, cocoa taste and acidity were lower in the extruded samples than in the commercial ones. Despite these differences, the obtained cocoas had similar sensory characteristics to the alkalinized powders.

The similar sensory patterns stress the suitability of extrusion to replace the traditional alkalization method. In a 92% shorter time and continuously, extrusion obtained cocoas with similar color and sensory characteristics, and reduced samples' associated energy and moisture content.

4. Conclusions

The effects of alkalization on cocoa physico-chemical properties are dominated by the alkali agent and its concentration, which makes the substitution of the traditionally employed technique possible. As we show here, extrusion has the capacity to speed up, reduce energy use and turn traditional alkalization into a continuous system, while making similar color and sensory changes to those of traditionally alkalinized products. Thus, this method has the capacity of replacing the traditional production techniques with more sustainable alternative.

Declaration of interest

None.

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Author declaration

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

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