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Cocoa applications in the food industry: Development of new uses and processing methods

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Valencia, November 2022

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CERTIFY:

That the work “Cocoa applications in the food industry: Development of new uses and processing methods” has been developed by Marta Puchol Miquel under their supervision in the Departamento de Tecnología de Alimentos of the Universitat Politècnica de València and in Olam Cocoa, as a Thesis Project in order to obtain the degree of Industrial PhD in Food Science, Technology and Management at the Universitat Politècnica de València.

Valencia, 8th of November 2022.

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Acknowledgements

Agradecimientos

Después de estos 5 años de tesis doctoral tengo que agradecer a muchas personas que esto sea finalmente una realidad. Esta tesis es gracias a todos ellos ya que sin sus ánimos y ayuda esto no hubiera sido posible.

En primer lugar, quiero dar las gracias a Édgar Pérez Esteve y a José Manuel Barat, personas que han sido esenciales para que este proyecto tomara forma y fuera una realidad. Gracias a ellos no solo esta tesis ha sido posible, sino que estoy trabajando desde hace 6 años en OFI y he podido compaginar el trabajo con la realización de este proyecto. Muchas gracias por la ayuda y el esfuerzo dedicado.

En segundo lugar, quiero dar las gracias a César Palomares Cano, quien desde el minuto uno que entré a trabajar en OFI ha confiado en mí, me ha apoyado y me ha dado alas para que esto fuera posible. Muchas gracias por el apoyo continuo, eres un jefe ejemplar.

Como no a mi familia, mis hermanas, mis padres y pareja, que han sido, son y serán los pilares fundamentales en mi vida. Me apoyan, me dan fuerza y viven cada uno de mis logros y metas como suyos. Es impresionante teneros cerca.

Por último, a mis amigos, los de toda la vida, los que he ido conociendo y los que se han quedado en el camino, todos han aportado un granito de arena en este pequeño logro.

También al Ministerio de Economía, Industria y Competitividad y el Fondo Europeo de Desarrollo Regional (Proyecto RTC- 2016-5241-2) por hacer posible diferentes proyectos que forman parte de esta tesis.

Os estaré eternamente agradecida a cada uno de vosotros por formar parte de mi vida, me siento muy afortunada.

Abstract

"Applications of cocoa in the food industry: development of new uses and processing methods" is an industrial doctoral thesis that aims to respond to many of the challenges that the cocoa processing industry faces as a result of growing social demands and recent legislative changes. These challenges include the sustainability of the entire value chain, the scarcity of raw materials, and the increases in demand, adaptation to new market trends (clean labels) and growing product consumer demands. To respond to these challenges, the thesis is divided into four chapters, each of which is aligned to a different challenge.

Chapter I studies the main problems that cocoa plantations face today. These problems can be grouped into two blocks: environmental problems (poor tree productivity, deforestation, pollution, etc.) and social problems (bad conditions for farmers, child labour, etc.). These problems have led to the creation of associations and support platforms from three different perspectives: international movements, local governments and multinationals from the world of cocoa. By way of conclusion in this chapter, it can be stated that consumers are increasingly aware of sustainability problems in the world of cocoa but are not as informed about the certification programs that are being carried out. Lack of information available to consumers and the fact that they more and more routinely place purchases mean that there is still a long way to go before sustainable labelling is really appreciated by consumers. For all these reasons, the cocoa industry faces an enormous challenge in forthcoming years to find a way for consumers to value and learn about all these sustainability programs. These actions will help the cocoa industry to position itself on the market, move toward a more sustainable future and differentiate itself from its competition. These movements of recent years have to be the beginning of a new era, with continuous progress toward improving social, economic and environmental sustainability to ensure that this food is valued by all so that chocolate does not compromise the well-being of either our planet or the people who grow it.

Abstract

Chapter II looks at the effect of the type of alkalinisation (in cocoa chips or cake), the type of alkaline agent used (K_2CO_3, KOH and $NaHCO_3$) and the intensity of alkalinisation (medium or strong) on the physico-chemical and sensory quality of a product made from cocoa powder produced with these variables: chocolate-flavoured sponge cake. It is generally considered that between both alkalinisation types there is a difference in costs that makes alkalisation in cake more profitable. However in flavour terms, alkalisation in nib has always been considered better. In recent years, shortage of potassium salts has been observed, which have been the most widely used for alkalinisation in the recent past. Therefore, at a time when cake alkalinisation can help to alleviate fluctuations in the price of alkalised cocoa, and substituting potassium carbonate salts for other cheaper salts could make processes cheaper and simpler, this chapter aims to clarify whether these differences are actually evident in the final application into which cocoa is incorporated. To do so, several batches of alkalised cocoa were made under different conditions, and chocolate-flavoured biscuits were made with them. The obtained conclusions show differences between studied the processes and parameters. The use of KOH as alkalinising salt resulted in a darker and reddish cocoa powder, while $NaHCO_3$ gave a lighter cocoa powder. These effects were also observed in both dough and the final cake. No significant differences were found in colour and texture when comparing the use of cocoa alkalised with K_2CO_3 in nibs or cake. However, the rheology tests revealed that the dough made with cocoa powder alkalised in nib was more elastic. Despite all this, consumers did not appreciate many differences between alkalinisation in chips and cake, nor between the different studied alkalising agents, although the darkest was perceived as being tastier. These conclusions can help the industry to gain a wider margin with possibilities of raw materials employed for the alkalinisation process because today some materials are not readily available, such as potassium salts.

The objective of Chapter III is to study a new path to help baked goods companies to adapt to the new "Clean label" trend in chocolate-flavoured biscuit production. This chapter is divided into two phases. In them, the replacement of alkaline cocoa with natural cocoa (the first phase) and medium alkaline cocoa (the second phase) is studied while increasing sodium bicarbonate levels (commonly used to make biscuits). The intention is to study two current market trends: cleaner labels (clean label) and avoid labelling alkali content above 7% (a growing trend in some countries). The results show that it is possible to obtain biscuits with similar colours and flavours to those made with medium alkaline cocoa using natural cocoa and from 1.5- to 1.8-fold the amount of standard sodium bicarbonate, employed as a leavening agent. It is also possible to obtain strong alkaline cocoa using medium alkaline cocoa and 1.8-fold the amount of standard baking soda.

In the last chapter, Chapter IV, the use of cocoa butter and cocoa cake as a substitute for cocoa liquor is studied to find alternative methods to traditional chocolate processing in preparation for increased chocolate demands and to avoid the high tariff costs of liquor in some countries. The two parts of this work consist of formulating chocolates from reconstituted cocoa liquor and high cocoa content (95%) and comparing their physico-chemical and sensory properties to those of traditionally made chocolate containing the usual percentages of cocoa (70%). The results reveal that, for the same percentage of cocoa, the chocolates formulated from reconstituted liquor are the same colour and have similar sensory acceptance despite having less viscosity and a slightly lower content of total polyphenols and antioxidant capacity than those formulated with cocoa liquor. Despite these differences, a principal component analysis and a sensory analysis reveal that the physico-chemical differences associated with formulation are less important than those caused by raising the percentage of cocoa. Consequently, the proposed method represents an interesting alternative to prepare cheaper chocolate in certain countries or at given times of the year when the price of cocoa liquor (a common ingredient in the traditional formulation) goes ups.

Resumen

“Aplicaciones del cacao en la industria alimentaria: desarrollo de nuevos usos y métodos de procesado” es una tesis doctoral industrial que tiene por objetivo dar respuesta a gran parte de los retos a los que se enfrenta la industria de transformación del cacao fruto de las crecientes demandas sociales y últimos cambios legislativos. Entre estos retos se incluyen la sostenibilidad de toda la cadena de valor, la escasez de materias primas y el aumento de la demanda, la adaptación a las nuevas tendencias del mercado (clean label) y las crecientes demandas de producto por parte de los consumidores. Para dar respuesta a estos retos, la tesis se ha dividido en cuatro capítulos, estando alineados cada uno de ellos con un reto diferente.

En el capítulo I, se estudian los problemas principales a los que se enfrentan hoy en día las plantaciones de cacao. Estos problemas se pueden agrupar en dos bloques: problemas medioambientes (baja productividad de los árboles, deforestación, contaminación…) y sociales (malas condiciones de los agricultores, trabajo infantil…). Estos problemas han hecho que se creen asociaciones y plataformas de ayuda desde tres visiones distintas: movimientos internacionales, gobiernos locales y las multinacionales del mundo del cacao. Como conclusión a este capítulo se extrae que el consumidor es cada vez más consciente de los problemas de sostenibilidad en el mundo del cacao, pero no está tan informado sobre los programas de certificación que se están llevando a cabo. La falta de información disponible para el consumidor y el hecho de hacer la compra cada vez mas de forma rutinaria, hace que quede mucho camino por recorrer para que el etiquetado sostenible sea realmente apreciado por los consumidores. Por todo ello, la industria del cacao tiene un gran reto en los próximos años buscando la manera de que los consumidores valoren y conozcan todos estos programas de sostenibilidad. Estas acciones ayudarán a la industria del cacao a posicionarse en el mercado, progresar hacia un futuro más sostenible y diferenciarse de la competencia. Estos movimientos que se han desarrollado en los últimos años tienen que ser el comienzo de una nueva era y un progreso continuo hacia la mejora de la sostenibilidad tanto social, como económica y ambiental, para poder asegurar que este alimento tan valorado por todos como es el chocolate no comprometa el bienestar del planeta ni de las personas que lo cultivan.

En cuanto al capítulo II, se ha estudiado el efecto del tipo de alcalinización (en virutas de cacao o en torta), el tipo de agente alcalino utilizado (K_2CO_3, KOH and $NaHCO_3$) y la intensidad de la alcalinización (media o fuerte) en la calidad físico-química y sensorial de un producto elaborado a partir de cacao en polvo producido con estas variables: bizcocho con sabor a chocolate. Generalmente se considera que entre ambos tipos de alcalinización hay una diferencia de costes que hacen más rentable la alcalinización en torta, aunque a nivel de sabor siempre se ha considerado mejor la alcalinización en nib. Además, en los últimos años se está observando una escasez de sales de potasio, las cuales han sido las más utilizadas para la alcalinización en los últimos años. Por tanto, en un momento en el que la alcalinización en torta podría ayudar a paliar las fluctuaciones en el precio del cacao alcalinizado y donde la sustitución de sales de carbonato de potasio por otras sales más económicas podría abaratar y simplificar los procesos, el objetivo de este capítulo es esclarecer si en realidad estas diferencias son tan evidentes en la aplicación final donde se incorpora el cacao... Para ello, se realizaron varios lotes de cacao alcalinizado en diferentes condiciones, y con ellos se prepararon con consiguientes bizcochos con sabor a chocolate. Las conclusiones obtenidas evidencian diferencias entre los procesos y parámetros estudiados. El uso de KOH como sal alcalinizante dio como resultado un cacao en polvo más oscuro y rojizo mientras que con el $NaHCO_3$ se obtuvo un cacao en polvo más claro. Estos efectos también se observaron tanto en la masa como en el bizcocho final. No se encontraron diferencias significativas en color y textura cuando se comparó la utilización de cacao alcalinizado con K_2CO_3 en virutas o en torta. Sin embargo, a través de ensayos de reología se observó que la masa elaborada con cacao en polvo alcalinizado en nib era más elástica. Pese a todo esto, los consumidores no apreciaron muchas diferencias entre la alcalinización en virutas y en torta, ni entre los distintos agentes alcalinizantes estudiados, aunque los más oscuros fueron percibidos como más sabrosos. Estas conclusiones ayudan a la industria a tener un margen más grande de posibilidades de materias primas para el proceso de alcalinización, ya que en la actualidad se está observando escasez de algunos materiales, como por ejemplo las sales de potasio.

Por otro lado, el objetivo del capítulo III es estudiar una nueva vía de desarrollo para las empresas de productos horneados que les ayude a adaptarse a la nueva tendencia del “Clean label” en la elaboración de bizcochos con sabor a chocolate. Este capítulo está dividido en dos fases. En estas, se estudia el reemplazo de cacao alcalino por cacao natural (primera fase) y cacao alcalino medio (segunda fase) a la vez que se incrementan los niveles de bicarbonato de sodio (utilizado comúnmente en la elaboración de bizcochos). Con esto se pretende estudiar dos tendencias actuales en el mercado: etiquetas más limpias (clean label) y evitar el etiquetado del contenido de álcali mayor del 7% (tendencia en auge en algunos países). Los resultados mostraron que es posible obtener bizcochos con colores y sabores similares a los realizados con cacao alcalino medio utilizando cacao natural y 1.5-1.8 veces la cantidad de bicarbonato de sodio estándar, utilizado como agente leudante. Por otro lado, es posible obtener un cacao alcalino fuerte utilizando cacao alcalino medio y 1.8 veces la cantidad de bicarbonato de sodio estándar.

En el último capítulo, capítulo IV, se estudió el uso de manteca de cacao y torta de cacao como sustituto del licor de cacao con el objetivo de buscar métodos alternativos al procesado tradicional del chocolate, para poder estar preparados ante un aumento de la demanda de producto o evitar los altos costes arancelarios del licor en algunos países. Las dos partes de este trabajo consistieron en formular chocolates a partir de licor de cacao reconstituido y alto contenido de cacao (95%) y comparar sus propiedades físico-químicas y sensoriales con las del chocolate elaborado tradicionalmente que contiene los porcentajes habituales de cacao (70%). Los resultados mostraron que, para el mismo porcentaje de cacao, los chocolates formulados a partir de licor reconstituido eran del mismo color y tenían una aceptación sensorial similar a pesar de poseer menos viscosidad y un contenido de polifenoles totales y capacidad antioxidante ligeramente menor que los formulados con licor de cacao. A pesar de estas diferencias, un análisis de componentes principales y un análisis sensorial revelaron que las diferencias físico-químicas asociadas con la formulación son menos importantes que las causadas por el aumento del porcentaje de cacao. En consecuencia, el método propuesto representa una alternativa interesante para preparar chocolate más barato en determinados países o en determinadas épocas del año en las que se incrementa el precio del licor de cacao (ingrediente habitual en la formulación tradicional).

Resum

“Aplicacions del cacau en la indústria alimentària: desenvolupament de nous usos i mètodes de processament” és una tesi doctoral industrial que té per objectiu donar resposta a gran part dels reptes als quals s'enfronta la indústria de transformació del cacau fruit de les creixents demandes socials i últims canvis legislatius. Entre aquests reptes s'inclouen la sostenibilitat de tota la cadena de valor, l'escassetat de matèries primeres i l'augment de la demanda, l'adaptació a les noves tendències del mercat (clean label) i les creixents demandes de producte per part dels consumidors. Per a donar resposta a aquests reptes, la tesi s'ha dividit en quatre capítols, estant alineats cadascun d'ells amb un repte diferent.

En el capítol I, s'estudien els problemes principals als quals s'enfronten hui dia les plantacions de cacau. Aquests problemes es poden agrupar en dos blocs: problemes medioambientes (baixa productivitat dels arbres, desforestació, contaminació…) i socials (males condicions dels agricultors, treball infantil…). Aquests problemes han fet que es creuen associacions i plataformes d'ajuda des de tres visions diferents: moviments internacionals, governs locals i les multinacionals del món del cacau. Com a conclusió a aquest capítol s'extrau que el consumidor és cada vegada més conscient dels problemes de sostenibilitat en el món del cacau, però no està tan informat sobre els programes de certificació que s'estan duent a terme. La falta d'informació disponible per al consumidor i el fet de fer la compra cada vegada mes de manera rutinària, fa que quede molt camí per recórrer perquè l'etiquetatge sostenible siga realment apreciat pels consumidors. Per tot això, la indústria del cacau té un gran repte en els pròxims anys buscant la manera que els consumidors valoren i coneguen tots aquests programes de sostenibilitat. Aquestes accions ajudaran la indústria del cacau a posicionar-se en el mercat, progressar cap a un futur més sostenible i diferenciar-se de la competència. Aquests moviments que s'han desenvolupat en els últims anys han de ser el començament d'una nova era i un progrés continu cap a la millora de la sostenibilitat tant social, com a econòmica i ambiental, per a poder

assegurar que aquest aliment tan valorat per tots com és el xocolate no comprometa el benestar del planeta ni de les persones que el cultiven.

Quant al capítol II, s'ha estudiat l'efecte de la mena d'alcalinización (en encenalls de cacau o en coca), el tipus d'agent alcalí utilitzat (K_2CO_3, KOH and $NaHCO_3$) i la intensitat de l'alcalinización (mitjana o forta) en la qualitat físic-química i sensorial d'un producte elaborat a partir de cacau en pols produïda amb aquestes variables: bescuit amb sabor de xocolate. Generalment es considera que entre tots dos tipus d'alcalinización hi ha una diferència de costos que fan més rendible l'alcalinización en coca, encara que a nivell de sabor sempre s'ha considerat millor l'alcalinización en nib. A més, en els últims anys s'està observant una escassetat de sals de potassi, les quals han sigut les més utilitzades per a l'alcalinización en els últims anys. Per tant, en un moment en el qual l'alcalinización en coca podria ajudar a pal·liar les fluctuacions en el preu del cacau alcalinitzat i on la substitució de sals de carbonat de potassi per altres sals més econòmiques podria abaratir i simplificar els processos, l'objectiu d'aquest capítol és esclarir si en realitat aquestes diferències són tan evidents en l'aplicació final on s'incorpora el cacau.,. Per a això, es van realitzar diversos lots de cacau alcalinitzat en diferents condicions, i amb ells es van preparar amb consegüents bescuits amb sabor de xocolate. Les conclusions obtingudes evidencien diferències entre els processos i paràmetres estudiats. L'ús de KOH com a sal alcalinizante va donar com a resultat un cacau en pols més fosca i vermellós mentre que amb el $NaHCO_3$ es va obtindre un cacau en pols més clara. Aquests efectes també es van observar tant en la massa com en el bescuit final. No es van trobar diferències significatives en color i textura quan es va comparar la utilització de cacau alcalinitzat amb K_2CO_3 en encenalls o en coca. No obstant això, a través d'assajos de reologia es va observar que la massa elaborada amb cacau en pols alcalinitzada en nib era més elàstica. Malgrat tot això, els consumidors no van apreciar moltes diferències entre l'alcalinización en encenalls i en coca, ni entre els diferents agents alcalinizantes estudiats, encara que els més foscos van ser percebuts com més saborosos. Aquestes conclusions ajuden la indústria a tindre un marge més gran de possibilitats de matèries primeres per al procés d'alcalinización, ja que en l'actualitat s'està observant escassetat d'alguns materials, com per exemple les sals de potassi.

D'altra banda, l'objectiu del capítol III és estudiar una nova via de desenvolupament per a les empreses de productes enfornats que els ajude a adaptar-se a la nova tendència del “Clean label” en l'elaboració de bescuits amb sabor de xocolate. Aquest capítol està dividit en dues fases. En aquestes, s'estudia el reemplaçament de cacau alcalí per cacau natural (primera fase) i cacau alcalí mitjà (segona fase) alhora que s'incrementen els nivells de bicarbonat de sodi (utilitzat comunament en l'elaboració de bescuits). Amb això es pretén estudiar dues tendències actuals en el mercat: etiquetes més netes (clean label) i evitar l'etiquetatge del contingut d'álcali major del 7% (tendència en auge en alguns països). Els resultats van mostrar que és possible obtindre bescuits amb colors i sabors similars als realitzats amb cacau alcalí mitjà utilitzant cacau natural i 1.5-1.8 vegades la quantitat de bicarbonat de sodi estàndard, utilitzat com a agent leudante. D'altra banda, és possible obtindre un cacau alcalí fort utilitzant cacau alcalí mitjà i 1.8 vegades la quantitat de bicarbonat de sodi estàndard.En l'últim capítol, capítol IV, es va estudiar l'ús de mantega de cacau i coca de cacau com a substitut del licor de cacau amb l'objectiu de buscar mètodes alternatius al processament tradicional del xocolate, per a poder estar preparats davant un augment de la demanda de producte o evitar els alts costos aranzelaris del licor en alguns països. Les dues parts d'aquest treball van consistir a formular xocolates a partir de licor de cacau reconstituït i alt contingut de cacau (95%) i comparar les seues propietats físic-químiques i sensorials amb les del xocolate elaborat tradicionalment que conté els percentatges habituals de cacau (70%). Els resultats van mostrar que, per al mateix percentatge de cacau, els xocolates formulats a partir de licor reconstituït eren del mateix color i tenien una acceptació sensorial similar malgrat posseir menys viscositat i un contingut de polifenoles totals i capacitat antioxidant lleugerament menor que els formulats amb licor de cacau. Malgrat aquestes diferències, una anàlisi de components principals i una anàlisi sensorial van revelar que les diferències físic-químiques associades amb la formulació són menys importants que les causades per l'augment del percentatge de cacau. En conseqüència, el mètode proposat representa una

alternativa interessant per a preparar xocolate més barat en determinats països o en determinades èpoques de l'any en les quals s'incrementa el preu del licor de cacau (ingredient habitual en la formulació tradicional).

Contents

1. Objectives

The main objectives of the present thesis appear in four blocks to: i) study the current sustainability status in the cocoa world and the influence on consumer perceptions; ii) adjust cocoa processing parameters to be prepared to face price fluctuations in cocoa ingredients and the shortage of potassium-alkalising salts; iii) develop clean label alternatives for cake recipes traditionally prepared with alkalised cocoas; iv) design new transformation processes to help the cocoa and chocolate industries to fight the consequences of new markets opening and the scarcity of raw materials.

In order to fulfil the main objectives, four different research lines are defined:

A. Understand the importance of sustainability in consumers' purchase intention of cocoa-derived products. The specific objectives are to:
   a. Determine the environmental and social problems in cocoa production and transformation.
   b. Study the General and Specific Sustainable Certifications for Cocoa Products.
   c. Analyse the influence of Cocoa and Chocolate Sustainability Labels on consumer perceptions and their willingness to pay more.
B. Adjust the cocoa processing parameters to be prepared when faced with the shortage of raw materials and price fluctuations. The specific objectives are to:
   a. Study the suitability of using alkalised cake-alkalised cocoa powders to prepare high-quality bakery product.
   b. Evaluate the impact of the type of alkalisation process and type of alkali on the physico-chemical and sensory properties of chocolate cakes.
C. Design new bakery products/processes to fulfil the new "clean label trend" when making dark cocoa cakes. The specific objectives are to:
   a. Study the effects of replacing of high-alkalised cocoa powders with natural or medium-alkalised cocoa powders (clean label products)

by increasing the levels of sodium bicarbonate used in cake formulation.

   b. Evaluate the proposed *in situ* alkalisation as an alternative to avoid the labelling of alkali agents in bakery products.

D. Design new transformation processes to ensure the chocolate demand on new markets. The specific objectives are to:

   a. Study chocolate formulation from reconstituted cocoa liquor and high cocoa content; to compare its physico-chemical and sensory properties to those traditionally prepared.
   b. Examine the influence of cocoa content in chocolate recipes (from 70% to 95% cocoa content).

2. General introduction

1. Cocoa as a commodity

Cocoa (*Theobroma cacao* L.) is a commodity of high economic value, and cocoa and chocolate products are among the most consumed luxury foods worldwide. In fact the world's estimated average chocolate consumption amounts to 0.9 kg/year per capita per year (CBI, 2021). The popularity of chocolate is essentially due to its pleasant sensory properties (Magagna et al., 2017) and the positive emotions that its consumption engenders (Magagna et al. 2017; Konar et al. 2016). Due to these characteristics, the market shows growing demand (ICCO, 2007; Technoserve, 2015) along with erratic prices due to instable markets in the countries where cocoa is planted (ICCO, 2007; The World Bank, 2017). Cocoa has increased 95 USD/MT, or 3.77%, since the beginning of 2022 according to trading on a contract for difference (CFD) that tracks the benchmark market for this commodity.

Cocoa primary production centers in African countries (Ivory Coast, Ghana, Nigeria and Cameroon) (77.4%), with some from America (17.5%) and the rest from Asia and Oceania (5.1%). (ICCO, 2020). However, cocoa products are usually processed in the European Union (35.6%), and some in Asia and Oceania (23.6), Africa (21.3%) and America (19.5%) (ICCO, 2020). So this supply chain is very pyramidal with millions of farmers producing cocoa beans at its bottom and very few traders distributing them at the top (Technoserve, 2015).

2. Cocoa production process

Cocoa products are obtained from cocoa pods, which are collected from *Theobroma cacao* trees. It takes approximately 3 years after planting before trees are fruitful enough to harvest pods (Olam Cocoa, 2016). After harvesting, cocoa pods are subjected to different postharvest and industrial processes to obtain distinct cocoa products: cocoa nibs, cocoa liquor, cocoa butter, cocoa powder (Di Mattia et al., 2014: Aprotosoaie, Luca, & Miron, 2016).

Cocoa pods are firstly cut down from trees and opened to collect cocoa beans. Then cocoa beans are fermented and dried (normally by sun drying) for several days (Suazo, Davidov-Pardo, & Arozarena, 2014). The fermentation process is characterized by a succession of microbial activities of three groups of microorganisms (yeasts, lactic acid bacteria, and acetic acid bacteria), which results in well-fermented fully brown cocoa beans (De Vuyst L., & Weckx, S., 2016). The main objective is to develop proper colour and flavour. During drying, moisture content lowers and flavour also develops. Inadequate drying can result in a musty or acetic taste (Adriaenssens, 2010).

Then beans are ready to be shipped worldwide for further processing and to be transformed into different cocoa products. When cocoa beans arrive at processing plants, bean shelling provides nibs and the first by-product: shells (Tan & Kerr, 2018). The process continues by roasting nibs. During roasting, moisture content lowers and cocoa flavour develops, with a reduced microbial load. Then nibs are ground to obtain cocoa liquor. In the next step, cocoa liquor is pressed (using high pressure and temperature) and two products are obtained: cocoa butter (used mostly in cosmetics and chocolate products) and cocoa cake (raw material to obtain cocoa powder). Depending on the applied pressure, cocoa cake can have different fat % (10-12%, 20-22% or 22-24%) (Oliviero, Capuano, Ca, & Fogliano, 2009). Finally, cocoa cake is subjected to a milling step to provide cocoa powder.

Optionally, another important step to develop colour and flavour, which is called alkalisation or dutching process, can be performed in different cocoa products: cocoa nibs, cocoa liquor, cocoa cake or cocoa powder (Pérez-Esteve, Lerma-García, Fuentes, Palomares, & Barat, 2016). Cake and nib alkalisation is the most widely used in industry. Cake alkalisation is the best economical option because cocoa butter neither enters the production process nor undergoes any alteration process. However, the colouring capacity and intense aroma of these cakes are considered to be lower (Dyer, 2003). Besides, more aromatic products are obtained during nib alkalisation, whose colours are more reddish and intenser, and less alkali is used in many cases (Olam Cocoa, 2016). Alkalisation is normally carried out by adding sodium or potassium carbonate at high temperature and controlled pressure. However, other alkaline agents can be used, such as alkali agents in cocoa processing sodium carbonate, sodium bicarbonate, sodium hydroxide, ammonium carbonate, etc. (Codex Alimentarius, 2019).

According to the final pH, cocoa powders can be classified as natural (pH 5-6), light-alkalised (pH 6-7.2), medium-alkalised (pH 7.2-7.6) and strong-alkalised powders (pH > 7.6) (Miller et al., 2008). Light-alkalised cocoa powders are light brown, but darker than natural ones, and their flavour is less astringent and less acidic than those of natural powders. Strong-alkalised cocoa powders are very dark and have a much stronger flavour than medium-alkalised ones (Kostic, 1997). These different types of cocoa powder are introduced into the formulations of several food products depending on the final characteristics that industry needs (bakery products, frozen desserts, confectionery coatings, dairy products, instant premixes).

Fig. 1 Summary of the transformation process of cocoa pods into cocoa butter and cocoa powder.

3. Cocoa food industry concerns about new changes in cocoa production, transformation, consumer demands and international legislation

After explaining the production process of the cocoa bean by-products (liquor, butter, cocoa powder), it is important to highlight what problems the cocoa industry faces to understand its challenges for forthcoming years. There are four fundamental points to deal with: concerns about the social and environmental sustainability of cocoa production and transformation; control of production/cost increases and price fluctuations; new markets; new regulations in the sector.

3.1 Concerns about the social and environmental impacts of cocoa production and processing

Despite being one of the most valued ingredients in the food industry, in recent years the cocoa sector lies in a centre stage. On the one hand, in environmental terms current cacao cultivation expansion and increased cocoa consumption are associated with deforestation, forest degradation, biodiversity loss and high greenhouse gas (GHG) emissions. Global concerns about emissions associated with tropical commodity production are increasing. Consequently, there is a need to change the present cacao-growing practice to make it a more climate-friendly cultivation system. On average, the production of 1 kg of cacao beans is associated with emissions of 1.47 kg CO_2 equivalent (Vervuurt et al., 2022).

On the other hand, in social terms cocoa production is predominantly carried out by smallholders because more than 90% of the world's cocoa farmers have plots of land covering between 2-5 hectares. Cocoa farmers remain the weakest point in the value chain. As a result, farmers still have poor living, or near-poverty, conditions with no access to basic social services, and without the tools or incentives to implement environmentally-friendly production practices (ICCO, 2021).

These facts have been critical for consumers who are aware of the negative impacts of cocoa production and are demanding more sustainability products and initiatives. Therefore, different organisations and cocoa producers have established sustainability programs to ensure that produced cocoa products are more sustainable from the social and environmental points of view.

To create a more sustainable cocoa sector, cocoa industries should focus their future on creating and improving control throughout the cocoa process, from plantation to selling the product to final consumers. It is necessary to coordinate efforts at different key points: origin (helping farmers and improving the quality of cocoa plantations); during transport (reducing emissions to the atmosphere and making strategies to cut distances); during cocoa processing (reducing emissions, energy use and contamination during processing). This will be a trend and an important key for following years because sustainability (environmental sustainability, social sustainability, economical sustainability) will play a key role to improve and distinguish companies from their competitors.

3.2 Cocoa scarcity and price fluctuations

The three described cocoa products (cocoa liquor, cocoa butter, cocoa powder) are used in different food industries for several end products (mostly cosmetic and food products). The cocoa market is continuously finding solutions to manage cocoa product stocks at the same rate (cocoa liquor, cocoa butter, cocoa powder). The cocoa liquor price is linked directly with the price of beans, while cocoa powder and cocoa butter are traded independently, and depend on demand. Normally when cocoa butter demand increases, so does its price, and the cocoa powder value goes down. So, the price of cocoa butter/cake can fluctuate even if the price of beans does not (Gilbert, 2016).

Another reason for price fluctuation is the fact that Africa is the largest global cocoa producer and supplies more than 70% of the world’s cocoa. Supply fluctuations result from a number of factors, which range from political and civil unrest to labour issues, and the effect of weather, diseases and pests on crop yields. For example, long periods of dry weather do not lead to cocoa bean growth, but result in supply shortages (Investopedia, 2021).

Another important point that should be analysed lies in changes in cocoa butter quality during nib alkalisation. As previously explained, cocoa butter is affected during this alkalisation process. So with time, with scarcity it is necessary to find differences between this alkalisation type and the cake alkalization process in the final application (used mostly in bakery products).

3.3 Changes in international regulations

Consumer beliefs and behaviours are rapidly changing. To anticipate these changes, and to perhaps even have an influence, companies must leverage profound consumer insights. Bearing this in mind, the cocoa industry faces challenges in forthcoming years, which generally focus on consumer trends and needs. Nowadays consumers are much more interested in information about production methods and ingredients in the food products that they eat (Asioli et. Al., 2017). For the cocoa industry, this movement has two different effects: regulation of alkali content and declaring alkali content on labels.

On the one hand, the EU additives Regulation defines the levels of certain authorised alkalising agents used as additives in foods (the level of alkalising agents used in cocoa powders sold to final consumers is currently set at 7% expressed as potassium carbonates, on dry, fat-free matter). According to the United States (US) Code of Federal Regulations (CFR) Title 21 Part 163, food labelling requires alkalised cocoa powder or liquor to be declared as "alkali-treated cocoa (liquor)" (Food and Drug Administration, 2020). On the other hand, depending on the region and alkalisation level, alkalised cocoa powders must be labelled as “cocoa processed with alkali” or with an E-number on the ingredient list, and should never allow a '100% Natural' to influence consumers’ attitude towards the product. For example, due to US regulations, labels show the ingredient as “cocoa processed with alkali”. In Europe, only if the percentage used is above 7% must a label indicate an E-number (Food ingredients 1st, 2019). In Europe, for products with less than 7% alkali, it is not mandatory to include the E-number or the “alkali used”, but this will probably change in the near future.

The future of labelling is clearly a new goal for industry. Therefore, to prepare for this change, in forthcoming years the cocoa industry needs to explore different processing techniques to achieve cocoa powders with similar flavour and colour to the cocoa alkalised ones by simply changing process conditions (temperature, water amount, pressure, etc.) or using ingredients already included in formulations. Of these, the baked goods industry is one of the markets that uses the most strong-alkaline cocoa because the final colour in their products is important for consumers. Industries, bakery companies and cocoa producers should work together to find solutions that will have benefits for all.

3.4 Opening new markets

In the last few years, some markets are increasing/starting chocolate consumption. One clear example is India, which currently represents one of the world's fastest growing chocolate markets. Moreover, the Indian chocolate market is projected to grow at a CAGR (calculate a compound annual growth rate) of 8.12% during the forecast period (2022-2027) (Mordorintelligence, 2022). Custom duties depend on the type of product and importing country. By way of example, for India, importing cocoa liquor, butter and powder from countries that do not belong to the Association of Southeast Asian Nations (ASEAN) or liquor from ASEAN countries implies custom duties of 33%. However, for powder and butter from ASEAN countries, import duties are 0%. Thus the goal for the chocolate industry is to find new formulations to produce chocolate more cheaply.

A study into the future climate in West Africa (the main cocoa producer) predicts an increase in temperature, which will reduce the size of the current growing area in Ghana and the Ivory Coast (CIAT, 2011). This means that the suitable area to harvest cocoa will reduce, and farmers should adapt their agronomic techniques to the new conditions. However in November 2021, high demand, coupled with tightening supplies, has led the cocoa price to sharply rise, which is the main ingredient in chocolate. Cocoa prices have risen by more than 8% since December 2021 (New York post, 2022).

As this will influence cocoa prices and availability, industry should evaluate the whole cocoa process to find new methodologies or to apply that with a lower impact on end products and manufacturing costs. One example is the alkalisation process. As described before, nib alkalisation strongly impacts cocoa butter quality and manufacturing costs. Cake alkalisation has fewer cost impacts, and cocoa butter is of high quality. So industry should probably find a way to focus more on improving the alkalinisation process in cake by seeking to reduce costs and environmental impacts, and on improving butter quality.

4. Conclusions

The food industry is always changing and attempting to be prepared for consumer expectations and trends. Accordingly, in forthcoming years the cocoa industry should focus on new demands and consumer preferences. All this have been studied and described in the Introduction. The drawn conclusions are:

- Consumers are apparently and increasingly concerned about the sustainability of the products they consume. However, the ethical and sustainable management of processes implies increasing the price of raw materials and finished products. Therefore, it is worth wondering: will consumers be willing to pay the cost of more sustainable production by industry?
- Cocoa nib alkalisation has always been considered that which produces higher quality cocoa powders. However now that raw materials are scarce, is it advisable to alkalise nibs and, therefore, negatively affect butter properties? Or do applications exist in which consumers will note no difference between the alkalinisation type and alkali used?
- Clean label legislation may pose a risk for alkaline cocoa consumption and, therefore, for the availability of the products made with it. Is there a new way to produce products with similar characteristics to those that employ alkaline cocoa, but which follow clean label principles?
- Growing chocolate demand as a result of increased desire for this product and of generating new markets makes us rethink the production process to be able to use, in addition to liquor, surplus butter and cake. However, will consumers sensorially accept this product? As liquor will be reconstituted from butter and cocoa powder, can the percentage of cocoa powder in formulations be increased to improve functional and sensory properties?

The answers to these questions with implications for the cocoa industry are the starting point of this doctoral thesis, with a mention of industrial doctorate, which is entitled “Cocoa Applications in the Food Industry: Development of New Products and Study of the Effect of Cocoa Type on the Physico-Chemical and Sensory Properties of the End Product".

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3. Chapter I

Chapter I: Sustainability labeling in the perception of sensory quality and consumer purchase intention of cocoa and chocolate

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In Galanakis, C.M. (eds) Trends in Sustainable Chocolate Production. Springer, Cham.
https://doi.org/10.1007/978-3-030-90169-1_9

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Abstract

Chocolate companies have been the focal point in recent years due to consumers' perceiving bad practices in their plantations (child trafficking, child exploitation, poor working conditions, no control of plantations, etc.). In this context, companies have developed many sustainability programs to improve farmers' needs and to certify that raw material production is done following ethical principles. When a company complies with all certification program requirements, it can include the so-called sustainability labels. So, sustainability labeling acts as a tool that informs customers about the certifications and environmental and social actions that companies work on. However, are consumers willing to pay more for certified products? Do they better perceive them? This chapter aims to identify the more widely used sustainability labels in chocolate and to investigate the relation between chocolate labeling and purchase intention and perception. The results conclude that sustainability labeling information influences consumers' purchase decisions and sensory scores. Hence a significant number of consumers worldwide are indeed willing to pay extra money for cocoa and chocolate manufactured following ethical principles and, thus, with sustainability labels (Fairtrade, Rainforest Alliance, organic cocoa, etc.) on the packaging.

Keywords Sustainability, Labelling, Cocoa, Consumers, Purchase decision, Sensory attributes, Willingness to pay

1. Introduction

Since cocoa farming takes place only 15 degrees north or south of the Equator, cocoa cultivation is an agricultural activity of great economic and social importance in tropical, hot, and humid regions. Cocoa takes approximately three years after planting before trees are fruitful enough to harvest pods (Olam Cocoa 2016). This is when ripe cocoa pods are cut down from trees and opened to collect cocoa beans. These cocoa beans are placed on banana leaves or in wooden boxes for the fermentation step that lasts 7 days. Next, cocoa beans are dried (usually utilizing sun drying) for several days. Afterward, beans are ready to be shipped worldwide for further processing and transformed into cocoa butter, cocoa cake, and cocoa powder (See Fig. 1).

Fig. 1 Cocoa processing diagram: from cocoa bean to cocoa products.

The fascination of cocoa consumers (and its most precious by-product, chocolate) that the global cocoa production demand grows every year. At the beginning of the 21st century, cocoa production was about 2,000,000 tons. However, in only 10 years this value increased a 50% reaching a of approximately 3,000,000 tons. In economic figures, in 2019, the global chocolate market was estimated at USD 130.56 billion, and an annual growth rate (CAGR) of 4.6% is expected during the 2020-2027 period (Gran View research 2020).

Behind the positive aspects of the growth of such a pleasant sector to our senses, covert actions are not so friendly. In recent times, the cocoa sector has faced several deeply embedded and interrelated challenges, including the use of old trees with low tree productivity, negative environmental impacts, such as deforestation, soil degradation, and pollution…. In social terms, cocoa production is characterized by low farmer and worker incomes, persistent poor labor conditions as well as political instability in many of the significant cocoa-origin countries (Ruf and Siswoputranto 1995; Nkamleu et al. 2010; Matissek Reinecke et al. 2012; Fountain and Hutz-Adams 2015). These facts have been critical for consumers who are aware of the negative impacts of cocoa production.

To improve farmer conditions, cocoa quality, and reducing problems on lands, and making prices fairer for farmers, cocoa producers and organizations have established sustainability programs to ensure that produced cocoa powder is more sustainable from the social and environmental points view. These can be divided into three different groups: Voluntary standards schemes (Fairtrade Labelling Organizations International, Rainforest Alliance, and International Federation of Organic Agriculture Movements (IFOAM)); Corporate sustainability initiative (The Nestlé Cocoa Plan, Cocoa for Generations 2017 (Mars), Olam Cocoa Compass, etc.) and network, association and platform initiatives (World Cocoa Foundation (WCF), International Cocoa Organization (ICCO); National Confectioners Association (CAOBISCO and ECA)).

Consumers are becoming increasingly aware of the importance of sustainability concerning food consumption. Among its demands is the reduction of food waste, the substitution of animal sources of protein for vegetable ones, as well as the promotion of the consumption of seasonal, local ecologically-labeled products (Rejman 2019).

Considering these sustainability programs and their increasing importance for consumers, in this chapter, we analyze the problems on cocoa plantations, farmers, and child labor conditions that have been the origin of current sustainability programs emerging, which are available for the cocoa market its main action points. After describing the most known and globally implemented problems, we will analyze consumer behavior towards these sustainability labels and their influence on consumers' sensory and willingness-to-pay perception of these products.

2. Environmental and social problems related to cocoa and chocolate production

In recent years, the cocoa sector, including all stakeholders, has been accused of unsustainable and unethical production practices. These practices have been aggravated by growing pressure to increase cocoa production and to meet the growing worldwide chocolate demand. The consequences of this fast growth of the sector have soon been evidenced: the impact of cocoa production on the environment, economy, and society of producing countries has become more robust. In this section, environmental and social problems related to cocoa and chocolate production, which are the origin of sustainable certification programs, are discussed. These problems have been classified into four groups (Ruf and Siswoputranto 1995; Nkamleu et al. 2010; Matissek Reinecke et al. 2012; Fountain and Hutz-Adams 2015).

2.1 Bad labor conditions for farmers

Cocoa cultivation and production form a crucial market for African regions and are the main economic livelihood of most people who use their land to grow cocoa trees. In all these countries, as the cocoa market is the basis of many families' economies, the increasing pressure of cocoa production and low-profit margins for cocoa producers are essential to understand the poor working conditions and low wages of those farmers who cultivate cocoa.

On the one hand, millions of cocoa farmers work under challenging conditions and do generally not earn enough to cover their own basic needs (food, house, education). To understand the seriousness of the matter, imagine that a chocolate bar costs a dollar. Of that dollar the cocoa producer only receives 6 cents. Thus, how the farmer is going to pay good salaries to their workers? All this is even more dramatic if we are aware that, of the entire value chain, farmers are the workers exposed to the worst working conditions: handling pesticides without having the appropriate personal protective equipment, working for long hours and handling of very dangerous tools. In addition, workers often face ethnic and gender discrimination. All of this leads to communities often lacking the necessary resources to develop, and still today do not have access to sufficient food, water, or education. (Make chocolate Fair 2020).

On the other hand, children in some countries are forced to work on cocoa plantations. Such is the level of poverty in Western Africa that in order to support their families, they start working from childhood. In the worst scenario, families are sometimes forced to sell their own children as workers to cocoa farms owners, thus depriving them of their childhood and education. Of course, today abusive child labor and child trafficking are serious violations of international human rights standards and are prohibited by international labor law (ILO standards 182 and 138) and the United Nations Convention on the Rights of the Child (32/1). However, despite being in the 21st century, they are still a reality (Make chocolate Fair 2020).

Specifically, most of the cocoa produced in Africa comes from Côte d'Ivoire and Ghana. Of these two, Côte d'Ivoire, which accounts for more than one-third of the total world production and is expected to produce approximately 2.18 million tonnes in 2021, is one of the largest cocoa producers. So important is cocoa for this country that the cocoa market represents more than half of its annual exports (see Fig. 2).

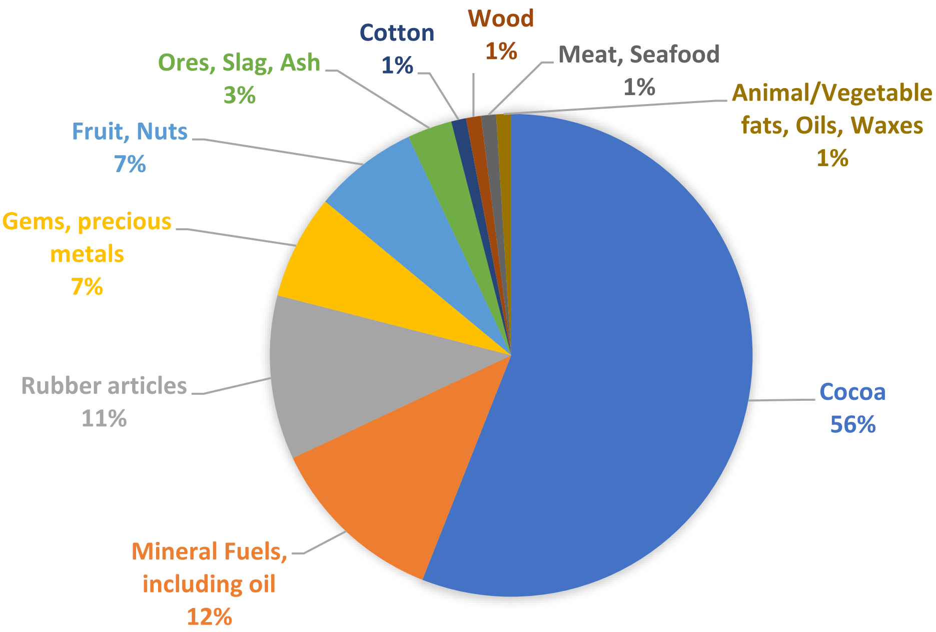

Fig. 2 Top 10 exports from Côte d'Ivoire (source: Bartalks 2020).

In an attempt to improve this situation, governments, world cocoa industry, cocoa producers, cocoa workers and non-governmental organizations agreed to abolish exploitative child labor through the signing of the voluntary Harkin-Engel Protocol in 2001. The objective of this protocol was to eliminate the "worst forms of child labor" and forced adult labor on cocoa farms in West Africa. The protocol's target was to reduce the worst forms of child labor by 70% by 2020. Two decades after the protocol was signed, children continue to be trafficked in Côte d'Ivoire and subjected to forced labor on cocoa farms (Make chocolate fair 2020). According to a new report by the National Opinion Research Center at the University of Chicago (NORC 2020), more than 1.5 million children still work in the cocoa production in Côte d'Ivoire and Ghana. In addition, the most dramatic thing is that, of them, 95% are exposed to the worst forms of child labor, such as the handling of dangerous tools or harmful pesticides. Other figures show that an estimated 2.1 million children work in the cocoa fields of Ghana and Côte d'Ivoire (CBI 2020a). The different forms of child labor exploitation in these countries are shown in Fig. 3.

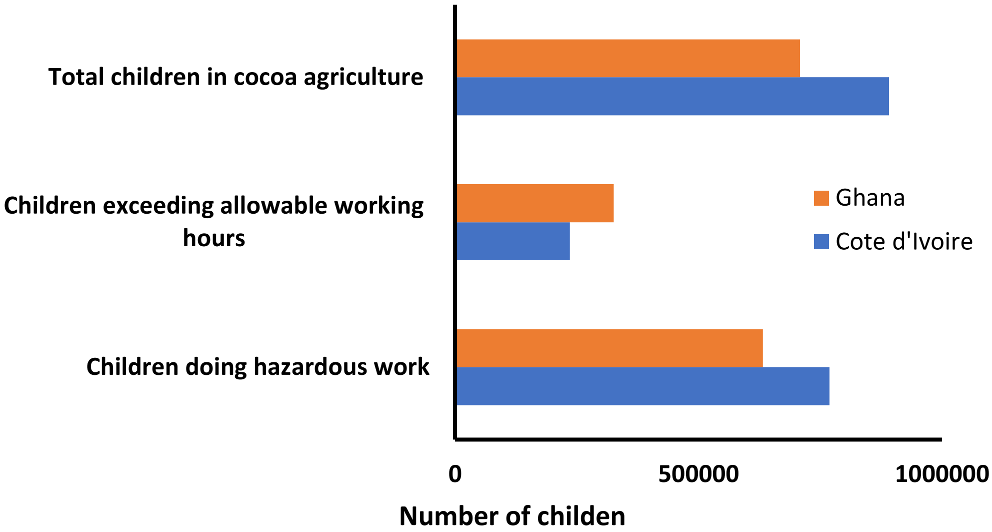

Fig. 3 Child labor in cocoa production in 2019 (Source: S&P Global 2019).

2.2 Instability in profit margins

Another critical problem that cocoa farmers face is price fluctuation and low economic benefits. The Cocoa Barometer (2015) estimates that cocoa farmers receive less than 7% of the total value added to 1 ton of cocoa beans. The distribution of each actor's contribution to the final cocoa price is seen in Fig. 4.

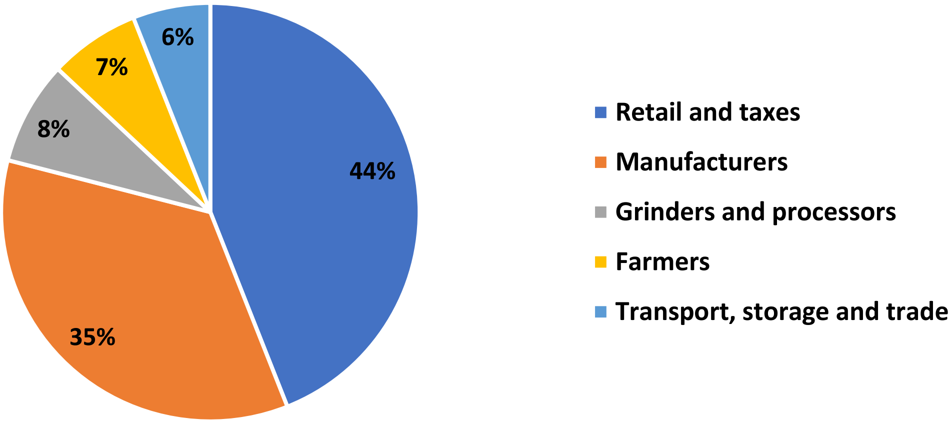

Fig. 4 Contribution of each actor to the final cocoa price as a percentage.

Since the 1990s, cocoa market is liberalized. It means that exporters and traders are buying and selling cocoa using *London Cocoa Futures* market prices, exposing cocoa farmers to high global price fluctuations (Vellema and Laven 2012; Vellema et al. 2006).

The consequence of this price fluctuation that farmers receive at farm gates, combined with high input prices required to modernizes fields, low loans, and small farm sizes, is meager income. Thus, if farmers do not receive money from the fields, they cannot invest all the money required to the fields maintenance, to control pest and tree diseases… An easy way to make more profit is to use a child in their plantations (ICCO 2007; Wessel and Quist-Wessel 2015). However, this is not the solution. As these practices do not improve yields, incomes from cocoa will remain low for the next harvest, and the circle will turn again. This circle can only be stopped when peasants receive a fair wage and investments are made in plantations (See Fig 5).

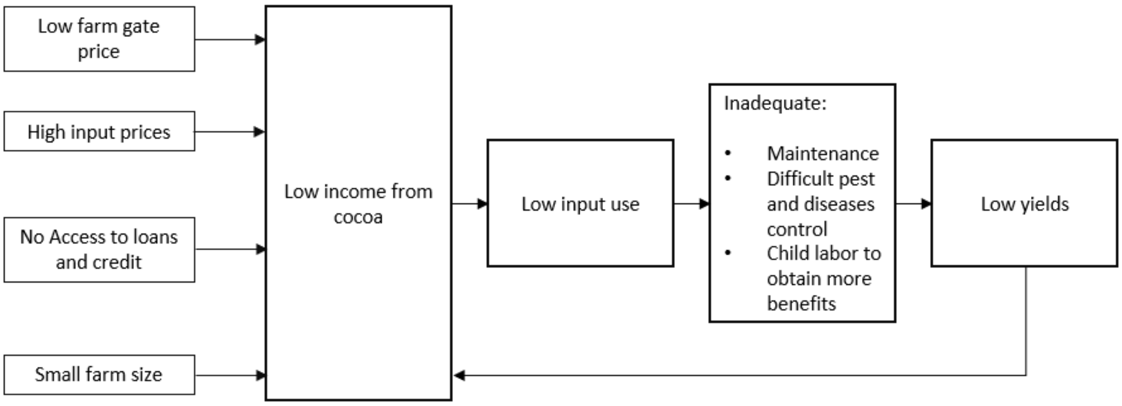

Fig. 5 Connection between cocoa issues resulting in problems in the sector (adapted from Wessel and Quist-Wessel 2015).

2.3 Problems on cocoa plantations

The pressure on increase cocoa production as a result of growing consumer demand generates different problems in producing countries, which are aggravated by the low yields resulting from high pest and disease incidence, old cocoa tree age, and lack of soil nutrients (Wessel and Quist-Wessel 2015). By clearing land for cocoa plantations, farmers modify the ecosystems in which many species thrive and, thereby, biodiversity is drastically reduced. (Bentley et al.

2004). Moreover, as soil care and irrigation are poor, soil nutrients begin to leak out, which increases soil erosion (Piasentin and Klare-Repnik 2004).

The more intense farming practices are, the more they damage the ecosystem. In most cases, cocoa farmers wear out soil and cut further into forests to obtain new land. This means that cocoa farming becomes a destructive circle for plantations and these processes stress soil and cacao trees. The mid-term results are lower yields, which is the exact opposite of what farmers expect (Asase et al. 2010).

2.4 Environmental impact of the supply chain during cocoa manufacturing

Regarding the supply chain, it is essential to realize that cocoa beans are recollected, fermented and dried, and usually shipped to other regions to be further manufactured. The nature of this supply chain, and the process itself, to transform cocoa products into chocolate involve several resources (see Fig. 6). For cocoa and chocolate manufacturing processes, factories need vast amounts of energy and water. Such is the amount of energy required to process and transform cocoa into chocolate that many studies suggest that it is responsible for between 6% and 28% of the environmental impact of chocolate production. (Miah et al. 2018; Neira 2016; Recanati et al. 2018). Regarding water, although very little research is available about its use during chocolate production, experts consider it also to be important.

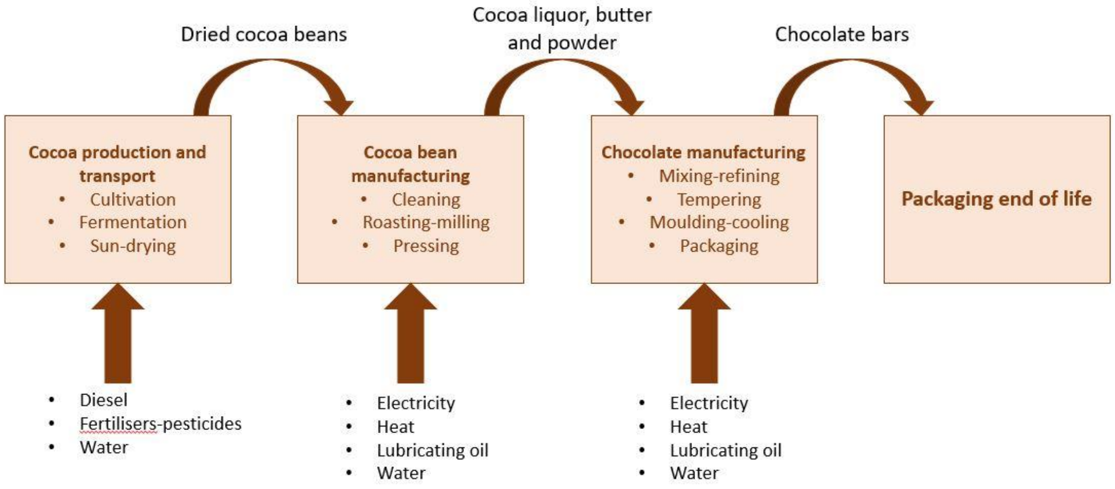

Fig. 6 The cocoa processing supply chain.

Despite these numbers, the environmental impact of the supply chain is supposed to reduce shortly because of increased cocoa grinding in producing countries. As an example, large multinationals such as Cargill, Olam and Barry Callebaut are betting on milling at source as a strategy to reduce production costs. Thus, while in the 2015/2016 season the percentage of grinding at source was 43%, this figure rose to 48% in the 2018/2019 season. Of this percentage, as Fig. 7 illustrates, 37% of cocoa beans are processed in Europe, 23% in Asia and Oceania, 21% cocoa is ground in Africa, and 19% in America.

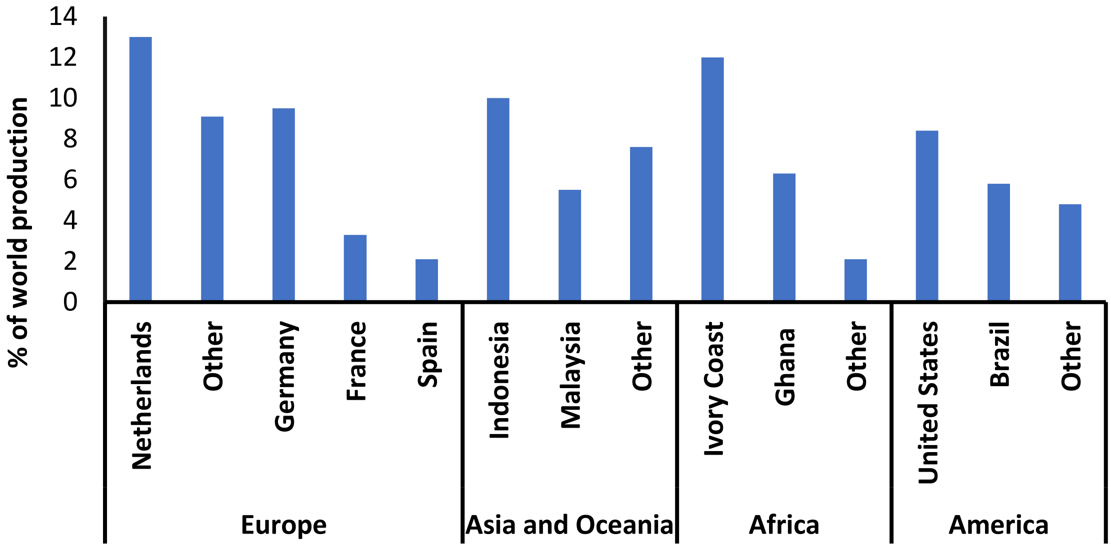

Fig. 7 Estimated cocoa bean grinding per region and country for 2018/2019. Source: CBI 2020b.

2.5 Impact of COVID-19 on cocoa farmers

Apart from all these problems, it is worth mentioning the impact COVID-19 has had on farmers in cocoa fields by making them even more vulnerable to existing health and well-being deficiencies. Since the pandemic took hold of the world in 2020, the progress made to fulfill sustainable development goals, particularly eradicating poverty and hunger, has been halted. In this way, what was originally born as a health pandemic, has ended up becoming a pandemic of hunger and poverty. Specifically, it has been estimated that around 135 million people have reached level C of food insecurity, or what is the same, are unable to survive without external food assistance. In addition, around 100 million people are after COVID-19 below the definition of the monetary poverty line, which is currently $1.90 a day. (Olam Group 2021). In the same line, a survey conducted by Olam with more than 3,400 farmers in 19 countries has shown the impact that the COVID-19 crisis has had on small farmers. Some of the conclusions drawn from this study reveal that around 50% of farmers have seen their income reduced and have had to find new ways to generate revenue. In addition, almost 1 in 4 farmers have had to clear land to increase their yields, and 5 in 10 African farmers saw lower demand for their products (Olam Group 2021).

3. General and specific sustainable certifications for cocoa products

To improve farmers' labor conditions, the sustainability of cocoa plantations, and the stability of the economy associated with the cocoa market, different certification programs have emerged in recent years.

These sustainability programs have been able to help lots of people who work on cocoa plantations and their families. Cocoa and chocolate companies have partnered and invested in the professionalization of cocoa farmers to intensify good agricultural production through certifications by increasing sensory quality.

Given the difficulty of establishing direct relationships with each cocoa producer, the adoption of certification systems is shown as an excellent alternative to monitor environmental, social and economic factors, granting greater process control and credibility over agricultural production systems. In this context, nowadays, the cocoa-chocolate sector has three internationally accepted certification bodies for cocoa production: Fairtrade Labelling Organizations International, Rainforest Alliance (emerged with UTZ in 2018), and International Federation of Organic Agriculture Movements (IFOAM). The three sustainable programs share the common objective of improving farmers' conditions and environmental impacts, but with some differences. In the following sections, all these programs and the cocoa sustainability projects owned by manufacturing companies and other new initiatives are described in detail.

3.1 Fairtrade certification

The Fairtrade certification initiative was created to inform that a certain product (in that case cocoa and chocolate) meet the social, economic and environmental standards set by Fairtrade Labeling Organizations International. This organization founded in 1997 is an association of 24 organizations that work to ensure better conditions for producers in the South. In its beginnings, it started as an international network to rise the political and social consciousness about the difficult situation of small-scale coffee producers around the world. However, with the years, certification has expanded and now it covers various products such as cotton, flowers, sugar, honey, fruits, tea or cocoa, among others.

According to Fairtrade philosophy, the best way to end poverty is by paying producers fair prices for their products and guaranteeing decent wages for workers. In this way, this program aims to improve lives and reduce poverty through ethical trade practices. Thus, when a company is Fairtrade-certified (see the logo in Fig. 8), regardless of fluctuations in market prices, workers will receive a fair price and, furthermore, if these farmers promote organic production, the economic value of the harvest will be even more favored.

Fig. 8 The Fairtrade logo.

Moreover, farmer organizations also receive a Fair-trade Premium which they can use to invest in different projects such as the renovation of plantations, replacing old trees with younger and more productive ones, or the modernization of both, the agricultural machinery and the facilities used for the collection, storage, transport or processing of cocoa. This organization is also creating cooperatives and associations and engaging farmers in them to better negotiate trade terms and reach broader markets.

Apart from the Fairtrade Trader Standard, Fairtrade has established a concrete standard for cocoa. It applies to small producing organizations and traders and contracts production setups in the Pacific region. This standard covers the production, purchase, and sale of cocoa beans, processed cocoa, secondary products, and their derivatives. It includes actions that control traceability, production practices, contracts, pricing, payment terms, pre-finance, sourcing plans, and a plan for premium products. If a cocoa company wishes to be certified with this standard, it must comply with both the "Fairtrade Trader Standard" and the "Fairtrade Standard for Cocoa" (Fairtrade 2017). Apart from this, Fairtrade works with the confectionary industry to source large volumes of sustainably produced cocoa.

Thanks to the efforts made by Fairtrade to extend its values around our planet, the number of Fair-trade areas continues to grow. As seen in Fig. 9, in 2016, the cocoa production area covered by the Fairtrade program was 722,060 ha in 2019, and this area is now 1,372,820.29 ha (Fairtrade 2021).

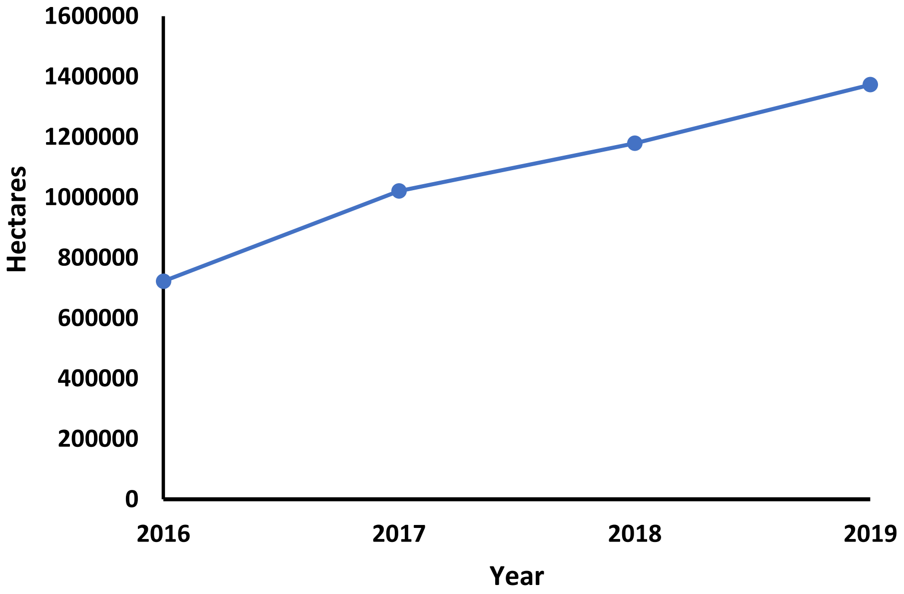

Fig. 9 Development of Fairtrade areas during the 2016-2019 period.

These hectares are distributed around different countries, such as Côte d'Ivoire, Ghana, the Dominican Republic, Peru, etc. However, they can all be seen in Fig. 10, and around 68% of the hectares included in the Fair-trade programs are in Côte d'Ivoire.

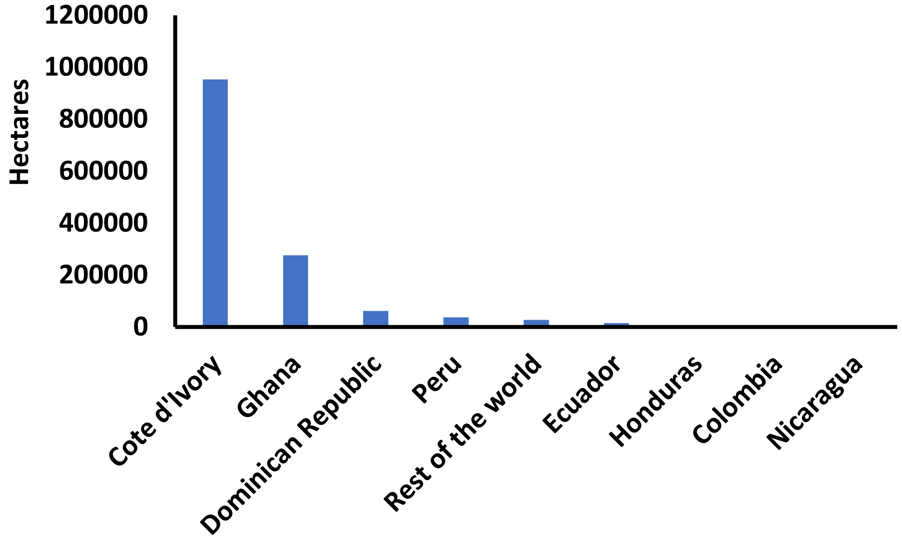

Fig. 10 Hectares of Fair-trade cocoa per country in 2019.

3.2 UTZ, Rainforest and Rainforest Alliance Rainforest Alliance

Rainforest was started in 1987 and was the world's first sustainable forestry certification. The goal was to improve farms productivity and resilience without altering the biodiversity (Rainforest Alliance 2021a). Years later, in 1992, the UTZ program was created in the Netherlands (UTZ 2021). It aimed to create a better future for people and nature, addressing thus two types of requirements: agricultural and environmental management practices, and the social and living conditions of the involved communities. In 2014, UTZ was reported to be the most extensive program for sustainable coffee and cocoa farming in the world (Potts et al. 2014).

Given the similarities between both programs (fight against deforestation, climate change, systemic poverty, and social inequity), these two organizations merged in 2017 creating the Rainforest Alliance (Rainforest Alliance 2017; Reuter events 2018). This international non-governmental organization (NGO) aims to connect the interests of companies, farmers, communities and consumers with the goal of leading sustainable products and services.

In the work with farmers and forest, the Rain Forest Alliance promotes land management practices that improve rural livelihoods without impacting nature. On the other extreme, they force cocoa and chocolate companies to foster responsible business practices along the whole supply chain. Finally, they impulse sustainability transformation through the creation of responsible policies, being necessary for it to collaborate with governments and civil society organizations (Rainforest Alliance 2021b). The e current logos of both certification programs, UTZ and Rainforest Alliance, are shown in Fig. 11.

Fig. 11 Current labels of the UTZ and Rainforest Alliance certification programs.

Actually, from its headquarters is in New York, it acts in more than 60 countries (Rainforest Alliance 2021b). Current critical impact areas of the Rainforest programs include forests and biodiversity, climate, rural livelihoods, human rights. The interventions of this program focus on four different locations. On the one hand, the Rainforest Alliance is a global leader in sustainability certification. More than two million farmers follow its agriculture standards in more than 70 countries around the globe. On the other hand, the Rainforest Alliance undertakes and implements conservation and community development programs in different regions where commodity production threatens ecosystem health and the well-being of rural communities.

Despite the growth of this certification standard, certification of products like pineapples, coffee, cocoa, bananas, tea, palm oil, among others under the brand of UTZ is still possible. Due to this reason, as seen in Fig. 12, number of hectares under the UTZ certification is bigger than the ones under the new Rainforest Alliance certification. Concretely, In 2020, Rainforest Alliance Certified cocoa was produced in 12 countries. In Latin America: Costa Rica, the Dominican Republic, Ecuador, and Peru; in Africa: Cameroon, Côte d'Ivoire, Ghana, Nigeria, and Tanzania; in Asia: India, Indonesia, and Papua New Guinea. The estimated production area dropped by 33% compared to 2019. This drop resulted from the Rainforest Alliance's decision to not certify the different labels of the same group, Rainforest Alliance and UTZ certification, at the same time in Côte d'Ivoire and Ghana. With Colombia added and Tanzania no longer producing UTZ-certified cocoa, the number of countries with UTZ-certified cocoa farmers remained stable at 17 in 2020. Regarding the production area, the estimated production area slightly dropped by 5% vs. 2019 due to a decrease in Africa.

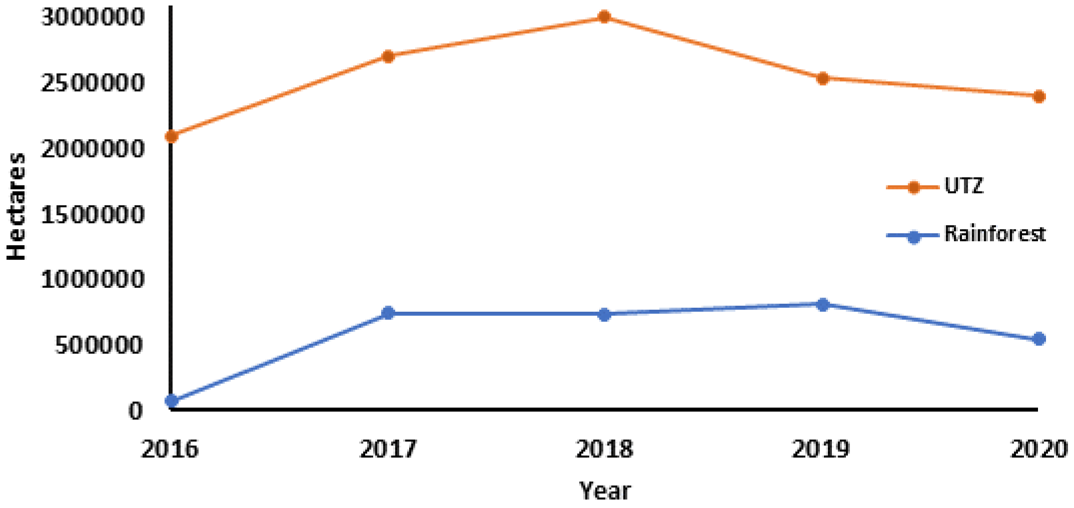

Fig. 12 Development of Fairtrade cultivation area in the period 2016-2020. Source: Cocoa Certification Data Report 2020.

3.3 Organic cocoa and chocolate certification

An organic certification is a seal that is granted to agricultural or food producers who have undergone a control process that guarantees the organic quality of what they produce in accordance with the corresponding regulations and according to the destination market where that product will be marketed.

product. Among the most common requirements for a production to be considered organic are the use of natural resources, without using synthetic chemicals, or genetically modified organisms (GMOs) - neither as fertilizer nor to combat pests.

In the specific case of cocoa, organic certification indicates that cocoa has been produced and processed using techniques, such as crop rotation, fertilization through compost or biological pest control. Implementing organic cocoa production practices is not an easy task, especially in small plantations. However, in the long run this practice can contribute to improved yields, product quality and consumer acceptance. In Europe, for example, organic fine aroma cocoa is increasingly in demand. Therefore, certification is a way to open up to new market niches (CBI 2020c).

Despite the existence of the International Federation of Organic Agriculture Movements (IFOAM), a global umbrella organization for the organic farming movement, there is no global certification program that allows a universal label to be obtained. On the contrary, each production area can establish its certification mechanisms and provide the corresponding logo to the products with fulfilled strict conditions regarding how they are produced, transported, and stored. In some territories such as the European Union, the United States, Japan or Canada, the term "organic" can only be used by certified producers, being the governments themselves who, through specific laws, formulate and review compliance with organic standards. The opposite case is made up of countries without organic laws that regulate organic certification. In these cases, the certification falls on non-profit organizations and / or private companies. A representation of different organic labels given by various certification agencies worldwide is shown in Fig. 13.

Fig. 13 Examples of types of organic certification labels from different parts of the world.

Such is the awareness for organic production that, according to the Research Institute of Organic Agriculture (FIBL), it is practiced on 72.3 million hectares of land and is managed by at least 3.1 million farmers in 187 countries. In economic data, it can be said that world sales of organic food and beverages amounted to more than 106,000 million euros in 2019 (FIBL 2021). The main consumer country of organic products is the United States, with Europe the second (CBI 2020d).

3.4 Other certification programs

Not at odds with this global trend of certifying sustainable cocoa production, in 2019, the International Standard Organization (ISO) launched the ISO 34101 series. This ISO is comprised by four different parts, which have as a main goal to address sustainable and traceable cocoa production, including economic, social, and environmental requirements. In the first part, criteria to implement and improve an effective management system that guarantees cocoa sustainability in their business are provided. Following these criteria provides a starting point for farmers to progressively meet the requirements of a sustainable cocoa production. The general, economic, social, and environmental performance requirements for all three levels of conformity (entry, medium and high) of a sustainable cocoa production are specified in part 2. The third part stipulates the requirements for traceability of sustainably produced cocoa.

Finally, part 4 establishes the requirements that the certification systems must meet. Therefore, it is especially aimed addresses the owners of certification schemes, certification bodies, and anyone seeking compliance with the ISO 34101 series. As with other certification schemes (ISO 9001 or ISO 22000), this certification requires high-level management systems (ISO 2019).

Another vital certification that focuses on emissions caused by-products throughout the process (from its origin to its arrival at the supermarket) is the carbon footprint. Carbon footprint is a well-known method to measure the number of greenhouse gases released during a product or a service (Druckman et al. 2011; Carbon trust 2007; Plassmann et al. 2010). This certification has no direct impact on farmers and cocoa plantation conditions. However, this certification provides an evidence of the commitment of companies to reduce current and future carbon emissions through the achievement of concrete actions. Thus, it is essential tool for consumers to know the food product's impact on the environment and compare different brands and how they are involved in these issues.

3.5 Cocoa sustainability projects owned by manufacturing companies

In addition to these general cocoa certifications, cocoa and chocolate manufacturing companies have been developing their sustainability programs. Hence, they seek to improve farmers' conditions and raise consumer awareness of sustainable cocoa production. Although each company follows its sustainability strategy, there are generally common patterns that go through using similar certifications to those described above. They implement their sustainability projects or combine both options. The following sections present the main sustainability projects in cocoa production of each company in the sector.

3.5.1 The Nestlé Cocoa Plan

The Nestlé cocoa sustainability project is called "The Nestlé Cocoa Plan" (NCP). It started in 2009, and its principal objective is to source 100% cocoa beans through its Nestlé Cocoa Plan by 2025 (Nestlé cocoa plan 2021a). This program focuses on the one hand on performing better cultivation techniques to make cocoa more profitable for producers. The principal action points are farmer training to improve farming practices, using better quality plants to improve yields that are more disease-resistant, and respecting the environment to avoid deforestation. On the other hand, it also wishes to improve farmers' living conditions and eradicate child labor from its supply chain. At this point, the principal actions include eliminating child labor through transparency and monitoring. Some of its plan's objectives also promote gender equality to improve not only family income but also water and sanitation. The last point of this program is to obtain better cocoa by enhancing the transparency of its supply chain and cocoa quality. To fulfill these goals, the idea is to build loyal customer-farmer group relationships, improve supply chain traceability, and reward NCP farmers for certification and sound quality (Nestlé cocoa plan 2021b).

3.5.2 Cocoa for Generations 2017 (Mars)

The Mars sustainable plan started in 2017. This program focuses on three key areas: Healthy Planet, Thriving People, Nourishing Well-being (Mars 2021). Regarding the Healthy Planet action plan, Mars cushions environmental impacts to help the planet and reduce emissions. Attention is paid to reduce the ecological footprint, fight climate change, water stress, deforestation, and unsustainable packaging use. With the Thriving People principle, Mars is committed to significantly improving the lives of 1 million people to better their livelihoods and respect human rights. Lastly, to guarantee a nourishing well-being, it is essential for to supply safe products with excellent nutritional value at the same time that transparency and social responsibly are assured (Mars 2021).

3.5.3 The Cocoa Life Programme (Mondelez)

The Mondelez cocoa life program was launched in 2012. The main guidelines in Mondelez’ action plan include three types of actions. On the one hand, those proposed to increase transparency and to connect consumers with the problems of farmers. The second is to empower cocoa communities to lead their own development and improve their livelihoods, promoting “self-sustainability” and the respect of human rights, overall those of children and women. The last is to work together with farmers and communities in the conservation of the land where cocoa is grown, (Cocoa life 2021).

3.5.4 Farming Programme (Lindt & Sprüngli)

The farming program of Lindt and Sprüngli was launched in 2008. Its objective is to obtain 100% cocoa sourced through sustainability by 2025 (Lindt & Sprüngli farming program 2021).

This program is divided into five action points. The first is traceability and farmer organization for cocoa beans. This traceability level guarantees that the cocoa beans that form part of this program are processed and transported separately from others and can be traced back to their origin. The second involves training and knowledge transfer by helping farmers to improve and professionalize their way of farming. The third is farmer investments to enable farmers to diversify and increase their income and strengthen their resilience. The fourth is community development to support communities in their development. The program provides access to drinking water by constructing water systems. The fifth and last one is the program's continuous progress and verification, which is an essential step towards its overall long-term sustainable supply chain aim (Lindt & Sprüngli farming program 2021).

3.5.5 Forever Chocolate (Barry Callebaut)

The Barry Callebaut sustainability program was launched in 2016. The principal objective is to make sustainable chocolate the norm by 2025 (Barry Callebaut 2021). The four main action plans and objectives are to help farmers prosper by modernizing agricultural and cultivation methods, increasing yields, diversifying income, and professionalizing farming to improve cocoa farmer livelihoods. The objective is that by 2025, more than 500,000 cocoa farmers will have left poverty behind. The second objective is zero child labor by remediation activities, including providing school kits and birth certificates. This requirement enables a child to go to school and support families and communities with education and training in child labor awareness. The objective is to eradicate child labor from its supply chain by 2025. The third objective is thriving nature by reducing emissions. The aim for 2025 is to be carbon- and forest-positive. The final action plan is 100% sustainable chocolate by 2025. In addition, Barry Callebaut has created the Cocoa Horizons Foundation, with the aim of promoting a more productive and sustainable agriculture, which has as a consequence the development of communities, as well as the protection of children and nature. To guarantee the independence of this foundation, it is supervised by the Swiss Federal Foundation Supervisory Authority (Cocoa horizons 2021).

3.5.6 Cocoa Promise (Cargill)

The Cargill Cocoa Promise program started in 2012. The principal objective is to achieve better incomes and living standards for farmers and their communities while cocoa sustainably grows (Cargill 2021). To meet this goal, this program is focused in strengthening the socio-economic resilience of cocoa farmers and their communities while ensuring a sustainable cocoa supplyAnother action plan is community well-being to enhance the safety and well-being of children and families in cocoa-farming areas. The last involves protecting the planet by promoting environmental best practices in the business and supply chain (Cargill 2021).

3.5.7 Cocoa compass (Olam)

The Olam cocoa compass project was launched in 2019. Cocoa Compass sets measurable targets in three areas: put children first, help farmers achieve a living income, and protect the environment (Olam group 2020). One of the main working areas focuses on farmers. Farmers must earn enough to cover their basic food, water, housing, education, healthcare, transportation, and clothing needs and afford unexpected costs. The goal by 2030 is to have 150,000 cocoa farmers in its supply network to achieve better living income. Another important working area is empowering communities to grow as thriving ones. Here the objective is to gain access to education and freedom from child labor. The critical outcome here is that they form part of a thriving local community, to eradicate child labor from its supply chain by 2030 and for all children to access education. The last one involves investing in nature. Olam focuses on the co-existence of prosperous farms and thriving communities with healthy ecosystems to both reduce and eventually reverse deforestation (Olam group 2020).

3.6 Network, association, and platform initiatives

There are also other initiatives that different networks, associations, and platforms have started in several regions. The most important ones are the actions performed by the International Cocoa Organization (ICCO), the World Cocoa Foundation (WCF) and the European Associations cocoa (ECA), and the Association of Chocolate, Biscuit and Confectionery Industries (CAOBISCO).

The International Cocoa Organization (ICCO) is an intergovernmental organization based in Abidjan – Côte d'Ivoire. ICCO was created during the negotiations of the first International Cocoa Agreement in the frame of the United Nations International Cocoa Conference that took place in Geneva in 1973.

Its vision is to see that the objectives set in the Global Cocoa Agenda for a Sustainable World Cocoa Economy are fulfilled. The aim is to achieve sustainable production, a sustainable industry chain, sustainable consumption, and strategic management of the cocoa sector (ICCO 2021).

More recently, in 2000, the World Cocoa Foundation (WCF) was created to assure a sustainable future for cocoa and the farmers whose livelihoods depend on this crop, by merging the efforts of the US Chocolate Manufacturers Association (CMA) and the American Cocoa Research Institute (ACRI). The members who form part of this program are on the one hand farm-level input providers, farmer cooperatives, cocoa trading companies, cocoa processors and chocolate makers and manufacturers, and on the hand, financial institutions, ports, warehousing companies, and retailers (World Cocoa Foundation 2021). The focus areas are prosperous farmers (to improve the livelihoods of cocoa farmers worldwide), Empowered Communities (to fight child labor in the cocoa supply chain), and a Healthy Planet (to end cocoa-related deforestation and take climate action). In 2017, the Sustainable Trade Initiative (IDH) joined the WCF to create and coordinate the Cocoa and Forests Initiative. This new platform aimed to provide a common framework to tackle deforestation by means of working hand to hand with cocoa industry, financiers, governments and civil society. In this moment, IDH operates in over 40 countries worldwide.

In Europe, the Association of Chocolate, Biscuit and Confectionery Industries of Europe (CAOBISCO) was created in 1959 to ensure an economic, environmental and socially responsible production and transformation of cocoa, at the same time that the production of sufficient quantity and quality of cocoa to satisfy the needs of consumers is guaranteed. For this, CACAOBISCO works with different partners throughout the cocoa supply chain, including the governments of the countries of origin and local authorities. Such is the importance of this association, that in this moment it represents more than 13,000 European chocolate, biscuits and confectionery manufacturing companies, 99% of which are small- and medium-sized enterprises (CAOBISCO 2021).

Finally, the European Cocoa Association (ECA) was founded in 2000. This trade association includes leading European companies involved in cocoa processing, as well as those related to cocoa trade or logistics activities. Among its actions for sustainability, it highlights the activities of the ECA Sustainability Working Group, which has among its activities the monitoring of the evolution of deforestation, child labor in plantations ... In addition, this work group is highly focused on monitoring the development of the new standard ISO 34101 on Sustainable and Traceable Cocoa, as well as the new African Regional cocoa Sustainability standard (ECA 2021).

4. Influence of cocoa and chocolate sustainability labels on consumer perceptions

Previous sections have shown that cocoa producers and consumers are increasingly concerned about the environmental, social, and ethical impacts of food production, which is why sustainability labels that consider these aspects are becoming more and more critical every day. However, for the percentage of cocoa or chocolate sold with any globally recognized sustainability label to no longer have a residual value, consumer awareness and a broad market offer are not enough. For this to happen, it is necessary for understanding to be translated into attitudes towards purchase intention. Yet, how do organic and fair-trade labels influence consumer opinions and behavior?

In recent years, much effort has been made to investigate how sustainability labels influence consumer opinions and behavior. These studies have focused on two different approaches: what motivates consumers to purchase organic- (e.g., Hughner et al. 2007; Hjelmar 2011; Rana and Paul 2020; Tandon et al. 2020), Fairtrade- (e.g., Annunziata et al. 2011; Pedregal and Ozcaglar-Toulouse 2011; Andorfer and Liebe 2012) or Rain Forest Alliance-certified food products (Chao, 2015); Consumers' demographic characteristics of organic (e.g., Wier et al. 2008; Feil et al. 2020; Marreiros et al. 2021; Furno 2021) or ethical (e.g., Newhouse and Buckles 2020) labeled products.

One of the most extensive studies to evaluate the relation linking consumer motivation, understanding, and using sustainability labels on food products (both environmental and ethical labels) is carried out by Grunert et al. (2014). In this study, 4,408 respondents participated from the UK, France, Germany, Spain, Sweden, and Poland. The results indicated that their understanding of the sustainability concept was limited, but understanding the selected labels (Fairtrade, Rainforest Alliance, and Carbon Footprint) was better as some seem self-explanatory. Moreover, in agreement with most of the studies above, motivation, understanding, and use of the labels mentioned above are affected by demographic characteristics, human values, and country differences.

By focusing exclusively on the product of this book, cocoa, the following section describes the relationship between cocoa and chocolate sustainability labels and customer perceptions. For a better understanding of this matter, four different approaches can be analyzed: are consumers able to identify the sustainable labels associated with cocoa and chocolate production? do consumers trust cocoa and chocolate sustainability labels? are sustainably produced products perceived as more desirable than traditional ones? does sustainable production affect the sensory perception of cocoa and chocolate?

4.1 Consumers' capacity to identify cocoa and chocolate sustainability labels

When we talk about perception and preference, it might appear that if two products are similar, but one carries a sustainability label, consumers should choose the latter. However, for this to happen, consumers should first consult label information and then recognize different certifications.

About the first of the actions, offering consumers the opportunity to find sustainability information on labels does not necessarily mean that they will use them because this depends on their motivation. In line with this, Adamowicz and Swait (2013) demonstrate that for most people, given the many food choices that consumers make every day, they usually avoid reading extra information on labels to minimize cognitive efforts.

Regarding recognition and considering that most sustainability labels are over 20 years old, it would seem consistent to think that consumers should recognize them when they form part of a food label. However, this is not what the scientific literature indicates. In a study carried out with students of Environmental Economics of Belgian nationality (Rousseau 2015), the participants were asked to identify three commonly used sustainability labels. The results showed that 60% of the respondents were able to locate the Fairtrade label correctly. However, only 8% of respondents correctly recognized the EU ecolabel, and a minimum of 6% admitted the EU organic label.

More recently in a study carried out in Brazil with 126 consumers of dark chocolate, 30% were male, and 70% were female of ages ranging from 18 to 50 years. However, 74% of them stated that they were interested in certified products. The majority could not recognize the Rainforest label (84.1%) and only 56.3% identified the organic seal (de Andrade Silva et al. 2017).

4.2 Consumers' confidence in sustainability labels

In the study of Rousseau (2015), the surveyed population had to select the statement (from a set of 5) that best reflected their opinion about organic or Fair-trade labels. The results showed that most respondents linked fair trade labels

(30%) and organic labels (40%) with the idea of these labels being marketing tools that do not imply socially desirable results. In contrast, only a tiny percentage (16% for organic labels and 22% for fair trade labels) indicated that the presence of these labels guarantees a sustainable and pesticide-free production process or an equitable and sustainable trade process, respectively. Lack of consumer trust in labeling schemes was also found by, among others, Aertsens et al. (2009) and Padel and Foster (2005).

4.3 Consumer associations with cocoa and chocolate sustainability labels

In order to evaluate if chocolates containing sustainable labels are more desirable than traditional ones, Rousseau (2015) asked the study population to select from a list of nine statements which attributes they associated with organic- or Fairtrade-labelled chocolate bar. The three more popular answers about organic chocolate were: chocolate causes less pollution caused by production (46.4%); it uses sustainably produced cocoa (40.8%); it is more expensive (39.6 %). In addition, 16% of those surveyed indicated that organic chocolate uses fair-trade cocoa, but there does not have to be a direct relationship between both concepts. Finally, despite chocolate not being considered a particularly healthy product, 15.7% of the population indicated that organic chocolate is more beneficial than conventional chocolate. This was also observed in Lee et al. (2013), in which about 15% of the respondents indicated that organic chocolate is healthier than conventional chocolate. This is known as the health halo effect.

When looking at fair trade chocolates, the respondents made three leading associations: chocolate is made with fair trade cocoa (70.6%), its consumptions improves the living conditions of farmers in developing countries (62.0%) and chocolate is more expensive (54.1%). A significantly lower number of respondents associated the consumption of fair trade chocolate with positive health effects (16% versus 3% reported for chocolates labeled organic). Finally, and although the trade label is not strictly linked to sustainable and environmentally friendly agricultural practices, 11% of consumers indicated that the production of Fairtrade certified chocolates causes less contamination.

Based on all the mentioned ideas it can be stated that customers can select this sustainability labeling for different reasons: (1) a purely altruistic environmental reason: (2) a warm-glow effect satisfying consumers' utility or ego (Andreoni 1990); (3) a selfish reason, when a green characteristic correlates positively with other characteristics, such as health benefits and taste (Bougherara and Combris 2009); (4) a positional effect which indicates purchasers' high income (Grolleau et al. 2012).

4.4 Effect of sustainability labeling on cocoa and chocolate consumers' sensory perception

As demonstrated in previous sections, the flavor is one of the most influencing parameters to affect customer perception. Therefore, at this point, we wonder, is there any relation between the sensory quality of cocoa/chocolate and sustainability labeling?

In order to answer this question, we have to bear in mind two dimensions: the effect of sustainable labeling on cocoa bean composition (which is ultimately linked with sensory quality) and the impact on consumers' perception.

With the first approach, it is commonly accepted that the sensory quality of cocoa and chocolate is strictly linked with the sensory quality of the cocoa beans used to produce them. Thus much research has been done to determine which factors are responsible for this cocoa sensory quality. In these studies, it has been pointed out that cocoa quality is a combination of intrinsic factors, such as the grain's genotype, and extrinsic factors, such as soil type, cocoa tree age, post-harvest treatments (pulp preconditioning, fermentation, and drying) and industrial processes (i.e. roasting) (Kongor et al. 2016). As seen, except for industrial processing variables, they all depend on factors related to the origin of cocoa beans and farmers' practices.

Generally, given the characteristics of cocoa-producing countries, it is difficult to directly control each farmer's practices on their plantations. In this context, the incorporation of standards and certifications like organic production, sustainable agriculture, or Rainforest Alliance will imply the adoption of quality management systems. This will lead to lead to greater traceability, better control of good agricultural practices and the use of proper monitoring systems in cultivations. Thus, something that cannot be denied is that all these efforts should contribute to a better sensory quality of products.

Regarding the effect of sustainability labeling on consumers' perception, we must once again resort to perception studies with consumers.

In this sense, it must be said that the number of studies focused on clarifying the reactions of consumers to organic foods with respect to expectations and sensory perceptions have been very abundant. These studies have repeatedly found that consumers generally have higher expectations of organic foods than to conventional ones (Ellison et al. 2016; Lee et al. 2013; Prada et al. 2017). This better consideration of organic foods has been called the 'organic halo effect” and it is so important that, even in studies where there is no correlation between expectations and reality through blind evaluations, the effect is maintained (De Andrade Silva et al., 2017). In addition, it is known that this effect is more important in people with good health than those with health problems (Apaolaza et al., 2017). Something curious about this effect is that its power is different depending on whether the product is consumed to satisfy a nutritional need or for pleasure (Ellison et al. 2016). Finally, it should be mentioned that, although it only points out in a low number of studies, the presence of the organic label can also lead to a worse expectation about the nutritional and sensory properties of the products (Schuldt and Hannahan 2013).

About chocolate, De Andrade Silva et al. (2017) demonstrated that sustainable labeling has a positive influence on the chocolate quality and sensory attributes. To reach this conclusion, the authors asked their study participants to taste six dark chocolate samples with different quality labels (including organic and rain forest alliance certifications) and percentages of cocoa during two sessions. In the first session a blind test was carried out. In the second one, all the judges were informed about the label of each sample. The results showed that information about sustainability labels positively affects the attributes of flavor, aroma, melting, and overall impression acceptance scores of samples with sustainability labeling, since scores of the seconds test where higher than those of the first one (blind test).

Similar results were described by Enax et al. (2015) and Didier and Lucie (2008). The authors of the first study described the relation between taste and fair trade products and concluded that adequate trade labeling has a positive influence on perceived chocolate taste. Didier and Lucie (2008) concluded that taste positively influences the Willingness to pay for organic or Fair-trade certified products in the second work.

5. Influence of cocoa sustainable labels on Willingness to pay for cocoa and chocolate products

As it has become quite clear that consumers are increasingly aware of the need to consume more respectful products with the environment and produced ethically and sustainably, we wondered, how does sustainable labeling affect consumers' Willingness to pay? To answer this question, the first thing we must make clear is the meaning of the willingness-to-pay (WTP) concept, which refers to the maximum price that a buyer accepts to pay for a given number of goods or services" (Le Gall-Ely 2009).

This concept is so important that many studies have dealt with consumer WTP for environmentally friendly foods and their determinants of different products and in various countries in recent years. In 2002, Loureiro et al. evaluated if consumers would pay a premium for eco-labeled apples. Likewise, Marette et al. (2012) experimented with 114 people between 18 and 69 years in France to evaluate consumers' WTP for eco-friendly apples with different labels. In 2009, Bougherara and Combris investigated whether selfish or altruistic motives drove WTP for an eco-labeled product. Janssen and Hamm (2012) assessed consumer preferences and WTP for different organic certification logos. The WTP for organic food in urban Turkey has been evaluated by Akgüngör et al. (2010). The factors that influence the WTP price premium for organic food have been studied by India Gumber and Rana (2017). Similar works have been done in almost every part of the world. See, for instance, the studies carried out in Pakistan (Sana et al. 2018), China (Yu et al. 2014), Greece (Krystallis et al. 2006), Mexico (Husted et al. 2014), Ghana (Owusu 2013), or Australia (Lockie et al. 2004). More recently, Katt and Meixner (2020) reviewed the drivers influencing consumers' WTP for organic food.

It is easy to find publications that have evaluated WTP for social sustainability attributes in the same vein. Most studies on WTP for fair trade products have focused on coffee because it is the most popular and well-known appropriate trade product to date. By way of example, Pelsmacker et al. (2005) wondered if consumers care about ethics. To know this, they studied consumers' WTP for fair trade coffee in Belgium. Similar studies on coffee have been done in the US and Germany (Basuand Hicks 2008), China (Yang et al. 2012), or South Africa (Lappeman et al. 2019). With the same goal, but with wine, Pomarici and Vecchio (2014) studied attitudes to sustainable wine of millennial costumers from Italy. In 2017, Miller et al. compared WTP for social responsibility in fruit and vegetable products in four countries: The United Kingdom, Japan, India, Indonesia.

These studies allow us to conclude that the purchase intention of consumers is strongly influenced both by quality and price, as well as by other more subjective characteristics such as sustainability labels. In general, it is evident that products with sustainable labeling are more expensive, however, this does not stop their consumption by a large part of the population. However, other types of consumers neither know nor care to understand the meaning of sustainability labels, therefore, they are not available to pay more for them. These conclusions agree with Mai (2014), who concluded that despite consumers' WTP for products with ethical attributes than those without, around half of them are still unwilling to pay more. One step forward was taken by Van Doorn and Verhoef (2011), who quantified this value, and estimated that consumers are willing to pay a price premium of up to 13% for organic products. However, these premiums vary between countries. In a meta-analysis on WTP for socially responsible products, Tully and Winer (2014) found that the mean percentage premium is 16.8 percent. On average, 60 percent of respondents are willing to pay a positive premium for socially responsible products. They also found that WTP for products where the socially responsible element benefits humans are higher than those that help the environment. In a study that held interviews with 1,192 people from five European countries (Austria, Germany, Italy, Switzerland, the UK) in front of supermarkets or organic food shops, Zander and Hamm (2010) noticed that consumers' WTP 10% surcharges for Fairtrade-labelled products. Finally, such studies remark that for consumers to find extra value in certified products, they must also be associated with personal benefits, such as increased product quality (Delmas and Grant 2014).

Having evaluated the influence of sustainable labels on WTP for ecological or fair trade products, the following sections focus on cocoa and chocolate. Different studies have been done to study WTP for sustainable cocoa and chocolate products to understand consumer behavior. This extra cost is focused mainly on organic and fair trade products.

5.1 WTP for organic cocoa and chocolate

Very few studies have centered on describing the effect of sustainable labeling of chocolate and cocoa products on consumers' WTP and the socio-demographic features of the potential consumers of these products.

In a study carried out by Tagbata and Sirieix (2008) with a sample of 102 consumers, the authors demonstrated that consumers are willing to pay €+0.55 for organic chocolate than for a non-certified one. These results contradict those of Rousseau (2015), whose study found that the presence of an organic label on chocolate bars harms consumer choices, and the price premium for a 100 g chocolate bar with an organic label is €−0.37 on average.

5.2 WTP for Fairtrade cocoa and chocolate

Contrarily to what happens with organic labels, the number of studies about the influence of the Fairtrade label on WTP is much larger.

Rousu and Carrigan (2008) conducted an auction in a grocery store and found that participants are willing to pay a premium of €0.08/100 g for Fair-trade chocolate. They also found that between 14-18% of participants would switch to or from the Fairtrade chocolate bar by providing reliable information. Authors also found that having reliable information on fair trade issues would change the consumption choice of the 14-18% of the surveyed population.

According to Tagbata and Sirieix (2008), the price that consumers were willing to pay for a standard chocolate bar was 70 eurocents. However, when this same tablet had the organic or Fairtrade labels, the price increased to € 1.25 and € 1.31, respectively. Tagbata and Sirieix (2008) also found that consumers' WTP for organic and Fair-trade chocolate is less than the sum of the WTP for organic and the WTP for Fairtrade chocolate separately. Finally, they observed that some consumers even prefer organic chocolate to be organic and Fairtrade chocolate. Thus, a single message seems preferable to multiple messages (Poelman et al. 2008).

In the same way as evaluating the WTP of organic products, Rousseau (2015) assessed the WTP of Fairtrade chocolates. This time the results revealed that consumers are willing to pay a positive premium for chocolate with a Fairtrade label than conventional chocolate. Based on the conditional logit estimation, the price premium that respondents are willing to pay for a 100 g chocolate bar with a Fairtrade label is €2.03 on average.

In the same year, Vecchio and Annunziata (2015) carried out a study with 80 people aged between 18 and 35 from Italy. They found that the surveyed sample is generally ready to pay more for chocolate bars carrying sustainability labeling (i.e., Fairtrade, Rainforest Alliance, and Carbon Footprint).

All these studies point out that consumers are willing to pay more for certified products than for those without certification (Mai 2014) and, for certificates, they are willing to pay more for "Fairtrade" than for other certifications (Rain Forest Alliance or Carbon Footprint) (Vecchio and Annunziata 2015).

5.3 Profile of consumers willing to pay for sustainable certified cocoa and chocolate products

Finally, having described the impact of organic and fair trade labeling on chocolate costumers' WTP, the time has come to study if there is a consumer profile for those consumers.

In a first approach to understand the socio-demographic profile of costumers' WTP for sustainably certified products, it is worth mentioning that according to Laroche et al. (2001), consumers' WTP for green products is influenced by specific characteristics like demographics, knowledge, values, attitudes, and behaviors. According to their values, Ryan (2006) defines green product consumers as those with the following characteristics: have a broad awareness for the environment, be committed to sustainable products, and showing a responsible consumption behavior, choosing those products produced by green companies.

When examining specific studies with cocoa-derived products, it must be considered that research works are limited. However, there are enough of them to have an idea about what consumers are like who are willing to pay more for products deriving from cocoa with sustainability certification.

In the study carried out by Didier and Lucie (2008), the authors found three clusters of consumers according to their WTP organic and fair trade-labeled cocoa products. The first cluster (42% of the sample) represents people who are insensitive to labels. This group, whose average age is around 35 years, comprises students and people with no socio-professional category. The second group (41% of the sample) is formed by consumers for whom the image of a chocolate bar is positively enhanced by the presence of "organic and fair trade" labels. The average age of this group is 45 years and comprises women (71%) primarily. Professionally, they work as executives, salespersons, perform other activities (43%), or are employees and retired people (35.7%). Finally, the valuation of the 'organic and fair trade' label by the people in the third cluster is determined by a product's taste. This cluster consisted of the 17% of the surveyed population, and was formed overall by people (32 years of average), especially women (88%) with any specific socio-professional category.

In a survey carried out in Belgium with university students Rousseau (2015), the participants were asked what aspects determine their choice when buying chocolate. For this question, 95% of them answered that the most critical factor is the chocolate type (white, milk, dark). In the second and third positions came price and flavor with 49% and 48%, respectively. This study showed that the most important attributes for young consumers are two: sensory experience -defined overall by taste-- and price. This falls in line with the existing literature, such as Torres-Moreno et al. (2012). On the contrary, sustainability aspects such as fair trade or environmental impact were only valued by less than 10% of the surveyed population. At the opposite extreme, it has also been evidenced that more mature chocolate consumers have an increasing preference for premium products, understood as those labeled as cocoa single origin, organic or fair trade and with better nutritional and functional properties (i.e. high cocoa content and low in sugars) (ICCO 2007).

For the socio-demographic variables of the population participating in the study by Vecchio and Annunziata (2015), several characteristics had a positive and statistically significant effect on WTP for all the chocolate bars. Concretely, it was highlighted that being woman, adult and having a high economic income are factors that predispose towards the consumption of sustainable products. Specifically, the study found that for Faitrade products, women were willing to pay a premium of 14 euro cents more than men. The premium was 13 cents for products with the Rain Forest label and 9 cents for those with the Carbon Footprint label.

As all four studies revealed, the socio-demographic profile of potential consumers of sustainable-certified cocoa-derived products indicates middle-aged or older women with an excellent socio-professional status. This was why the WTP in the study of Rousseau (2015) performed with young students, for these products was so low.

6. Conclusions and future perspectives

Awareness of the impact of mass cocoa and chocolate production on the environment and producing communities is globally increasing. In the global culture of environmentalism and fair trade context, this fact has led to the creation of different certification programs (international and specific for cocoa) by certification bodies worldwide or even by the companies that transform cocoa into chocolate. Of all these sustainable production labels, the most important in terms of the number of certified cocoa fields are UTZ, Fairtrade, Rainforest, and organic farming.

Over the years, it has been found that a significant proportion of consumers are willing to pay higher prices for organic or fair trade products. These consumer profiles are generally made up of women with a high socio-professional category. However, there is still a long way to go before the production of certified cocoa, especially its consumer purchase preference, becomes the general trend. Even when food carries a sustainability label, and consumers are aware of the importance of consuming cocoa and chocolates produced with the minimum environmental, social and ethical impacts, these sustainably certified products are not always those that end up in shopping baskets.

One of the reasons for this is that consumers are not always aware of sustainability labels on the products they buy. This occurs when consumers have very little time to shop or because buying is such a routine action that it becomes instinctive. The second reason is that, by assuming consumers are aware of labels, they would not spend time understanding what they mean or searching for information. The third cause appears when, after identifying labels, consumers do not make correct interpretations or labels do not convey trust. Finally, other reasons include the product being more expensive or its taste is not as good as the usual product.

All these factors should be considered in forthcoming years to design packaging and awareness effective campaigns that imply an actual change in consumer habits, especially those of younger consumers with fewer economic resources to invest in food products.

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4. Chapter II

Chapter II: Effect of the type and degree of alkalization of cocoa powder on the physico-chemical and sensory properties of sponge cakes

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LWT, 2021, 152, 112241.

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Abstract

Alkalization is a crucial process during cocoa processing to reduce its bitterness, improve solubility and develop color. Alkalization can be performed out at several points of the process (nib or cake), with different agents and at various intensities. All these variables may affect cocoa properties, but also physico-chemical and sensory properties of derived products (i.e. cakes). This work aims to evaluate the impact of alkalization type (nib vs. cake), alkalizing agent (K2CO3, NaHCO3 and KOH) and process intensity (mild and strong) on the physico-chemical and sensory properties of sponge cakes. For this aim, 8 different alkalized powders were industrially produced and used in the preparation of sponge cakes. Alkalizing conditions significantly affected cocoa properties (pH, color, sensory properties) and those of the corresponding cakes (cake doughs color and rheology, as well as baked cake color and texture). In general, doughs prepared with cocoas alkalized under strong conditions were a 55% darker and a 15% less elastic. After baking, the corresponding cakes were a 17% darker (L*) and a 12% harder in texture. Despite these differences, all the cakes were equally rated by consumers in sensory terms demonstrating that for this application, alkalization variables do not condition consumer acceptability.

Keywords Dutching, bakery, quality, consumer’s acceptance

1. Introduction

Cocoa powder is widely used in the food industry as one of the main ingredients in confectionery, bakery and pastry products.

Obtaining cocoa powder begins with cocoa beans, which undergo fermentation, drying, deshelling and roasting processes (Miller et al., 2008). Unshelled and roasted cocoa beans are ground and liquefied by heating to obtain cocoa liquor, which is pressed to obtain a fatty fraction (cocoa butter) and a partially defatted fraction (cocoa cake). After subjecting the cocoa cake to a pulverization process, natural cocoa powder is obtained (Frauendorfer & Schieberle, 2006), which is characterized by its light brown color, and having a slightly acidic pH (5–6) (Kostic, 1997) and astringent taste (Quelal-Vásconez, Lerma-García, Pérez-Esteve, Talens & Barat, 2020).

In order to broaden their technological applications, cocoa nibs, cocoa liquor, cocoa cake and cocoa powder can be subjected to direct treatment with alkali, which is known as alkalization or the Dutching process (Miller et al., 2008; Rodríguez, Pérez, & Guzmán, 2009; Kealey et al., 2005; Minifie, 2012). This process consists of mixing any of the above-mentioned cocoa sources with an alkali solution and treating this mixture with the combined effects of temperature and pressure.

During the alkalization process, pH increases to a range from 6 to 8 (Kostic, 1997). In addition to neutralizing the acids present in cocoa, the reactions between cocoa pigments and the alkali in the presence of oxygen and heat allow cocoa color to develop. In this way, the alkalized cocoa powder color darkens and its flavor is milder than that of natural cocoa powder. If cocoa powder is highly alkaline, it provides an even more intense flavor and a darker color, which is consistent with consumers' expectation of dark chocolate (Chau Loo, Tesén, & Valdez, 2013). For this reason, medium- and strong-alkalized cocoa powders are generally used in bakery applications.

In short, it can be stated that the alkalization process improves solubility, develops a darker color, removes acidity, astringency and bitterness (Valverde-García, Perez-Esteve, & Barat-Baviera, 2020). However, the intensity of these changes depend on the cocoa process stage in which alkalization takes place (nib, liquor, cake or powder), the type and concentration of alkali, and the intensity of other process variables (time, pressure, temperature, water percentage, etc.) (Dyer, 2003).

Alkalizing agent is generally established insofar as potassium carbonate and sodium hydroxide are the most widely employed alkali agents during alkalization. In line with the World Health Assembly's commitment to reduce the mean population sodium chloride intake by 30% to < 5 g/day by 2025 (WHO, 2013) in the cocoa industry, sodium hydroxide has been replaced with potassium hydroxide. However, other alkaline agents are authorized, such as ammonium hydroxide, ammonium or magnesium carbonate, sodium, potassium or ammonium bicarbonate, ammonia gas, magnesium oxide, and mixtures of these (Codex Alimentarius, 1981). The alkali agent added during the cocoa alkalization process can impact baking properties in the same way as baking soda does. For this reason, sodium bicarbonate alkali is a good option in bakery products (Olam Cocoa, 2017).

The most economical option is cake alkalization as cocoa butter does not enter the production process and does not undergo any alteration process due to high temperatures and saponification processes: changes of fatty acids profile or setting characteristics, modification of unsaponifiable fraction... However, these cakes are traditionally less appreciated because they are considered to have a lower coloring capacity and a less intense aroma (Dyer, 2003). Moreover, during alkalization with nibs, more aromatic products are obtained whose colors are more reddish and intense, and less alkali is used in many cases (Olam Cocoa, 2017). For this reason, and although the product is more expensive because butter can alter and lose part of its commercial value, nib-alkalized cocoas are usually considered a better product (Moser, 2015).

Despite the large body of scientific literature on the effects of alkalinization on cocoa's nutritional, functional, microbiological and sensory characteristics (Valverde-García, Pérez-Esteve, & Barat-Baviera, 2020), there is still a research gap in the field to clarify the impact of cocoa powder characteristics on the physico-chemical and sensory properties of the different applications in which it can be used to, thus, evaluate how the food matrix empowers or masks these attributes.

In this context, the present work studies the effect that cocoa type has according to its processing (alkalization type, degree and type of alkali) on the physico-chemical and sensory properties of dough and cake whose formulations contain alkalized cocoa powder.

2. Materials and Methods

2.1 Chemicals and ingredients

2.1.1 Ingredients for preparing cocoa powder

All the cocoa powders herein employed were supplied by Olam Food Ingredients S.L. (Cheste, Spain), who especially prepared these products for our study. The origin of the cocoas used as raw materials for the different alkalization treatments (cocoa cake and cocoa nibs) was Côte d'Ivoire. Three different alkalis were utilized: potassium carbonate (K_2CO_3) (Quimialmel, Castellón, Spain), sodium bicarbonate ($NaHCO_3$) (Barcelonesa, Cornellà de Llobregat, Spain) and potassium hydroxide (KOH) (Quimialmel, Castellón, Spain).

2.1.2 Cake preparation ingredients

The essential ingredients for preparing cakes, such as wheat flour (Aragonesa, Huesca, Spain), butter (Hacendado, Pozoblaco, Spain), white sugar (Pfeifer & Langer, Colonia, Germany), eggs (Huevos Guillen, Paterna, Spain), baking powder (Hacendado, Novelda, Spain) and pasteurized semi-skimmed milk (Hacendado, Urnieta, Spain), were bought in a local supermarket.

2.2 Cocoa alkalization process

Eight different alkalized cocoa powders were specifically prepared for this study at a pilot plant scale. They differed in terms of: a) the process stage in which alkalization took place: cocoa nibs (N) and cocoa cake (C-); b) alkalizing agents (potassium hydroxide -KOH-, potassium carbonate -K_2CO_3- and sodium bicarbonate -NaHCO3-); c) alkalization intensity (mild and strong). Both alkalization process were done using batches of 100 kg of cocoa (nibs or cake), previously roasted. Nib alkalization was performed exclusively with potassium carbonate (K_2CO_3) as it is the most widespread one. Cake alkalization was performed with K_2CO_3, sodium bicarbonate ($NaHCO_3$) and potassium hydroxide (KOH) to study the effect of the alkaline agent on the properties of both the resulting cocoa powder and the final product. Processing parameters conditions such as amount of water or alkalizing agent, solution temperature, reaction time, pressure, drying time… were set to assure equivalent alkalization degrees between the nib and cake-alkalized processes. Values of these parameters are shown in Table 1.

Table 1. Processing conditions for medium and strong alkalization intensities.

	Mild conditions	**Strong conditions**
Batch weight (kg)	100	100
Alkalizing salt (kg/100 kg of cocoa)	3	6
H_2O (kg/100 kg of cocoa)	20	30
Solution temperature (ºC)	75	75
Reaction time (min.)	50	60
Pressure range (mbar)	1400-1600	1800-2000
Reaction set point (ºC)	110	140
Drying time (min. after reaching 100 ºC)	5	5

In order to allow the equivalent raw material and manufacturing treatments in all the samples, they were especially produced for this study in various processing plants belonging to Olam Cocoa. Cake alkalization was performed in the pilot plant of Olam Food Ingredients Spain (Cheste, Valencia, Spain). The nib-alkalized cocoa powder processed under mild conditions (NM) was produced at the Unicao factory (Abidjan, Ivory Coast). Finally, the nib-alkalized cocoa powder processed under strong conditions (NS) was prepared at the deZaan factory (Koog aan de Zaan factory, The Netherlands). All the products were dried by using hot air (80ºC) until a moisture content of 35-45 g/kg was obtained.

2.3 Cocoa powder characterization

2.3.1 Extractable pH

The extractable pH in the cocoa powder and cocoa liquor was determined by following the methodology described in The deZaan Cocoa Manual (Olam Cocoa, 2017). For this purpose, a suspension of 2.5 g of cocoa powder/liquor 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 left to cool down to room temperature. Data collection was carried out in triplicate (n=3) using a Crisonbasic 20+ pH meter (Barcelona, Spain), previously calibrated with technical solutions of known pH (4.01, 7.00 and 9.21 at 25ºC, Crison Instruments SA, Barcelona, Spain).

2.3.2 Extrinsic and intrinsic color

Extrinsic and intrinsic color was measured in the cocoa powder samples. To determine extrinsic color (dry cocoa powder color), a portion of dry cocoa powder was placed inside a methacrylate cuvette (20 mm thick) to ensure uniform powder distribution to guarantee sample opacity. To determine intrinsic color (cocoa dispersed in water), 5 g of the cocoa powder sample were suspended in 15 mL of distilled water at 60 ºC and were stirred for 1 minute. The mixture was left to cool down to room temperature. Then it was vigorously stirred to resuspend possible settled particles and placed inside a methacrylate cuvette. A CM-3600d (Konica Minolta, Azuchi Machi, Japan) spectrocolorimeter was used to measure both, extrinsic and intrinsic color.

The results were expressed according to the CIE-Lab system (D65 illuminant and 10° viewing angle). Measurements were taken with an 8-mm diameter diaphragm inset. The measured parameters were L* (L* = 0 (black), L* = 100 (white)), a* (+a* = red) and b*(+b* = yellow). Using the a* and b* values, we calculated hue (h*ab) and chroma (C*ab) by the following equations:

$$h_{ab}^{*} = \arctan\frac{b^{*}}{a^{*}} \quad \text{Eq. 1}$$

$$C_{ab}^{*} = \sqrt{a^{*2}+b^{*2}} \quad \text{Eq. 2}$$

The mean values and standard deviation from three replicate measurements (n=3) were calculated.

2.3.3 Sensory evaluation

Sensory analyses were performed according to ISO 6658:2017 by a trained panel made up of nine people (n=9). The members of the panel were selected and trained according to the ISO 8586:2012. To this end, 40 g of cocoa powders were mixed with 1L of tap water at 60° C and stirred until an homogeneous suspension was obtained. Around 50 mL of this suspension were poured into coded cups. Samples were tested at a temperature close to 50° C and seven different markers were analyzed: cocoa and chocolate taste, acidity, astringency, alkalinity, body, bitterness. The intensity of each attribute was scored from 1 to 5, where 0 represented no taste and 5 denoted a very intense taste. The coded samples were shown simultaneously and evaluated in a random order among the panelists.

2.4 Cocoa cake preparation

A typical cocoa sponge cake recipe was followed to prepare the different formulations. Each dough was prepared in a Thermomix TM 31 food processor (Vorwerk, Wuppertal, Germany) by mixing 150 g of sugar and 240 g of eggs at room temperature for 1 minute at the speed of 3. Subsequently, 30 mL of milk and 250 g of butter were added to the mixture, which was stirred for 2 minutes at the same speed. Then 240 g of flour and 60 g of alkalized cocoa (4 soft-alkalized and 4 strong-alkalized) were added, and the dough was mixed for 3 minutes by increasing the speed to 4. Finally, 16 g of baking powder were added and was mixed for 3 minutes at the speed of 4.

Once doughs were obtained, 700 g of each one was transferred to a previously greased metal mold (14.5 cm x 11.0 cm), and were cooked for 50 minutes with medium dry air ventilation at 165 ºC in a SelfCookingCenter® scc 62 oven (Rational, Landsberg am Lech, Germany). After baking, cakes were cooled to room temperature (approx. 2 h). Then the physico-chemical and sensory analyses were performed.

Each formulation was repeated 3 times on different days to include the maximum preparation variability. Every formulation was characterized the day of preparation following the procedures described in sections 2.5 and 2.6.

2.5 Dough characterization

2.5.1 pH

The pH in doughs was determined by a CrisonBasic 20+ pH meter (Crison, Barcelona, Spain) by embedding a puncture probe directly into dough. The pH measurements of doughs were taken in triplicate for each of the three independent formulation repetitions (n=9).

2.5.2 Rheology

The rheological properties of the different cocoa doughs were determined under the steady state and dynamic conditions by a controlled stress rheometer (RheoStress, Thermo Haake, Karlsruhe, Germany) using plate-plate sensor geometry (60 mm in diameter) with a 1 mm gap. A stress sweep from 0.1 to 200 Pa at 1 Hz and 25 °C was first performed to establish the linear viscoelastic region (LVR). Then a frequency sweep from 0 to 15 Hz at 1Pa and 25 °C was performed to record the values of the elastic and viscous moduli and parameters G' and G'', respectively. Tests were done in triplicate for each of the 3 independent formulation repetitions (n=9).

2.5.3 Color

The color determination in sponge cake doughs was measured in triplicate following the procedure described in Section 2.3.2 for extrinsic color (measuring the sample after being transferred to the methacrylate cuvette). Tests were done in triplicate for each of the 3 independent formulation repetitions (n=9).

2.6 Cake characterization

2.6.1 Moisture, water loss, density and rise

Moisture was determined by AOAC method 650.46 (AOAC, 1997). For this purpose, 3 g of sponge cake cooled to room temperature were weighed in duplicate and taken to an FD 115 heat/drying chamber (Binder, Tuttlingen, Germany), which was previously programmed at a temperature of 100±1 ºC overnight. Based on the difference in sample weight before and after drying, moisture content was determined by the following expression:

$$\text{Moisture (g/100 g)}= \frac{\text{Wi - Wf}}{\text{Wm}} * 100 \qquad \text{Eq. 3}$$

where Wi = weight of the crucible, plus the wet sample (g); Wf = crucible weight, plus the dry sample (g); Wm = sample weight.

The total water loss during baking was determined by the following expression:

$$\text{Water loss (g/100g)}= \frac{\text{Wi - Wf}}{\text{Wi}} * 100 \qquad \text{Eq. 4}$$

where Wi = weight before baking (g); Wf = weight after baking (g).

In order to determine density, cakes were cut into 30 mm diameter x 30 mm high cylinders with a metal punch. Density was calculated by the ratio between the weight of cylinders and their volume.

The rise of cakes was determined by measuring the height of the cakes at the highest point of three central sections with the help of a graduated measuring tape. Moisture determination, density and rise determinations were done in triplicate for each of the 3 independent cake repetitions (n=9).

2.6.2 Color determination

The baked cake color was measured with the help of a CM-700d spectrocolorimeter (Konica Minolta, Ramsey, USA), conditioned with a CM-A181 standard mask for 3 mm diameter SAV (with no license plate). For measurements, a 10º visual angle, a D65 illuminator and the excluded specular component mode (SCE) were selected. Color was measured at seven different locations on the crust and crumb for each of the 3 independent cake repetitions (n=21). The results were expressed in accordance with the equations described in Section 2.2.2.

2.6.3 Texture

The texture parameters hardness (N), elasticity (dimensionless), cohesiveness (dimensionless), and Resilience (dimensionless) defined by Bourne (1978) of sponge cakes were determined by a double compression test (TPA) in the TA-XT plus texture analyzer (Stable Micro Systems, Godalming, England), equipped with a SP/75 compression plate. The probe speed was 1 mm/s (pre-test and test) and 2 mm/s (post-test), with 50% deformation and a 30-second waiting time between compressions. For this analysis ten pieces of each cake were cut (30 mm diameter x 30 mm height) and analyzed (n=30).

2.7 Sensory analysis

The degree of acceptance of the different sponge cakes by a panel of consumers was evaluated by hedonic tests. The panel of tasters was formed by 40 students and research staff members from the Food Technology Department of the Universitat Politècnica de València (Spain), who were frequent chocolate cake eaters. Samples were evaluated in a tasting room equipped with individual cabins (ISO, 2010). They were coded with randomly chosen 3-digit numbers. Acceptance tests were performed on a 7-point hedonic scale (1 I absolutely dislike, 2 I considerably dislike, 3 I somewhat dislike, 4 I neither dislike nor like, 5 I somewhat like, 6 I considerably like, 7 I absolutely like). This scale was used to describe all the following parameters defined according to Standard UNE 87-001-94: color, sponginess, taste, chocolate aroma and overall appreciation. To minimize any residual effects, consumers were asked to rinse their mouths with water before testing each sample.

2.8 Statistical analysis

Normality was tested using Shapiro-Wilk test ($\alpha < 0.05$) and homogeneity of variance was tested using Levene's test. The differences between samples due to cocoa type (alkalization type, alkali type and the intensity of the alkalization process) employed in the formulation of the different cakes were determined by an analysis of variance (ANOVA), followed by Tukey's post hoc test were used when the data was normally distributed and the variance was homogeneous. For nonparametric statistics, the Kruskal-Wallis test and Dunn's multiple comparison test were used. Data were analyzed by XLSTAT 2020.3.1 (New York, USA). ANOVAs were done by using the STATGRAPHICS Centurion XVI v. 17.2.04 statistical software (Manugistics Inc., Rockville, MD, USA). All data presented in tables are expressed as averages and pooled standard deviations. Pooled standard deviations make no assumption about the distribution and are much more robust than standard deviations calculated on only part of the data. For its calculation it was followed the procedure suggested by Renard (2021).

3. Results and Discussion

3.1 Cocoa powder characterization

3.1.1 Extractable pH

The pH value is an indicator of the degree of cocoa alkalization (Valverde-García et al, 2020). This determination allows samples to be classified into different categories: light alkalized cocoa (pH 6.0 - 7.2), medium alkalized cocoa (pH 7.2 - 7.6) and strong alkalized cocoa (pH> 7.6), according to the guidelines of Miller et al., (2008). As shown in Table 2, the minimum pH in the alkalized samples was 6.6±0.1. Bearing in mind that the pH of the raw materials was 5.4±0.1, it can be stated that the alkalization process was successful in both the different alkalization treatments (nib and cake).

According to Miller's classification (Miller et al., 2008), by applying mild-alkalizing conditions, two different alkalization levels were achieved: light-alkalized

($NaHCO_3$, K_2CO_3) and medium-alkalized (KOH). However, under strong alkalizing conditions, the obtained products were classified as medium- ($NaHCO_3$) and strong-alkalized (K_2CO_3 and KOH). When K_2CO_3 was used as the alkalizing salt, no significant differences were found in pH between the samples alkalized in nib and cake, which confirmed the equivalent conditions of treatments (Olam Cocoa, 2017).

In this way, at the same alkali concentration, the alkalization salt determined the final cocoa pH (Moser, 2015). The salt with the highest capacity to increase pH was potassium hydroxide (KOH), followed by potassium carbonate (K_2CO_3) and sodium bicarbonate ($NaHCO_3$). This ability of hydroxides to increase the pH of cocoa during alkalization to a greater extent than carbonates or bicarbonates is because hydroxides are stronger bases (Srivastava & Misra, 2015).

Table 2. pH values of the obtained cocoa powders.

	Mild conditions	**Strong conditions**
N_K_2CO_3	6.7^{aA}	8.0^{bB}
C_K_2CO_3	6.8^{aA}	7.9^{bB}
C_KOH	7.4^{bA}	8.1^{bB}
C_$NaHCO_3$	6.6^{aA}	7.1^{aB}
Pooled standard deviation (n=3)	0.1	0.1

N#_K_2CO_3 = Nib-alkalized cocoa with K_2CO_3; C#_K_2CO_3 = Cake-alkalized cocoa with K_2CO_3; C#_KOH = Cake-alkalized cocoa with KOH; C#_$NaHCO_3$ = Cake-alkalized cocoa with $NaHCO_3$; #=M = mild alkalization conditions; #=S = strong alkalization conditions. Values with different lowercase letters in the same column indicate statistically significant differences ($p < 0.05$) between cocoa powders with different alkalizing agents or type of alkalization (Nib (N) or Cake (C)) for the same percentage of alkali. Values with different capital letters in the same column indicate statistically significant differences ($p < 0.05$) between cocoas with different percentages of alkali for the same alkalizing agent or type of alkalization. Data were analyzed with Kruskal-Wallis test and Dunn's multiple comparison test.

3.1.2 Extrinsic and intrinsic color

In order to evaluate the effect of alkalization type (cake or nib), alkalization intensity (mild or strong) and alkali type (KOH, K_2CO_3 and $NaHCO_3$) on cocoa powder color, this property was measured by two different approaches. On the one hand, the dried powder color (extrinsic color) was determined because it is the parameter that normally characterizes cocoa specification. However, this parameter is conditioned by the amount and polymorphic forms of cocoa butter (Olam Cocoa, 2017). Thus, two powders may appear different in terms of their extrinsic color and look like a similar color in a certain application. For this reason, the color of the cocoa suspended in water (intrinsic color) was also determined as it is considered to correlate better with the color of the powder in an application (Dyer, 2003). This has also been described by Moser (2015), who advises that, in order to properly evaluate cocoa impact when using cocoa in an application, it is always necessary to examine cocoa's true intrinsic color. In fact, early indicators can be misleading, such as extrinsic color.

Table 3 shows the color coordinates for both extrinsic and intrinsic colors. As we can see, the three processing variables (salt type, concentration and alkalization type) significantly affected both color types.

The sample made with $NaHCO_3$ was the lightest in color (highest L* value), in both the extrinsic and intrinsic colors at the mild- and strong-alkalization intensities. The darkest sample was that made with KOH. Significant differences were found between the mild-and strong-alkalizing intensities when comparing the same alkalizing salt.

For chroma (C*), differences were found between the alkalization intensities (mild and strong) in the extrinsic and intrinsic colors. The sample with the most saturated color was that formulated with $NaHCO_3$ for the mild- and strong-alkalizing conditions. The lower color purity was for the samples made with KOH.

In the values shown for h*, and also for extrinsic and intrinsic colors, the mild-alkalization conditions provided a higher h* value compared to the strong-alkalization conditions, which reaffirmed the capacity of alkalization to go from yellowish to reddish tones due to the polymerization of polyphenols (Valverde-García et al., 2020).

These differences between KOH, K_2CO_3 and $NaHCO_3$ were due to the different salt strengths (Rodríguez et al., 2009).

The correlation between extrinsic and intrinsic colors was quite notable. Regarding the L* value, the correlation was 0.80 for the cocoa powders alkalized under mild conditions and 0.95 for those processed under strong ones. Similar values were obtained for C* and h* with correlation values of 0.94 and 0.87 or 0.84 and 0.80 for the mild- and strong-alkalization conditions, respectively. Although a correlation existed, it was not 100%. Therefore, it was not possible to accurately predict intrinsic color from extrinsic color, so both parameters should always be measured.

Table 3. Extrinsic and intrinsic color of the obtained cocoa powders.

	Extrinsic color			**Intrinsic color**		
	L*	**C***	**h***	**L***	**C***	**h***
NM_K_2CO_3	36.8^{bB}	26.4^{bB}	55.2^{bB}	16.3^{cB}	19.2^{cB}	49.75^{bB}
CM_K_2CO_3	36.1^{aB}	26.1^{bB}	54.7^{bB}	15.5^{bB}	18.5^{bB}	49.2^{bB}
CM_KOH	35.7^{aB}	23.8^{aB}	52.7^{aB}	13.6^{aB}	16.2^{aB}	45.5^{aB}
CM_$NaHCO_3$	39.6^{bB}	28.2^{cB}	55.0^{bB}	18.6^{dB}	19.9^{dB}	51.4^{cB}
NS_K_2CO_3	25.5^{bA}	20.2^{bA}	47.7^{bA}	11.0^{cA}	9.8^{cA}	36.25^{bA}
CS_K_2CO_3	24.8^{bA}	18.6^{aA}	48.4^{cA}	9.1^{bA}	8.7^{bA}	36.1^{bA}
CS_KOH	22.0^{aA}	18.2^{aA}	46.0^{aA}	7.0^{aA}	7.9^{aA}	34.7^{aA}
CS_$NaHCO_3$	28.8^{cA}	20.7^{bA}	49.9^{dA}	12.8^{dA}	9.5^{cA}	41.4^{cA}
Pooled standard deviation (n=3)	0.3	0.2	0.4	0.3	0.3	0.4

N#_K_2CO_3 = Nib-alkalized cocoa with K_2CO_3; C#_K_2CO_3 = Cake-alkalized cocoa with K_2CO_3; C#_KOH = Cake-alkalized cocoa with KOH; C#_$NaHCO_3$ =

Cake-alkalized cocoa with $NaHCO_3$*; #=M = mild alkalization conditions; #=S = strong alkalization conditions. L * = luminosity; C * = chroma; h * = hue. Values with different lowercase letters in the same column indicate statistically significant differences (p <0.05) between cocoa powders with different alkalizing agents or type of alkalization (Nib (N) or Cake (C)) at medium (M) or strong (S) alkalization conditions. Values with different capital letters in the same column indicate statistically significant differences (p <0.05) between cocoas with different percentages of alkali for the same alkalizing agent or type of alkalization. Data were analyzed with Kruskal-Wallis test and Dunn's multiple comparison test.*

3.1.3 Sensory profile

Fig. 1 shows the sensory profiles of the obtained cocoa powders. The cocoas alkalized under mild conditions presented more cocoa, chocolate, body, acidity and astringency, and less alkalinity tones than those alkalized under the strong conditions.

Of the samples alkalized under the mild conditions, NM_K_2CO_3 and CM_K_2CO_3 cocoas presented more chocolate flavor, body, astringency, and alkali taste, while CM_KOH and NM_K_2CO_3 presented more bitterness. For the samples alkalized under the strong conditions, all the samples had a similar flavor profile. This finding highlights that CS_K_2CO_3 and CS_KOH had more intense bitterness and alkali taste, and that cocoa flavor was more present in the sample alkalized in nibs. These results confirmed the impact of the alkalization conditions of the final sensory attributes and also provide one of the few examples of published data on how the cocoa sensory profile is modified according to different alkalization parameters.

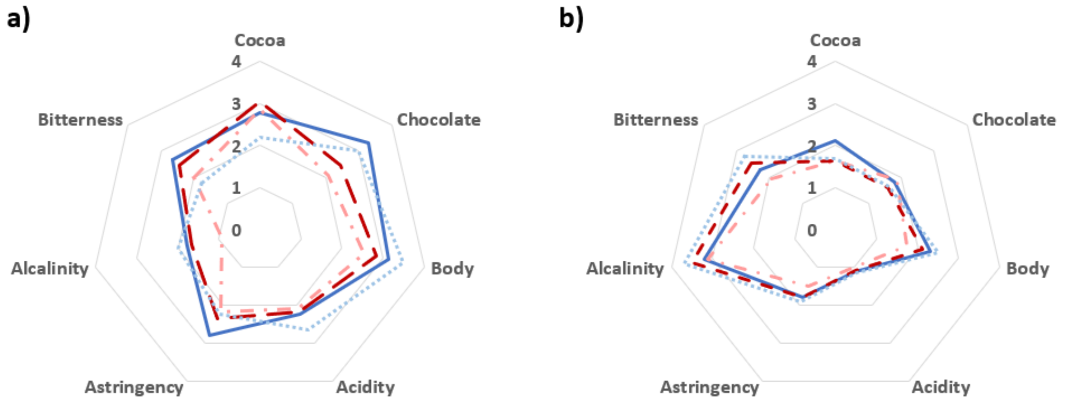

Fig. 1 Sensory profiles of cocoa samples alkalized in mild (a) and strong (b) conditions. *N_K_2CO_3 (dark blue solid line), C_K_2CO_3 (light blue dotted line), C_KOH (dark red dashed line), C_$NaHCO_3$ (light red dash-dotted line).*

3.2 Dough characterization

3.2.1 pH and color

Table 4 shows the pH and color values of the cake doughs prepared with the different alkalized cocoa powders. Any type and color of cocoa can be added to a bakery recipe, but much attention should be paid to pH (Moser, 2015). Generally, bakery doughs with a lower pH, linked with lactic acid production during fermentation, require a slightly shorter mixing time and are less stable than doughs with a normal pH level (Delcour & Honseney, 2010; Wehrle, Grau, & Arendt, 1997). In our case, although the pH of cocoas varied between 6.7 and 8.1, the pH of the doughs ranged between 7.4 and 7.7. These data confirmed that the cake dough pH is generally established by the main ingredients creating a buffering effect (Baik, Marcotte, & Castaigne, 2000) and are merely affected by the employed cocoa. Thus, the type of cocoa should not affect to the needed mixing time.

For color, statistically significant differences ($p < 0.05$) were observed between the samples due to the three factors: the degree, type of alkalization and the alkali agent.

In agreement with the color of the cocoa powders used in the formulation, the dough with the lighter color (lower L* value) was that prepared with the C#_ $NaHCO_3$ cocoa, followed by that prepared with N#_K_2CO_3 under both the mild (M) and strong (S) alkalizing conditions. In all cases, and as expected, the samples formulated under the strong-alkalization conditions were darker than those made under the mild ones.

Regarding color purity values (C*), the dough formulated with cocoas alkalized using a mild alkalization intensity exhibited a purer color than those prepared with the cocoas alkalized under strong conditions. The dough made with the C#_ $NaHCO_3$ cocoa was purer in color under the mild- and strong-alkalization conditions. The sample with less color purity was made with KOH.

Significant differences appeared in the h* values between the mild and strong alkalization conditions when each alkalized cocoa powder was employed. In accordance with cocoa powders (see Table 3), in all the cases strong conditions gave a more reddish hue. At the two alkalization conditions (M and S), statistically significant differences ($p < 0.05$) were found between the hue of the doughs made with the alkalized cocoa in the cakes with sodium bicarbonate (C#_$NaHCO_3$) and the rest. No statistically significant differences ($p < 0.05$) were observed between alkalization in nib (N#_K_2CO_3) and cake (C#_K_2CO_3) for either alkalization conditions.

When comparing the dough color values with the cocoa powder color results, the correlation between them was high. The correlation for the L* value was 0.86 if extrinsic color was compared and was 0.87 if intrinsic color was compared. The correlation values for C* and h* were 0.95 and 0.85 and 0.98 or 0.92 for extrinsic or intrinsic color, respectively. In short, the correlation between cocoa powder color and dough was quite relevant and higher if intrinsic color was compared. However, lack of a total correlation between cocoa powder and the corresponding cocoa dough indicates that cocoa color in a certain application not only depends on its own interaction, but also on its interactions with other food constituents, such as proteins, fat or polysaccharides.

Table 4. pH and color of the doughs prepared with different alkalized cocoa powders.

	pH	Color		
		L*	C*	h*
NM_K_2CO_3	7.5^{A}	18^{abB}	16.8^{abB}	47.4^{abB}
CM_K_2CO_3	7.5^{A}	19^{bB}	$16.^{abB}$	46.4^{aB}
CM_KOH	7.5	17^{aB}	15.8^{aB}	46.3^{aB}
CM_$NaHCO_3$	7.6	25^{cB}	18.8^{bB}	51.9^{bB}
NS_K_2CO_3	7.7^{bB}	13^{bA}	9.1^{bA}	39.9^{aA}
CS_K_2CO_3	7.7^{bB}	13^{abA}	9.0^{abA}	40.1^{abA}
CS_KOH	7.5^{ab}	11^{aA}	8.8^{aA}	40.1^{abA}
CS_$NaHCO_3$	7.4^{a}	14^{cA}	9.7^{bA}	42.9^{bA}
Pooled standard deviation (n=9)	0.1	2	0.5	0.6

*N#_K_2CO_3 = Nib-alkalized cocoa with K_2CO_3; C#_K_2CO_3 = Cake-alkalized cocoa with K_2CO_3; C#_KOH = Cake-alkalized cocoa with KOH; C#_$NaHCO_3$ = Cake-alkalized cocoa with $NaHCO_3$; #=M = mild alkalization conditions; #=S = strong alkalization conditions. L * = luminosity; C * = chroma; h * = hue. Values with different lowercase letters in the same column indicate statistically significant differences ($p < 0.05$) between cocoa powders with different alkalizing agents or type of alkalization (Nib (N) or Cake (C)) at medium (M) or strong (S) alkalization conditions. Values with different capital letters in the same column indicate statistically significant differences ($p < 0.05$) between cocoas with different percentages of alkali for the same alkalizing agent or type of alkalization. Data were analyzed with Kruskal-Wallis test and Dunn's multiple comparison test.*

3.2.2 Rheology

In addition to color and flavor, alkalization type is believed to affect the water-holding capacity of cocoa in pastry and confectionery products, and that nib-alkalized cocoa retains much more water than cake-alkalized cocoa to, thus, affect cocoa rheology (Olam Cocoa, 2017).

In order to evaluate this possible affects, the dynamic strain sweep data of all the doughs were studied. Figure 2 depicts the evolution of the storage modulus values (G ', which measures the elastic component) and the loss module (G", which measures the plastic component) according to the frequency with which cakes are prepared with the different types and degrees of cocoa powder alkalization. This measurement is important because cake volume and texture correlate with dough rheological properties (Sahin, 2008).

The doughs prepared with cocoas under the mild alkalization conditions (Fig. 1a) obtained higher G’ values than those for G", which indicates greater elastic behavior. This behavior was also evident in the sponge cakes under the high alkalization conditions (Fig. 1b).

Among the doughs prepared with the alkalized cocoa powders under the mild conditions (Fig. 2a), the dough prepared with the N#_K_2CO_3 cocoa showed dominating elastic and viscous modulus than the dough prepared with C#_K_2CO_3. When comparing the rheology of the doughs prepared with alkalized cake cocoas, alkalization with K_2CO_3 conferred dough more elasticity than the other alkalis. No statistical differences ($p>0.05$) in viscous modulus were observed.

Under the strong conditions (Fig. 2b), alkalization type (nib and cake) did not affect either elastic or viscous modulus. However, when comparing the values of the doughs containing alkalized cake powders, the dough containing the cocoa powder alkalized with KOH (CS_KOH) displayed more elasticity than the other doughs. No differences were found in viscous modulus among the different formulations. These data indicate that the degree of alkalization is the factor that most affects dough rheology when cocoa is incorporated, followed by alkalization type or the employed alkalizing agent.

By taking the rheology results into account, it can be concluded that alkalization type (nib or cake) affects dough rheology. However, in this formulation, this process variable could influence rheology to the same extent as the degree of alkalization or alkali type.

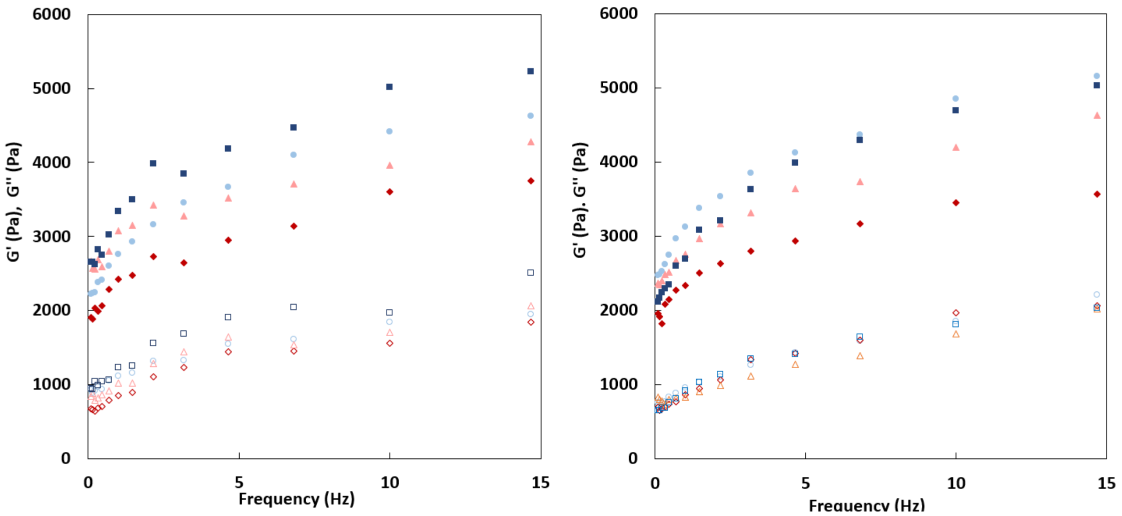

Fig. 2 Viscoelastic properties of sponge cakes made cocoa samples alkalized in mild (a) and strong (b) conditions. G' (filled symbols), G'' (white symbols). N_K_2CO_3 (dark blue squares), C_K_2CO_3 (light blue circles), C_KOH (dark red rhombuses), C_$NaHCO_3$ (light red triangles).

3.3 Cake characterization

3.3.1 Water loss, moisture, density and rise of cakes

Table 5 offers the values obtained for water loss, moisture, density and rise of cakes. It is important to study these variables because the alkali concentration might affect final product properties. For example, baking products can be affected by introducing certain alkalized cocoas due to the alkalizing agent's leavening effect (Olam Cocoa, 2017). However as observed, neither the type or degree of alkalization of the cocoa powder used in the sponge cake formulation had a statistically significant effect ($p > 0.05$) on the water loss, moisture, rise noted for doughs during baking and density. These data also confirmed that the possible water-holding capacity modification due to different alkalization process did not affect moisture or water loss after baking.

Table 5. Moisture, water loss, rise and density of the cakes prepared with different alkalized cocoa powders after baking.

	Moisture (g/100 g)	Water loss (g/100g)	Rise (cm)	Density (g/ml)
NM_K_2CO_3	26.0	10.2	7.3	0.47
CM_K_2CO_3	26.8	10.6	8.0	0.48
CM_KOH	26.7	10.5	8.5	0.472
CM_$NaHCO_3$	25.9	10.5	8.3	0.47
NS_K_2CO_3	26.6	11.0	9.0	0.47
CS_K_2CO_3	26.5	10.7	8.7	0.46
CS_KOH	26.4	10.6	8.0	0.47
CS_$NaHCO_3$	26.1	10.2	8.6	0.46
Pooled standard deviation (n=9)	0.9	0.4	0.4	0.02

N#_K_2CO_3 = Nib-alkalized cocoa with K_2CO_3; C#_K_2CO_3 = Cake-alkalized cocoa with K_2CO_3; C#_KOH = Cake-alkalized cocoa with KOH; C#_$NaHCO_3$ = Cake-alkalized cocoa with $NaHCO_3$; #=M = mild alkalization conditions; #=S = strong alkalization conditions. The differences found between cakes prepared with cocoa powders with different alkalizing agents or type of alkalization (Nib (N) or Cake (C)) at medium (M) or strong (S) alkalization conditions were not statistically significant (p> 0.05) using the Kruskal-Wallis test.

3.3.2 Color determination

Table 6 shows the L *, C *, h* values of cake crust and crumb. When the cake-alkalized cocoa with sodium bicarbonate under the mild and strong alkalization conditions (C#_ $NaHCO_3$) was used, sponge cake crust became lighter and had yellowish color with higher saturation. Under the mild-alkalization conditions, the darkest color with less color purity was obtained when using KOH as alkalizing salt. No statistically significant differences were found among cake- and nib-alkalized cocoas with K_2CO_3 for most of the analyzed parameters. These results agree with the color trends observed in the powder in which they were prepared.

Similarly, with sponge cake crumb, the use of cake-alkalized cocoa under the mild conditions of sodium bicarbonate (CM_ $NaHCO_3$) generated a lighter, more saturated and yellower crust. Under the strong alkalizing conditions, the cake-alkalized cocoa with potassium hydroxide (CS_KOH) conferred crumb more darkness and less color purity. The cake alkalinized with sodium bicarbonate (CS_ $NaHCO_3$) gave a more yellowish tone than the other samples.

When these data were correlated with the color coordinates of the cocoa powders, the correlation was around 0.95 for the L* value, 0.97 for the C* value and 0.86 for the h* value when the intrinsic color values were used.

Table 6. Color of the crust and crumb of the cakes prepared with different alkalized cocoa powders.

	Crust			**Crumb**		
	L*	**C***	**h***	**L***	**C***	**h***
NM_K_2CO_3	35^{bB}	17.0^{aB}	49.2^{aB}	21^{bB}	12.5^{aB}	42^{bB}
CM_K_2CO_3	34^{bB}	17.0^{aB}	50.1^{abB}	21^{bB}	12.6^{aB}	42^{abB}
CM_KOH	33^{aB}	16.4^{aB}	52.3^{bB}	19^{aB}	11.7^{aB}	41^{a}
CM_$NaHCO_3$	37^{cB}	18.3^{bB}	55.9^{cB}	22^{bB}	15.7^{bB}	46^{cB}
NS_K_2CO_3	29^{aA}	11.3^{bA}	42.7^{aA}	17^{bA}	9.5^{cA}	37^{aA}
CS_K_2CO_3	29^{aA}	10.0^{bA}	45.0^{bA}	17^{abA}	6.9^{bA}	39^{abA}
CS_KOH	29^{aA}	8.5^{aA}	46.2^{bA}	16^{aA}	5.5^{aA}	40^{b}
CS_$NaHCO_3$	32^{bA}	11.3^{bA}	49.0^{cA}	18^{bA}	10.0^{cA}	42^{cA}
Pooled standard deviation (n=21)	2	0.5	0.9	2	0.6	1

*N#_K_2CO_3 = Nib-alkalized cocoa with K_2CO_3; C#_K_2CO_3 = Cake-alkalized cocoa with K_2CO_3; C#_KOH = Cake-alkalized cocoa with KOH; C#_$NaHCO_3$ = Cake-alkalized cocoa with $NaHCO_3$; #=M = mild alkalization conditions; #=S = strong alkalization conditions. L * = luminosity; C * = chroma; h * = hue. Values with different lowercase letters in the same column indicate statistically significant differences ($p < 0.05$) between cocoa powders with different alkalizing agents or type of alkalization (nib or cake) for the same percentage of alkali; Values with different capital letters in the same column indicate statistically significant differences ($p < 0.05$) between cocoas with different percentages of alkali for the same alkalizing agent or type of alkalization. Data were analyzed with Kruskal-Wallis test and Dunn's multiple comparison test.*

3.3.3 Texture

Regarding cake texture, the texture profile analysis (TPA) found that the type of alkalization and alkali used to manufacture cocoas had a statistically significant effect ($p < 0.05$) on the hardness, cohesiveness, resilience and elasticity of cakes. Table 7 shows that the cakes with the cocoas prepared under the mild alkalization conditions presented greater hardness than those prepared under the strong alkaline conditions. For the mild alkalization conditions, the use of alkalized cocoa with potassium carbonate (K_2CO_3) in nib or cake conferred cake greater hardness than the other alkalis, and no statistically significant differences were observed between both. Under the strong alkalizing conditions, the hardness of the cake formulated with NS_K_2CO_3 was greater than when CS_K_2CO_3 was used.

Cakes prepared with cocoa alkalized with K_2CO_3 obtained lower cohesiveness (internal food structure resistance) and resilience (ratio of recoverable energy as the first compression is released) values than those prepared with KOH or $NaHCO_3$. Statistical differences were found ($p< 0.05$) for alkalization intensities (mild or strong).

Regarding elasticity, the cakes prepared with cocoas alkalized with mild conditions presented less elasticity than those prepared with cocoas alkalized in strong ones. Under the mild alkalization conditions, the alkalinized cake cocoa with potassium hydroxide (C#_KOH) provoked greater elasticity in sponge cakes than the other employed alkalis. Cakes prepared with cocoas alkalized under the strong conditions showed a lower elasticity. No statistically significant differences ($p> 0.05$) were observed for elasticity between cakes prepared with cocoas alkalized in nib (N#_K_2CO_3) and cake (C#_K_2CO_3) at either alkalization intensity.

Table 7. TPA parameters for sponge cakes prepared with different alkalized cocoa powders.

	Hardness(N)	**Cohesiveness**	**Resilience**	**Elasticity**
NM_K_2CO_3	13^{bB}	0.57^{aA}	0.23^{aA}	0.89^{aA}
CM_K_2CO_3	13^{bB}	0.58^{a}	0.24^{aA}	0.90^{aA}
CM_KOH	11^{aB}	0.63^{bB}	0.27^{bB}	0.92^{bB}
CM_$NaHCO_3$	10^{aB}	0.63^{bB}	0.27^{b}	0.91^{abA}
NS_K_2CO_3	11^{bA}	0.60^{aB}	0.25^{aB}	0.92^{bB}
CS_K_2CO_3	10^{aA}	0.60^{a}	0.26^{bB}	0.92^{bB}
CS_KOH	10^{aA}	0.59^{aA}	0.26^{bA}	0.90^{aA}
CS_$NaHCO_3$	10^{aA}	0.62^{bA}	0.27^{b}	0.92^{bB}
Pooled standard deviation (n=30)	2	0.03	0.02	0.02

N#_K_2CO_3 = Nib-alkalized cocoa with K_2CO_3; C#_K_2CO_3 = Cake-alkalized cocoa with K_2CO_3; C#_KOH = Cake-alkalized cocoa with KOH; C#_$NaHCO_3$ = Cake-alkalized cocoa with $NaHCO_3$; #=M = mild alkalization conditions; #=S = strong alkalization conditions. Values with different lowercase letters in the same column indicate statistically significant differences ($p < 0.05$) between cocoa powders with different alkalizing agents or type of alkalization (nib or cake) for the same percentage of alkali. Values with different capital letters in the same column indicate statistically significant differences ($p < 0.05$) between cocoas with different percentages of alkali for the same alkalizing agent or type of alkalization. Data were analyzed with Kruskal-Wallis test and Dunn's multiple comparison test, since only Hardness passed the normality and homoscedasticity tests.

3.3.4 Sensory analysis

In parallel to the instrumental evaluation, cake samples were sensory-evaluated by a panel of untrained consumers (n=40). To measure product liking and preference, the hedonic scale is a unique scale that provides reliable and valid results (Stone, Bleibaum, & Thomas, 2012). Consumers were asked to evaluate six sample attributes on a 7-point hedonic scale. The sensory test results are shown in Table 8. Despite the number of testers could limit the reliability of results, the statistical analysis revealed no statistically significant differences ($P > 0.05$) in color, sponginess, taste, chocolate flavor, mouthfeel and overall appreciation terms, and demonstrated the degree of similarity between the samples that differed in the process stage in which alkalization was produced (cocoa nibs and cocoa cake) with alkalizing agents (KOH, K_2CO_3 and $NaHCO_3$) and alkalization intensity (mild and strong). These results were surprising because it was considered that the selection of specific cocoas to prepare certain products would be important to guarantee consumer acceptance (Shankar, Levitan, Prescott, & Spence, 2009). In this case, and despite color and sensory profile determinations were significantly different among samples, consumer acceptance was similar. It indicates that the matrix can mask most cocoa attributes.

However, the data revealed that despite there being no correlation between instrumentally measured color and sensory preference, the instrumental color crumb values showed a good correlation ($r=0.77$) for the global evaluation. In this way, darker cocoa cakes (lower L^* values) obtained a better global evaluation value (KOH alkalizing agent), which confirmed what was previously established: darker products are generally better appreciated by consumers as color has a strong impact on perceived flavor (Spence, 2015).

Table 8. Sensory attribute scores for sponge cakes prepared with different alkalized cocoa powders.

	Color	Sponginess	Taste	Chocolate aroma	Global evaluation
NM_K_2CO_3	7^a	5	6	6	6
CM_K_2CO_3	7^a	6	5^A	6	6
CM_KOH	7^a	6	6	6	6
CM_$NaHCO_3$	5^b	6	5^A	6	6
NS_K_2CO_3	6	6	7	6	6
CS_K_2CO_3	7	6	7^B	6	6
CS_KOH	7	6	7	6	7
CS_$NaHCO_3$	7	6	7^B	6	6
Pooled standard deviation (n=40)	2	2	2	2	2

N#_K_2CO_3 = Nib-alkalized cocoa with K_2CO_3; C#_K_2CO_3 = Cake-alkalized cocoa with K_2CO_3; C#_KOH = Cake-alkalized cocoa with KOH; C#_$NaHCO_3$ = Cake-alkalized cocoa with $NaHCO_3$; #=M = mild alkalization conditions; #=S = strong alkalization conditions. Values with different lowercase letters in the same column indicate statistically significant differences ($p < 0.05$) between cocoa powders with different alkalizing agents or type of alkalization (nib or cake) for the same percentage of alkali; Values with different capital letters in the same column indicate statistically significant differences ($p < 0.05$) between cocoas with different percentages of alkali for the same alkalizing agent or type of alkalization. Data were analyzed with ANOVA and LSD post hoc test.

4. Conclusions

This is one of the first works aiming to understand the effect of alkalization type (nib or cake), alkali (K_2CO_3, KOH and $NaHCO_3$) and alkalization intensity (mild and strong) not only on cocoa powder quality parameters, but also on those of the corresponding doughs and cakes where they are included. The study evidences that KOH provides the darkest, most reddish and least saturated cocoa, while $NaHCO_3$ yields the lightest one. This general behavior is kept after the preparation of the dough and the cake. Comparing nib-and cake-alkalized powders with K_2CO_3, it can be noted that color differences are not significant for most of the parameters in both, cocoa powders and corresponding cakes. The same happens to texture, but not for rheology, where the doughs prepared with the nib-alkalized powders in mild conditions exhibit the higher elastic modulus. Despite these differences, consumers' satisfaction with different cakes was very similar, although darker products were perceived as tastier. By considering these attributes, the best conditions for processing cocoa if used to prepare cakes should be alkalization in cake (processing is more economical and does not reduce consumer perceived sensory quality). Moreover, KOH and strong alkalizing conditions should be preferred to obtain a product as dark as possible and thus, to allow consumers to perceive a more intense cocoa flavor.

Acknowledgements

The authors wish to acknowledge the financial assistance provided by the Ministerio de Economía, Industria y Competitividad (Spanish Government) and the European Regional Development Fund (Project RTC- 2016-5241-2).

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5. Chapter III

Chapter III: In situ cocoa alkalization during sponge cake baking: a new strategy to obtain clean label bakery products

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Submitted to LWT

Abstract

Alkalized cocoa powder has been widely used for years in the baking industry for its capacity to confer the products into which it is incorporated a really dark chocolate color. However, new labeling regulation trends, according to which alkalized cocoa powder or liquor should be declared on labels as "alkali-treated cocoa”, might pose a problem for those consumers who demand clean labels. In this scenario, in situ cocoa alkalization performed by sodium bicarbonate, a common processing aid used as a leavening agent during the baking process, is a promising strategy. The objective of the present work is to study the effect of increasing the levels of the sodium bicarbonate used in cake formulation on the physico-chemical and sensory properties of sponge cakes containing natural- and medium-alkalized cocoa. The results demonstrated that the obtained sponge cakes prepared with natural cocoa and 1.5-1.8-fold the amount of bicarbonate used as a leavening agent exhibited similar coloration, texture and flavor to those with medium-alkalized cocoa. In any case, acceptable sponge cakes with a comparable color to those baked with strong-alkalized cocoa were obtained. When using medium-alkalized cocoa powder and 1.5-1.8-fold the amount of bicarbonate, sponge cakes had similar sensory and texture attributes to those of strong-alkalized cocoa powders. These results confirm the suitability of using sodium bicarbonate for the in situ alkalization of cocoa powder, which acts as a leavening agent at the same time. As it is a common processing aid in cocoa cake formulation, its use would not affect consumer perception of what is considered a clean label and would not, thus, be rejected by consumers.

Keywords Clean label, natural cocoa powder, alkalized cocoa powder, sponge cake, alkali agents, sodium bicarbonate,

1. Introduction

Cocoa powder is known for being a nutritional ingredient with high diverse functional content. However, cocoa is used in most food industry applications to confer a myriad of end products (ice-creams, fillings, cakes, etc.) flavor and color. The importance of employing cocoa powder with high coloring capacity is highlighted by the general trend to restrict the use of artificial colors (Regulation EU No 1129/2011). Utilizing these additives is strictly regulated in the EU, the USA, and many other countries worldwide. There is growing concern about the safety of some frequently used legal food colorants and the general trend is to replace synthetic forms with natural products (Oplatowska-Stachowiak et al., 2017). Given this situation, alkalization is becoming so important. This process, also known as “Dutching”, was a treatment first conceived by Coenraad Johannes van Houten in the 19th century to enhance cocoa powder solubility. However after its implementation, industry discovered its capacity to modify color and flavor, and started using it with cocoa nibs, liquors and cakes (Olam, 2017).

In general, natural and light-alkalized powders are employed to prepare chocolates, milk chocolate, ice-creams, instant drink mixes, coatings and fillings. Medium- and strong-alkalized cocoas are generally used in ice-creams, cookies, cakes, coatings and chocolate truffles. Finally, black powders are utilized to prepare products with specific sensory characteristics, such as Oreo-type cookies. The selection of specific cocoas to prepare certain products is important because consumer studies have demonstrated that color has a strong impact on perceived flavor (Valverde et al., 2020). This point highlights the importance of modifying cocoa properties by the alkalization operation.

Due to these appealing properties, alkalization, although unknown to consumers, has for years been a very extended process to confer cocoa new and extraordinary coloring properties. According to Codex Stan 192-1995, the following additives can be used as alkali agents in cocoa processing: sodium carbonate, sodium acid carbonate (sodium bicarbonate), sodium hydroxide, ammonium carbonate, ammonium hydroxide, carbonate calcium, calcium hydroxide, magnesium carbonate, potassium carbonate, among others (Codex

Alimentarius, 2019). The desired products can be obtained by varying the proportion of these ingredients. Each one results in different aromas and functional attributes (Moser, 2015).

However, two recent legislative changes might affect the consumption of alkalized cocoa in forthcoming years.

On the one hand, the EU additives Regulation defines the levels of certain authorized alkalizing agents used as additives in foods (EU Commission Regulation No. 1129/2011). In general, the level of alkalizing agent employed in other food applications, including baked goods, certain dairy products and ice-creams, is currently set at Quantum Satis (the amount needed). However, the European Cocoa Association has provided a recommendation for cocoa powders which, when sold as such to final consumers, states that the level of alkalizing agents is set at a maximum level of 7% dry matter, without fat and expressed as potassium carbonates (ECA, 2019). Despite the fact that this amount is not really habitual, it might be needed to obtain certain reddish or black colors.

The second possible restriction to the future use of alkalized cocoas is related to the 2022 publication of the Code of Federal Regulation, Title 21, Volume 2, part 163. This regulation implies that when cacao nibs, or cacao beans from which they are prepared, are processed with alkali, the food name shall be accompanied by the "Processed with alkali" statement on labels (FDA, 2022). This new consideration goes against the new clean-label trend, which consists of consuming products produced free of ‘chemical’ additives, having easy-to-understand ingredient lists and being produced by traditional techniques with limited processing (Edwards, 2013). Thus in forthcoming years, the demand of strongalkalized cocoas it is expected to lower with the consequent loss in the offer of products that incorporate them.

Therefore, obtaining a product with similar characteristics to those of alkalized cocoa using natural cocoa would avoid having to state “treated with alkali”.

One of the alkaline cocoa applications that could benefit from this cleaning label is chocolate-flavored sponge cakes made with cocoa. Chemical leavening agents are used to bake them, and two components are involved: an acidulant and bicarbonate salt. The acidulant neutralizes bicarbonate salt in the presence of water to produce carbonic acid, which rapidly decomposes into carbon dioxide and water (Zhou, Therdthai, & Hui, 2014). Sodium bicarbonate, also known as "baking soda", is the commonest carbon dioxide source. It is low-cost, extremely pure and easy to handle, and leaves no after taste (Pop, 2007). Regarding the food safety of this additive, the Codex Alimentarius, in Codex Stan 192-1995, assigned the functional classes of leavening and alkalizing agents with no maximum usage dose. This dose is regulated by Good Manufacturing Practices (GMP) (Codex Alimentarius, 2019).

In this context, the present work aims to determine whether it is possible to substitute strong-alkaline cocoas (alkali content higher > 7%) for natural- or medium-alkalized cocoas to bake chocolate-flavored cakes while maintaining their physico-chemical and sensory properties. For this purpose, we propose studying the effect of increasing the amount of sodium bicarbonate on not only cocoa color and aroma development, but also on other physico-chemical and sensory cake properties.

2. Materials and methods

2.1 Materials

The ingredients employed to prepare cakes were flour (Aragonesa, Huesca, Spain), sunflower oil (Hacendado, Sovena, Spain), white sugar (Pfeifer & Langer, Colonia, Germany), egg powder (Catereasy, Barcelona, Spain), sodium bicarbonate (Hacendado, Alicante, Spain), skimmed milk (Hacendado, Urnieta, Spain), salt (Marismeña, Huelva, Spain), food-grade tartaric acid (La Tienda del Cervecero, Murcia, Spain), food-grade malic acid (Health Leads, UK) and cocoa powder. All the cocoa powders were supplied by Olam Food Ingredients S.L. (Cheste, Spain). The utilized cocoa powders were natural (N), light-alkalized (LA), medium-alkalized (MA) and strong-alkalized (SA).

2.2 Dough preparation

For each proposed formulation, 1000 g of dough were prepared in a Thermomix TM 31 food processor (Vorwerk, Wuppertal, Germany). The control samples were prepared by mixing 37 g of reconstituted powdered egg in 160 ml of water with 256 g of sugar for 2 minutes at speed 4. Subsequently, 65 mL of milk, 2.5 g of malic acid and 2.5 g of tartaric acid were added to the mixture, which was stirred for 1 minute at the same speed. Then 230 g of flour, 51 g of the N or alkalized cocoa (LA, MA and SA) powder, 8 g of sodium bicarbonate and 1.9 g of salt were added and mixed for 2 minutes at speed 3. Finally, another lot of 65 mL of milk and 118 g of oil were added and mixed for 3 minutes at speed 4. Each formulation was repeated 3 times on different days to include variability in sample preparation (n=3).

In parallel, the samples with the most sodium bicarbonate were prepared in two phases:

Phase I. Cocoa N and different levels of bicarbonate as a leavening agent (1.5-, 1.8-, 2, 3- and 4-fold the amount of the control recipe) were tested

Phase II. Cocoa MA and different levels of bicarbonate as a leavening agent (1.5-, 1.8- and 2-fold the amount of the control recipe) were tested

2.3 Cake preparation

Once doughs had formed (Section 2.2), three aliquots (300 g each) were placed inside a metal mold (16 cm x 8 cm) and left in a SelfCookingCenter® scc 62 oven (Rational, Landsberg am Lech, Germany) to be baked. In this way, each dough produced three cakes (n=9). The baking process took place at 190 ºC, with medium-high dry-air ventilation for 18 minutes. After baking, cakes were cooled to room temperature (approx. 1 h). Subsequently, physico-chemical and sensory analyses were carried out.

2.4 Cake characterization

2.4.1 Water loss

The percentage of total water loss during baking was determined from the weights of the cake dough before and after baking using the following expression:

$$Water\ loss = \frac{Mi - Mf}{Mi}$$

where: Mi = weight before baking (g); Mf = weight after baking (g).

2.4.2 Specific volume

The specific cake volume was measured by the millet seed displacement method using high-density polyethylene spheres as material (Sahin and Sumnu, 2006). The specific cake volume was calculated as the ratio between the volume displaced by cake (mL) and cake weight (g).

2.4.3 Color analysis

The baked cake color was measured with the help of a CM-700d spectrocolorimeter (Konica Minolta, Ramsey, USA) and a CM-A181 standard mask for a 3 mm-diameter SAV. For measurements, a 10º visual angle, a D65 illuminator and the included specular component mode (SCI) were selected. Color was measured at 12 different locations (n=108).

The results were expressed according to the CIE-Lab system (D65 illuminant and 10º viewing angle). Measurements were taken with a 3 mm-diameter diaphragm inset. The measured parameters were L* (L* = 0 (black), L* = 100 (white)), a* (+a* = red) and b*(+b* = yellow). Using color values L*, a* and b*, hue (h*ab) and chroma (C*ab) were calculated by the following equations:

$$h_{ab}^{*} = \arctan\frac{b^{*}}{a^{*}} \quad \text{Eq. 1}$$

$$C_{ab}^{*} = \sqrt{a^{*2}+b^{*2}} \quad \text{Eq. 2}$$

The global color difference (ΔE *) between the cakes made with different bicarbonate levels (phase I and phase II) and the corresponding control cakes was calculated by applying Equation 4 (Mokrzycki and Tatol, 2011).

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

2.4.4 Moisture analysis

Cake moisture was determined by the AOAC method 650.46 (AOAC, 1997). For this purpose, 3 g of sponge cake were left to cool to room temperature and taken to a heat and drying chamber FD 115 (Binder, Tuttlingen, Germany), which had been previously programmed at a temperature of 100±1 ºC overnight. By knowing the difference in sample weight before and after drying, moisture content was determined by this expression:

$$\%\ \text{Moisture} = \frac{\text{Wi - Wf}}{\text{Wm}} * 100 \qquad \text{Eq. 3}$$

where: Wi = crucible + wet sample weight (g); Wf = crucible + dry sample weight (g); Wm = sample weight. Determinations were done in duplicate for each cake (N=18).

2.4.5 Texture analysis

The texture parameters (strength, cohesiveness, resilience, elasticity) of sponge cakes were determined by a double compression test (TPA) using the TA-XT plus texture analyzer (Stable Micro Systems, Godalming, England) equipped with a probe (40 mm diameter). The probe speed was 1 mm/s (pre-test and test) and 2 mm/s (post-test), with 50% deformation and a 30-second waiting time between compressions. For this test, each cake was cut into six pieces (2 cm thick) with a metal cylinder. All the pieces underwent a texture analysis (n=54).

2.4.6 Imagen analysis

An image analysis was performed to study how the different cocoa powder types and the addition of differing amounts of sodium bicarbonate affected the crumb and cake structure of the baked sponge cakes. For this purpose, different cakes were cut into 2 cm-thick slices. Each slice was scanned on both sides in a Canon Lide 220 scanner (Amstelveen, Holland), which gave 12 images (readings) per cake.

To segment the pixels that could be considered bubbles or structure, the band threshold method was applied, followed by a growth process, as reported by other authors (Verdú et al., 2015). In the first step, the pixels with a value below the threshold that collected the darkest tones up to black (Th1) were classified as bubbles, while the pixels of the second threshold (Th2, which extended to white), were classified as structure/matrix. In the second step, the pixels between thresholds Th1 and Th2 (indeterminate pixels) were classified as bubbles or structure by considering the well-classified neighboring pixels, which implies a growth process. This technique was carried out based on previous works (Benlloch et al., 1995; Benlloch et al., 1996a; Benlloch et al., 1996b). With this information, the number, size, distribution and circularity of bubbles were calculated.

2.4.7 Sensory

The sensory evaluation of samples was carried out by the students and staff of the UPV's Food Technology Department, Spain (n=32) following Standard UNE-ISO 6658: 2019 guidelines (AENOR, 2019) in a tasting room designed according to Standard UNE-EN ISO 8589: 2010 (AENOR, 2010). The untrained tasters panel evaluated the product’s color, aroma, texture, taste and mouthfeel, and overall appreciation, on a 5-point hedonic scale (1 = I dislike it a lot, 5 = I like it a lot) in each sample, which were assigned a 3-digit code as indicated in Standard UNE-ISO 4121: 2006 (AENOR, 2006).

2.4.8 Statistical analysis

Differences between samples were determined by a multifactorial analysis of variance (MANOVA), with a confidence level of 95% LSD ($p < 0.05$). Data were analyzed by the STATGRAPHICS Centurion XVI v. 17.2.04 statistical software (Manugistics Inc., Rockville, MD, USA).

3. Results and discussion

3.1 Cake characterization

3.1.1 Water loss, moisture, and specific volume

Table 1 shows the moisture, water loss and specific volume values of the samples made with cocoa powder at different degrees of alkalization (considered the control samples). For these control samples, the moisture values ranged between 31.1±0.7% and 31.9±0.4%, those of water loss between 7.9±0.6% and 8.6±0.4% and those of specific volume between 2.7±0.1 mL/g and 2.8±0.2 mL/g. The statistical data analysis revealed that there were no statistically significant differences ($p > 0.05$) among the control samples.

Table 1. Cake moisture, water loss and specific volume.

		Moisture (g/100g))	**Water loss (g/100g)**	**Specific volume (mL/g)**
Control samples	N	31.8±0.7 ^{cd}	8.6±0.4 ^{d}	2.8±0.2 ^{de}
	LA	31.9±0.4 ^{d}	8.3±0.5 ^{cd}	2.8±0.3 ^{de}
	MA	31.1±0.7 ^{bcd}	8.5±0.3 ^{cd}	2.8±0.2 ^{de}
	SA	31.7±0.4 ^{cd}	7.9±0.6 ^{bc}	2.7±0.1 ^{cde}
Samples with N cocoa	1.5N	31.8±0.5 ^{cd}	7.9±0.6 ^{bc}	2.8±0.1 ^{de}
	1.8N	31.0±0.3 ^{bc}	7.9±0.6 ^{bc}	2.6±0.1 ^{bcd}
	2N	31.2±0.5 ^{bcd}	7.3±0.3 ^{ab}	2.7±0.1 ^{cde}
	3N	30.8±0.4 ^{ab}	7.0±0.2 ^{a}	2.5±0.1 ^{abc}
	4N	30.1±0.5 ^{a}	7.0±0.2 ^{a}	2.4±0.1 ^{ab}
Samples with MA cocoa	1.5MA	30.5±0.4 ^{ab}	8.2±0.3 ^{cd}	2.9±0.1 ^{e}
	1.8MA	30.1±0.4 ^{a}	8.0±0.1 ^{cd}	2.7±0.1 ^{cde}
	2MA	30.1±0.6 ^{a}	8.1±0.2 ^{cd}	2.3±0.2 ^{a}

Different lowercase letters denote statistically significant differences between cocoa percentages ($p < 0.05$).

Table 1 also shows the moisture, water loss and specific volume values for the samples made with cocoas N and MA and increasing amounts of sodium bicarbonate. Despite finding statistically significant differences, values were similar to those of the control samples, with the lowest values for the samples made with cocoa MA and a higher percentage of sodium bicarbonate. The mild effect of the amount of sodium bicarbonate on the moisture of different bread doughs has also been reported by Zolfaghari, et al, (2017).

For the water loss values, minimum values (7.0±0.2 g/100 g) were obtained in those samples in which the percentage of sodium bicarbonate exceeded 2-fold the established standard percentage.

Finally, the specific volume values related to the N cocoa and MA significantly lowered ($p<0.05$) when the percentage of sodium bicarbonate exceeded 2-fold the established standard percentage, with values of 2.3-2.4 mL/g instead of 2.8-2.9 mL/g. This contradicts that reported by Ali, et. al., (2012). These authors concluded that a leavening agent increases the specific volume of bread samples and their textural characteristics, especially hardness. This is partly related to the specific volume of bread samples. The reason for this may that at such high sodium bicarbonate concentrations, raising is so marked that the gluten network is unable to support the structure and, therefore, finally collapses. This effect was even worse in samples 3M and 4M because gluten network weakening was so great that the structure completely collapsed and no characteristic cake structure was obtained. Therefore, these formulations were removed from the study.

3.1.2 Color measurements

The color coordinates of the crumb of different cakes are shown in Figure 1. As expected, for the controls (Figure 1a), the minimum L*, C* and h* values were obtained with the samples made using cocoa SA because they were baked with the darkest and more reddish powder.

A very interesting result was obtained when using cocoa N or MA. Increasing the amount of sodium bicarbonate led the L *, C * and h* values to progressively lower, with statistically significant differences (p <0.05).

The darkening of flour doughs as a consequence of increasing the amount of bicarbonate levels has been previously reported by Vetter and Zeak (1989). Their study on chemical leavening agents in cookies and crackers concluded that leavening agents like sodium bicarbonate influence product color given their effect on pH. These agents impact pH due to the alkaline action of the carbon dioxide producer (soda). Heidolph (1996) studied systems with chemical leavening and concluded that a high pH favors Maillard reactions. This occurs in the baking stage of the brown color development phase. However in this case, besides the possible effect on Maillard reactions, bicarbonate also affects the pigments contained in cocoa powder because the obtained shades are more typical of alkalinized cocoa than of an alkali-treated mass.

From these data, it can be concluded that it is possible to obtain a similar color to that of the control cakes made with cocoas LA (L * = 24.8±2.3, C * = 17.6±1.9, h * = 46.6±2.4) and MA (L * = 24.8±2.1, C * = 17.8±1.9, h * = 46.4±2.1), using cocoa N and increasing the amount of bicarbonate in the formulation by 1.5-fold (L * = 23.6±2.3, C * = 18.2±1.9, h * = 45.4±2.9).

When comparing the SA control to formulations 4N and 2MA (see Figure 1), colors were darker (lower L* values). This means that by applying sodium bicarbonate additions, it is possible to obtain even darker colors than by employing cocoa SA. This fact would positively influence consumer appreciation. Moreover, the dark brown color in sweets is associated with increased chocolate taste (AINIA, 2012). On the other hand, it allows cocoas with alkali contents < 7% to be used, but the same color would be obtained. What is even more interesting is, in the best case, this strategy allows dark cocoa cakes to be obtained using cocoa N, which might allow product preparation with a cleaner label and not having to include the “treated with alkali” statement on the list of ingredients.

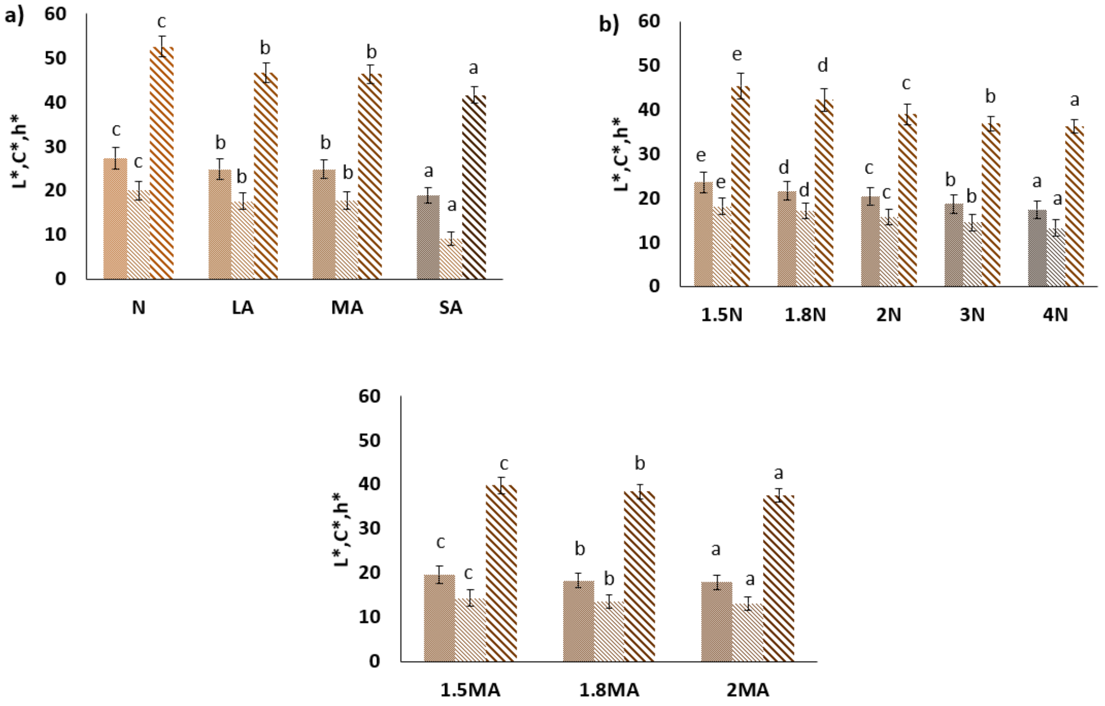


Fig. 1 Values of L * (solid), C * (fine screen) and h * (thick screen) measured in the crust of control cakes (a) and those elaborated with N (b) or MA (c) cocoa and increased amounts of sodium bicarbonate.

The different letters in the same series indicate statistically significant differences (p <0.05) between the different degrees of alkalization (a) or the different levels of bicarbonate (b and c). SD.: standard deviation.

Regarding crust color, Figure 2 shows the color coordinates of the different cakes prepared in this study. Similarly to crumb, by increasing either the degree of alkalization of the cocoa powder employed to prepare the control samples or the percentage of sodium bicarbonate in the samples prepared with cocoa N or MA led the L*, C* and h* values to lower. Moreover, these data allow us to conclude that it is possible to obtain similar color coordinates to those of the control LA (L * = 28.8±2.1, C * = 12.1±2.5) and MA (L * = 28.8±2, C * = 12.5±2.5) cakes by increasing 1.8-fold the amount of bicarbonate (L * = 28.8±2.3, C * = 12.5±2.6).

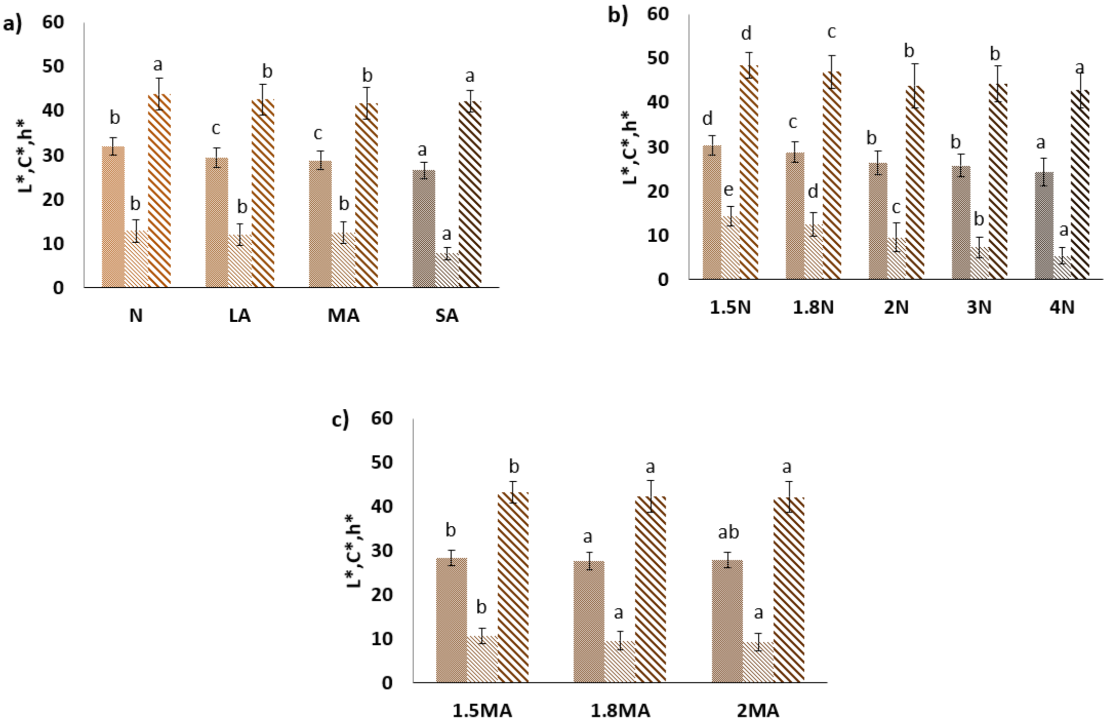


Fig. 2 Values of L * (solid), C * (fine screen) and h * (thick screen) measured in the crust of control cakes (a) and those elaborated with N (b) or MA (c) cocoa and increased amounts of sodium bicarbonate.

The different letters in the same series denote statistically significant differences (p <0.05) between the different degrees of alkalization (a) or the different levels of bicarbonate (b and c). SD.: standard deviation.

Finally, to evaluate how the color differences between the control cakes and those made with increasing amounts of bicarbonate would be perceived by observers, the global color difference was calculated by taking each control cake as a reference. As Tables 2 and 3 indicate, a cake with similar crust and crumb color to that obtained when employing commercial cocoas LA and MA could be obtained with cocoa N and increasing the amount of bicarbonate by 1.5- or 1.8-fold (Table 2). Likewise, a similar color to that provided by cocoa SA could be obtained by utilizing formulations 4N (Table 2), 1.8MA and 2MA (Table 3). In all these situations, the ΔE * values would be below 5, and only when color differences are more than five points can human eyes detect and identify differences (Pawłowska, 2018).

Table 2. Global color difference (ΔE *) between the cakes made with cocoa MA + increasing the amount of bicarbonate and the control cakes.

		Bicarbonate levels				
		1.5N	**1.8N**	**2N**	**3N**	**4N**
Crumb	**LA**	1.39	3.47	5.22	7.35	9.02
	MA	1.33	3.49	5.27	7.41	9.1
	SA	10.19	8.39	6.77	5.43	4.5
Crust	**LA**	2.97	0.82	3.49	5.61	8.13
	MA	2.71	0.74	3.75	5.91	8.42
	SA	7.69	5.22	1.83	0.95	3.37

Table 3. Global color difference (ΔE *) between the cakes made with cocoa MA + increasing the level of bicarbonate and the control cake.

	Bicarbonate levels		
	1.5 MA	**1.8 MA**	**2MA**
Crumb	5.23	4.46	4.18
Crust	3.36	2.08	1.91

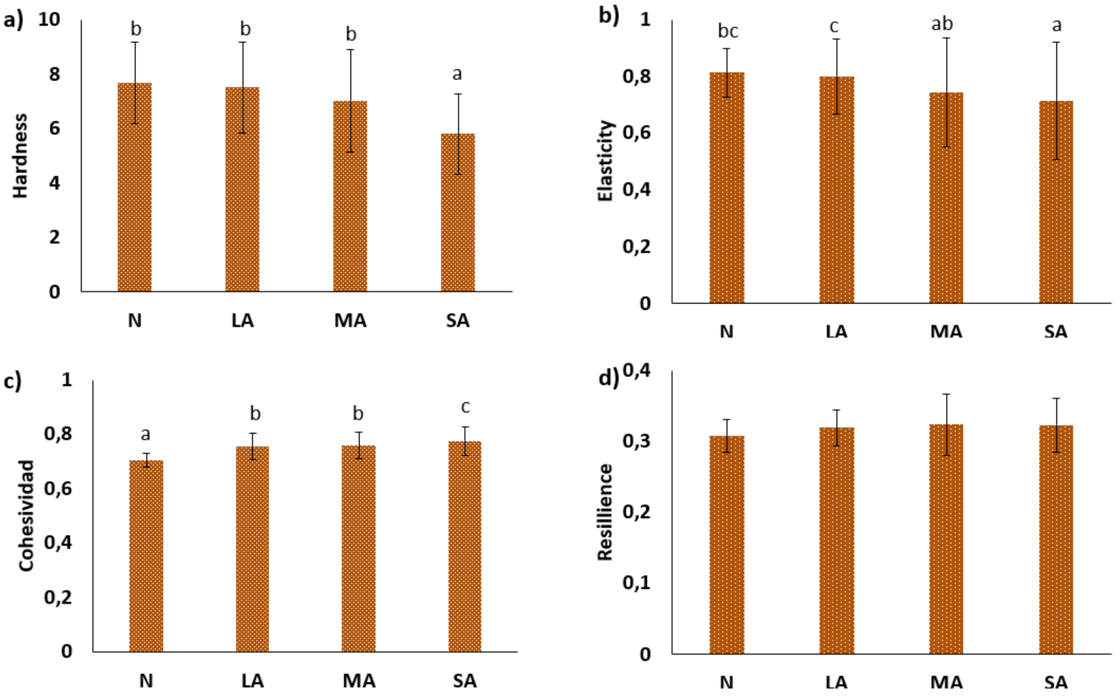
3.1.3 Texture

The influence of increasing sodium bicarbonate in the cakes made with cocoas N and MA in relation to the texture of the control samples was determined by analyzing the texture profile (Figure 3).

Figures 3a and 3b show the influence of the degree of alkalization of cocoa powder on the hardness and elasticity of the cakes made with the different cocoa powder types, respectively. The hardness values ranged between 7.7±1.5 (N) and 5.8±1.5 (SA). The elasticity values ranged from 0.8±0.1 (N and LA) to 0.7±0.2 (SA). With hardness, the increase in the degree of alkalization led values to statistically and significantly lower ($p < 0.05$), and the samples with the lowest hardness values were made with cocoa SA. No statistical differences for elasticity were found.

The effects of increasing the amount of bicarbonate in the cakes prepared with cocoas N and MA on their hardness and elasticity are shown in Figures 5e and 5f, respectively. For hardness, no statistically significant differences were observed between the cakes prepared with cocoa N and increasing the amounts of sodium bicarbonate. However in the samples prepared with cocoa MA, the higher the sodium bicarbonate content, the more the hardness values increase.

For elasticity, the statistical data analysis revealed statistically significant differences ($p < 0.05$), but only in the series of cakes prepared with cocoa N. This was generally due to the differences in the largest amount of bicarbonate. As elasticity is considered a good parameter of starchy products like cakes or muffins (Sanz, et. al. 2009), these results evidenced that cakes would be of maximum quality at up to the 2-fold sodium bicarbonate level.



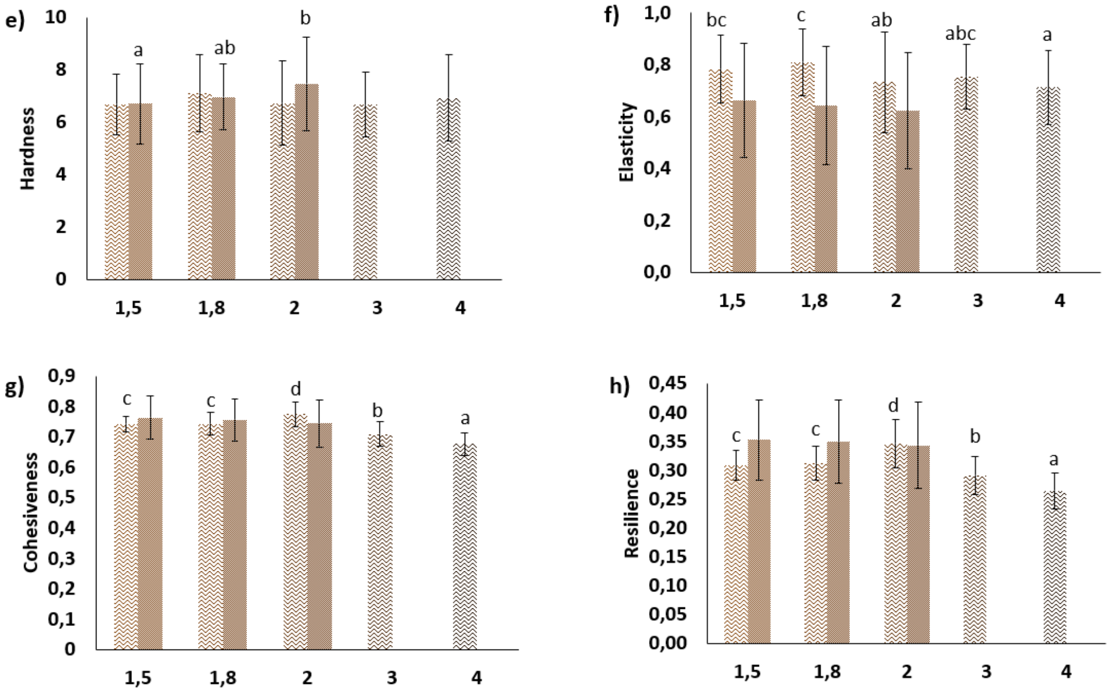


Fig. 3 Values (mean±SD) of the hardness, elasticity, cohesiveness and resilience values measured in the crumb of the control cakes (a, b, c, d), and those made with cocoa N or MA with increasing amounts of sodium bicarbonate (e, f, g, h). Cocoa N (zig-zag pattern). Cocoa MA (brown).

The different letters in the same series indicate statistically significant differences (p <0.05) between the different degrees of alkalization (a, c, e, g) or the different levels of sodium bicarbonate (b and c). SD.: standard deviation.

Figure 3c shows the influence of the degree of cocoa powder alkalization on cohesiveness. It depicts a progressively rising cohesiveness as the degree of cocoa powder alkalization increases. The highest cohesiveness value (0.78±0.1) was obtained with the sample made with cocoa SA. The statistical data analysis revealed statistically significant differences (p <0.05) for cohesiveness because different cocoa types were used. No statistically significant differences (p> 0.05) were found for resilience according to the applied degree of cocoa alkalization.

Figure 3g illustrates the effect on the cohesiveness and resilience (Figure 5h) for the samples made with different bicarbonate levels for both cocoas N and MA When cocoa N was used, the sample prepared with twice the amount of sodium bicarbonate obtained the highest values for cohesiveness (0.77±0.04) and resilience (0.35±0.04). From this point onward, cohesiveness and resilience statistically decreased ($p < 0.05$), with minimum values for 3N and 4N samples.

For the cakes baked with cocoa MA, the statistical analysis revealed no statistically significant differences ($p > 0.05$) for cohesiveness and resilience. According to these results, when working with bicarbonate levels between 1.5 and 2, the obtained values in both phases I and II, were similar to those of controls MA (phase I) and SA (phase II).

Based on the texture profile analysis, it is possible to replace the MA control by the cakes made with cocoa N and with bicarbonate levels between 1.5 and 1.8 to, thus, avoid employing alkalizing agents in cocoa powder. The same can be concluded for the SA control made with cocoa MA and the same bicarbonate levels.

3.1.4 Imagen analysis

2D image segmentation analyses were performed as complementary tests to determine textural characteristics. As Figure 4a depicts, the higher the degree of alkalization of cocoa powder, the more bubbles contained in samples. A similar effect was observed when increasing the bicarbonate levels (Fig. 4b). The size of air bubbles value lowered as the degree of cocoa powder alkalization (Fig. 4c) or the bicarbonate level (Fig. 6d) increased.

The distribution of bubbles decreased with increasing degrees of alkalization (Fig. 4e) and with rising bicarbonate levels (Fig. 4f). In the latter case, the decrease was less pronounced.

The bubble circularity value also lowered when the alkalization level rose, but the differences among samples were minimal (Fig. 4g and Fig. 4h). These values could explain the differences observed in texture. In this study, when the degree of alkalization or the bicarbonate level increased, so did the number of bubbles. Hence cakes incorporate more air. As air level is related to hardness, less incorporated air is associated with increased hardness (Chung et al, 2010). Decreasing bubble size as a consequence of a rising degree of alkalization or a rising bicarbonate level seemed to be compensated by a larger number of bubbles, and did not negatively affect product texture. With elasticity, when the number of bubbles grows, positively increasing baked products' quality (Sanz et al., 2009). However in this study, the samples with the most bubbles displayed less elasticity. This was perhaps due to the fact that the number of bubbles was disproportionate, or because the lowest values were obtained for the distribution (Fig. 4e and Fig. 4f) and circularity of bubbles (Fig. 4g and Fig. 4h).

From this analysis, we conclude that optimal textural characteristics can be obtained with intermediate levels for number of bubbles and bubble size. In addition, having a high distribution and circularity values are desirable factors, which can be achieved by working with intermediate bicarbonate levels.

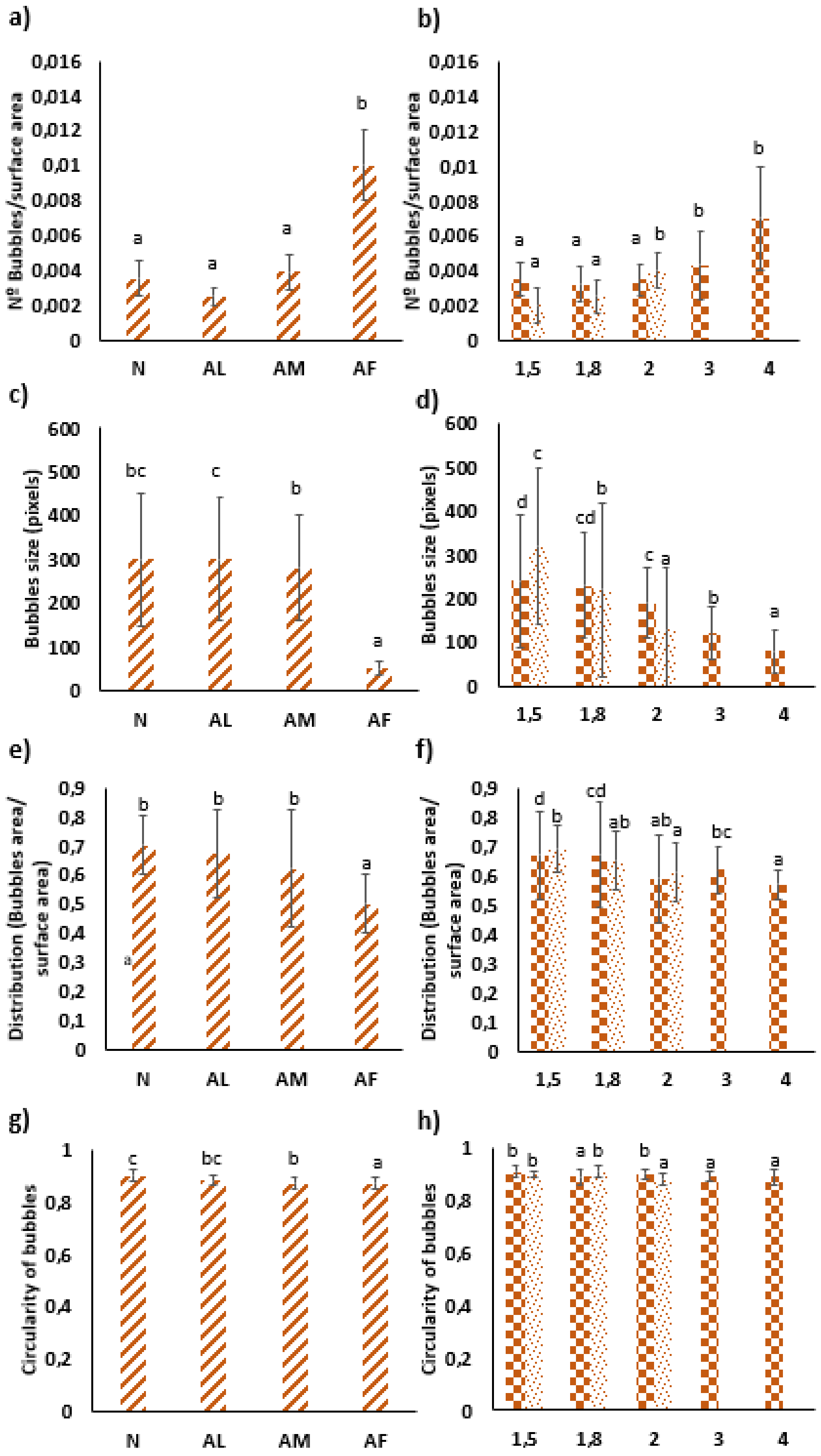


Fig. 6 Values (mean±SD.) of the 2D image segmentation analysis performed with the control cakes (a, b, c, d) and those made with cocoa N or MA, plus increased amounts of sodium bicarbonate (e, f,g, h). Cocoa N (zig-zag pattern). Cocoa MA (brown).

Different letters in the same series indicate statistically significant differences ($p < 0.05$) between the different degrees of alkalization (a, c, e, g) or different levels of bicarbonate (b, d, f, h). SD.: Standard deviation.

3.2 Sensory analysis

As the selection of specific cocoas for preparing certain products is important because consumer studies have demonstrated that color strongly impacts perceived flavor (Shankar et al., 2009), two sensory evaluations were made to determine the influence of *in situ* alkalization on potential consumers' sensory acceptance. The first was done with a cake baked with cocoa MA as the control sample and the second with cocoa SA as a control. For these tests, of all the possible recipes, we selected only the two recipes that provided the most similar colors to those of the control samples, and which exhibited similar texture parameters.

Figure 5a and 5b shows the scores that tasters gave the cakes made with MA cocoa (control) and cocoa N with a 1.8 bicarbonate level, and those made with cocoa SA (control) and cocoa MA, plus the 1.8 and 2 bicarbonate levels. We can see for all the attributes that the average score remained close to 4 (I like it). In addition, there were no significant differences ($p > 0.05$) for the color, aroma, texture, flavor, mouthfeel and global acceptance attributes in both Phases I and II.

These results also confirmed that, at certain levels, excess sodium bicarbonate did not imply modifications to the typical color of the control cakes or the appearance of unpleasant tastes, such as soda bite. On the contrary, in the other recipes that did not contain cocoa, excess sodium bicarbonate would confer biscuits an alkaline reaction, a yellowish crumb and surface coloration with an accompanying unpleasant taste (soda bite) (Manley, 2000).

Therefore for the sensory evaluation, it is possible to use cocoa N at the 1.8 bicarbonate level and obtain similar results as when cocoa MA is employed. It is also possible to use cocoa MA with bicarbonate levels 1.8 and 2 and obtain similar results to those acquired when employing cocoa SA.

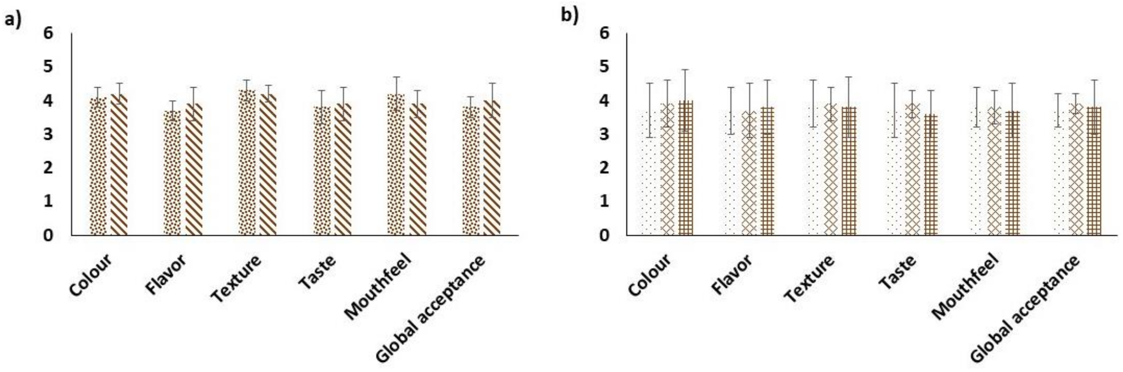


Fig. 7 Values (mean±SD) of the evaluation of color, aroma, texture, flavor, mouthfeel and global acceptance for: a) Phase I: the control sample made with cocoa MA (dotted plot), the sample with level 1.8 N (diagonal screen); b) Phase II: the control sample made with cocoa SA (dotted network), the sample with level 1.8 MA (rhombus network); the sample with level 2MA (squared network); SD: standard deviation.

4. Conclusions

It is possible to obtain sponge cakes with similar color and textural properties to those obtained when using alkaline cocoa starting from cocoa N and by increasing the proportion of sodium bicarbonate to 4-fold higher levels. However in textural or sensory terms, the cakes prepared with a bicarbonate level of > 2-fold the amount of the control recipe were unacceptable. Hence the most suitable sodium bicarbonate percentages for this new *in situ* alkalization strategy while baking cocoa-containing cakes is 1.8 for both cocoas N and MA. Using one or the other will depend on the expected final color: lighter or darker.

This is a positive conclusion for both the cocoa manufacturing and bakery industries because they can continue to use cocoa to prepare dark cakes with no labeling implications. In environmental terms, the reported *in situ* alkalization method would have a significant impact on energy saving by shortening or eliminating the industrial cocoa alkalinization process.

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6. Chapter IV

Chapter IV: Formulation and physico-chemical and sensory characterisation of chocolate made from reconstituted cocoa liquor and high cocoa content

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LWT, 137, 110492

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Abstract

Demand of dark chocolate with high cocoa content is increasing worldwide, which means having to find alternative processing methods that allow to dispense with the main ingredient in chocolate: cocoa liquor. To fulfil this goal, we propose using cocoa butter and cocoa cake as their price and duties can be lower than those of liquor. In line with this, the two objectives of this work were to formulate chocolate from reconstituted cocoa liquor and high cocoa content (95%) and to compare its physico-chemical and sensory properties with those of traditionally prepared chocolate containing the usual cocoa percentages (70%). The results showed that for the same percentage of cocoa, the chocolate formulated from reconstituted liquor were the same colour and had similar sensory acceptance despite them possessing less viscosity, and a slightly lower total polyphenols content and antioxidant capacity than those formulated with cocoa liquor. Despite these differences, a principal component analysis and a sensory analysis revealed that the physico-chemical differences associated with formulation are less important than those caused by increasing the cocoa percentage. Consequently, the proposed method represents an interesting alternative to prepare cheaper chocolate in certain countries or at given times of the year.

Keywords Alternative manufacture, consumer acceptability, functional properties, AESAN countries

1. Introduction

Chocolate, traditionally prepared by mixing, refining and conching cocoa liquor, cocoa butter and sugar, is a dense suspension of solid particles whose main ingredient is cocoa, which is responsible for its unique flavour and melt-in-the-mouth properties (Beckett, 2009).

The passion for this product has made chocolate demands increase worldwide. According to the Cocoa Association of Asia, the region's market for chocolate confectionery has grown at an annual rate of five percent due to the rise of affluent middle incomers who eat more chocolate (The Asean Post, 2019). In India, considered the fastest-growing chocolate consumer, chocolate manufacturers do not meet local demands and they need to import cocoa liquor despite increasing local bean production (Innova, 2019). When they import cocoa liquor, butter and powder from countries that do not belong to the Association of Southeast Asian Nations (ASEAN) or liquor from ASEAN countries, custom duties are 33%. However, for the powder and butter (two fractions obtained after pressing cocoa liquor) imported from ASEAN countries, duties are 0% (Central Board of Indirect Taxes and Customs, 2020). For these reasons, it might be cheaper to import butter and powder from these countries and then reconstitute the original cocoa liquor.

Moreover, the cocoa liquor price is linked directly with the price of beans, while cocoa powder and cocoa butter are traded independently, depending on demand. Cocoa butter is used mostly to make chocolate but is being increasingly employed in pharmaceuticals and cosmetics (Kalustian, 1985). Cocoa powder is utilised mainly by the food industry to prepare biscuits, cakes, ice cream and drinks (Olam, 2017). Normally when cocoa butter demand increases, so does its price, and the cocoa powder value goes down. So even when the price of beans does not change, the price of cocoa butter/cake can fluctuate (Gilbert, 2016).

All these facts made us rethink the way by which chocolate is prepared and contemplate manufacturing chocolate with the two independent cocoa liquor constituents: cocoa powder and cocoa butter. However, using reconstituted liquor to prepare chocolate is not an obvious step. It is generally considered that cocoa liquor is the dominant factor for determining consumers' experience with the sensory characteristics that characterise chocolate: texture and mouthfeel. Another important characteristic of chocolate is its viscosity, which is related to not only chemical composition, but also to the nature of the ingredients. One the one hand, fat in cocoa liquor coats the surface of particles and reduces their interparticle interaction to induce chocolate flow (Afoakwa, 2010). On the other hand, as liquor is considered thicker in viscosity than the butter and powder mix, lower yield values can be expected if formulations are made by mixing both components. This not only conditions the way in which chocolate flows in the mouth but might also modify its flavour because it has been proven that the time which the solid particles in chocolate taste takes to arrive at tongue sensory receptors depends on chocolate viscosity (Do, T.-A et al., 2007).

Apart from all this, as cocoa products are among the richest sources of polyphenols in our diet and are linked with potential benefits for cardiovascular health, antioxidant protection, cholesterol balance, and anti-allergic, antiviral, anti-inflammatory and anticarcinogenic properties (Rocha et al., 2017), the interest shown in the brands that prepare cocoa-derived products with the highest possible cocoa percentage is growing. Chocolate producers cannot ignore this trend and see this strategy as an effective way to improve their product’s functional and nutritional values. The higher the non-fat cocoa solid content in chocolate, the higher the polyphenol content (Jalil et al., 2008) and the lower the contribution of calories and simple sugars of chocolate, and all this ends up having a positive effect on human health (EFSA, 2012).

Bearing both concepts in mind, the objective of this work was twofold. On the one hand, to study the impact of liquor reconstitution from cocoa butter and cocoa powder on the physico-chemical, functional and sensory properties of the dark chocolate made from it. On the other hand, to evaluate how these properties are influenced by increasing the percentage of cocoa solids in the formulation. The study of both types of factors in the same research allowed us to determine the impact of each variable on the final chocolate characteristics.

2. Material and Methods

2.1 Chemicals and samples

The three cocoa-derived ingredients needed to prepare the different formulations of dark chocolates were processed in the factories belonging to Olam Food Ingredients with Ivory Coast beans to guarantee standarisation in the composition of the three products. Cocoa liquor was provided by Unicao (Abidjan, Ivory Coast), natural cocoa powder by Olam Food Ingredients Spain (Cheste, Spain) and deodorised cocoa butter by deZaan (Olam Cocoa BV, Koog aan de Zaan, Holland). The other ingredients were: powdered sugar (Hacendado, Valencia, Spain); lecithin (Solae LLC, St. Louis, Missouri, USA); vanillin (Borregaard Ingredients, Sarpsborg, Norway).

All the raw materials were donated by Olam Food Ingredients Spain SL. The reagents and solvents herein used were: methanol, n-hexane, hydrochloric acid, acetone, sodium carbonate (Na_2CO_3), Folin-Ciocalteu's phenol reagent, gallic acid (Scharlau, Barcelona, Spain), 1-diphenyl-2-picrylhydraz (DPPH) (Fluka, New York, USA) and trolox (Acros Organics, New Yersey, USA).

2.2 Fat, moisture and pH determination

The moisture and fat determinations in the cocoa liquor, cocoa butter and cocoa powder samples were made following Procedure 931.04, described by AOAC (2019) and Method 37/1990, described by the ICA (1990), respectively. For this purpose, 3 g of cocoa were weighed (M_0) and dried for 4 h at 102±2ºC (M_1). Moisture content was determined as the percentage of mass lost after drying ((M_0-M_1/M_0)*100). For the fat analysis, the dehydrated samples from the moisture analysis were placed inside the extraction units of a 6-possition semi-automatic Soxhlet extraction unit (Soxtec 8000, Foss, Denmark). Petroleum ether was then added to the extraction cups in a closed system, and cups were heated with an electric heating plate. The three-step extraction consisted of boiling, rinsing and solvent recovery. Fat content was defined as the percentage of mass of fat and other compounds extracted with petroleum ether and deposited in aluminium cups after recovering the solvent. Each sample was analysed in triplicate. From the cocoa fat and moisture values, the solid content was estimated by subtracting the value of moisture and fat from 100. These values were used to calculate the percentage of cocoa butter and cocoa powder that could be blended to reproduce the cocoa liquor composition.

The extractable pH in the cocoa powder and cocoa liquor was determined by following the methodology described in the deZaan Cocoa Manual (OLAM, 2017). For this purpose, a suspension of 2.5 g of cocoa powder/liquor was prepared in 12.5 mL of distilled water at 80ºC 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).

2.3 Chocolate preparation

In this study, two different dark chocolate formulations were compared: the traditional formulation consisting of blending cocoa liquor with cocoa butter and the necessary solids (F1); the new formulation consisting of blending cocoa butter, cocoa powder and the other necessary solids (F2). In order to increase the percentage of cocoa content to 80, 85, 90 and 95 g/100g, the amount of sugar was proportionally reduced.

Table 1 shows the percentages of the different ingredients blended to prepare traditional chocolate with several cocoa contents, as well as those of the chocolate prepared with a liquor reconstituted from its two fractions (cocoa butter and cocoa cake) using the same percentage of cocoa solids.

Experimental samples (5 kg of each formulation) were produced by mixing powder sugar and cocoa liquor in a mixer (Kitchenaid, Barcelona, Spain) at 58 rpm for 2 minutes, and then at high speed (220 rpm) for 3 minutes. Afterwards, samples were refined using a three-roller refiner (EXAKT 50 I, Exakt, Germany) operating at 732 rpm and yielding a particle fineness lower than 20 µm.

The refined chocolate was conched in a 5 kg-conch (Buhler, Uzwil, Switzerland) at low speed for 7 h at 60ºC. Then lecithin and cocoa butter were added and conched at high speed for 30 minutes at 60ºC. Samples were stored at room temperature. Each formulation was prepared in triplicate.

Table 1. Recipes used for the formulation of the dark chocolate.

	70 g cocoa/100g chocolate		80 g cocoa/100g chocolate		85 g cocoa/100g chocolate		90 g cocoa/100g chocolate		95 g cocoa/100g chocolate	
	F1	**F2**	**F1**	**F2**	**F1**	**F2**	**F1**	**F2**	**F1**	**F2**
Cocoa powder	25	35.34	33	44.37	38	49.89	42	54.40	47	59.92
Butter	25	34.66	24	34.63	24	35.11	24	35.60	23	35.08
Liquor	20	-	23	-	23	-	24	-	25	-
Sugar	29.6	29.6	19.6	19.6	13.6	13.6	9.6	9.6	4.6	4.6
Lecithin	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37	0.37
Vanillin	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03

2.4 Intrinsic colour determination

Prior to the colour determinations, samples were melted at 60ºC for 30 minutes. Then chocolate was dropped onto the surface of an optical glass where it solidified. A CM-700d (Konica Minolta, Tokyo, Japan) spectrocolorimeter was used to measure the colour of the different chocolate samples. The results were expressed according to the CIE-Lab system (D65 illuminant and 10º viewing angle). Measurements were taken with an 8-mm diameter diaphragm inset. The measured parameters were L* (L*= 0 (black), L*= 100 (white)), a* (+a*=red) and b*(+b*= yellow). Using colour values L*, a* and b*, we calculated hue (h^*_{ab}) and chroma (C^*_{ab}) by the following equations:

$$h^*_{ab} = \arctan\frac{b^*}{a^*} \qquad \text{E}$$

$$C^*_{ab} = \sqrt{a^{*2}+b^{*2}} \qquad \text{E}$$

The mean values of three replicate measurements and standard deviation were calculated.

2.5 Rheology analysis

The rheology properties of the different chocolate samples were determined by a controlled stress rheometer (RheoStress, Thermo Haake, Karlsruhe, Germany) using a cone-plate geometry (sensor type P61 with a C60/2 Ti rotor, Haake RheoStress 1, Karlsruhe, Germany). The rheological behaviour of dark chocolate was analysed. The equipment included a thermostatic bath, operated at 40ºC. Prior to the analysis, samples were incubated at 60ºC for 30 min for melting, which allowed the transfer to the cone-plate system.

Flow curves were determined by performing shear rate sweeps from 0 to 200 s^{-1}. Three consecutive rising and falling cycles were used to evaluate and eliminate the thixotropyc effect.

The experimental data obtained in the third down sweep were adjusted to the Herschel- Bulkley model for non-Newtonian fluids (Eq (3)).

$$\sigma = \sigma_0 + K\gamma^n \qquad \text{Eq (3)}$$

where σ is shear stress (Pa), σ_0 is yield shear stress (Pa), K is the consistency index (Pa s^n), γ is the shear rate (s^{-1}), and n is the flow viscosity index (dimensionless). The yield stress value employed in Herschel-Bulkley's model was previously obtained by fitting the experimental data to the Casson model (Eq (4)) (Tarrega & Costell, 2006). All the measurements were taken in triplicate.

$$\sigma^{0.5} = \sigma_0^{0.5} + K\gamma^{0.5} \qquad \text{Eq (4)}$$

2.6 Differential scanning calorimeter

The melting properties of the different chocolate were evaluated by differential scanning calorimeter (Stare System, Mettler-Toledo, Inc., Switzerland). First of all, 5 mg of each sample were weighed in a 40-mL capacity aluminium pan and sealed. Samples were analysed following the method reported by Afoakwa et al. (2008b) using a single scan: a first heating step from -60ºC to 200ºC at 10ºC/min, followed by cooling to -60ºC at 50 C/min. An empty aluminium pan was taken as the reference. Measurements were taken in duplicate for each sample in a nitrogen stream (20 mL/min). The onset temperature (T_{onset}) and end temperature (T_{end}) were calculated for each peak present in the obtained thermogram (Gloria and Sievert, 2001).

2.7 Particle size distribution

Particle size distributions were measured by a Lasentec FBRM Model M500 (Mettler Toledo, USA). A representative chocolate sample (250 ml) was melted at 50ºC in a 400-mL beaker glass. Before the analysis, ultrasonic dispersion was applied for 2 minutes to ensure that particles were independently dispersed. Then particle size distribution was analyzed for 10 minutes in 10 cycles lasting 1 minute each.

2.8 Cocoa polyphenol extraction

The determination of total polyphenols and antioxidant capacity was carried out from a hydroalcoholic phenolic extract obtained according to the method described by Martín et al. (2008) with some modifications. For this purpose, 1 g of a previously defatted sample was weighed and 20 mL of a solution of methanol and hydrochloric acid 16 mmol L^{-1} (50:50, v/v) were added. Samples were kept for 15 minutes in an ultrasonic bath (Elmasonic S40H, Singen, Germany) and centrifuged (Centrifuge 5804R, Eppendorf, Hamburg, Germany) at 13,000 g for 15 minutes at 4ºC. Subsequently, a second extraction step was performed under the same conditions. Then a third extraction cycle was run by suspending the precipitate of the second cycle in 20 mL of acetone and a distilled water mixture (70:30). The supernatants from the three extractions were combined and brought to a final volume of 60 mL with distilled water. Extracts were kept at 4ºC until analysed. Previously, samples were defatted by cold extraction with hexane. For this purpose, 3g of cocoa were mixed with 15 mL of hexane and vigorously stirred for 5 minutes. Then samples were centrifuged at 13,000 g for 15 minutes at 4ºC. After removing the supernatant, two new extraction cycles were performed. Finally, samples were dried using a vacuum.

2.9 Polyphenols and antioxidant capacity determinations

The total polyphenol content in the polyphenolic extract was determined spectrophotometrically following the Folin-Ciocalteu method by placing 50 µL of sample in a test tube, 450 µL of a methanol/water solution (1: 1), 4 mL of carbonate calcium and 5 mL of a Folin-Ciocalteu solution diluted at 1:10. Then it was kept in the dark for 1 h and absorbance was measured in a spectrophotometer (Helios Zeta UV-VIS, Thermo Scientific, UK) at 765 nm. The results were expressed as g gallic acid equivalents (GAE) per 100 g of fat free and dry sample (ffd). All the analyses were performed in triplicate. The antioxidant capacity of the phenolic extracts was determined by the DPPH radical method, which consists of adding 15 µL of sample to 285 µL of methanol and 2.7 mL of a methanolic solution of DPPH radical (25 mg L^{-1}). Samples were incubated in the dark and absorbance was measured in a spectrophotometer (Helios Zeta UV-VIS, Thermo Scientific, UK) at 517 nm. The results were expressed as g trolox equivalent (TE) per 100 g of fat free and dried sample (ffd). All the tests were carried out in triplicate.

2.10 Catechin and epicatechin determination

For the quantification of both epicatechin and catechin, an HPLC model 1260 Infinity II from Agilent Technologies (Madrid, Spain) was used. The analysis was run according to the method described by Niemenak et al (2006) with some modifications. The chromatographic conditions employed while measuring were: column temperature of 40ºC, UV detection at 280 nm, injection volume of 30 µL and flow rate of 1.2 mL/min. The filtered polyphenolic extracts were injected into a Liquid Purple C18 5 µm (250x4.4mm) reversed phase column from Análisis Vínicos (Tomelloso, Spain). The mobile phases were 2% aqueous acetic acid (phase A) and acetonitrile, water and acetic acid in the 40:9:1 v/v/v proportion (phase B). The gradient was 0-8 min, 90% phase A, 8-20 min, 90-85 phase A, 20-35 min, 85-10% phase A; 35-37, 10-90% phase A; 37-45 min, 90% phase A.

2.11 Sensory analysis

The different degrees of acceptance of chocolate indicated by a panel of untrained consumers were evaluated by hedonic tests. The panel of tasters was formed by 40 students and research staff members from the UPV Food Technology Department. The four extreme formulations (F1-70, F1-95, F2-70 and F2-95) were evaluated at 25ºC in a tasting room equipped with individual cabins (ISO, 1988), after being coded with randomly chosen 3-digit numbers. Acceptance tests were performed on a 7-point hedonic scale (1 I absolutely dislike, 2 I considerably dislike, 3 I somewhat dislike, 4 I do not like, 5 I somewhat like, 6 I considerably like and 7 I absolutely like). This scale was used to describe all the following parameters defined according to Standard UNE 87-001-94: colour, aroma, texture in mouth, fat sensation, sweetness, flavour and overall appreciation. To minimize any residual effects, consumers were asked to rinse their mouths with water before testing each sample.

2.12 Statistical analysis

The differences between samples due to the formulation (liquor or reconstituted liquor) and percentage of cocoa were determined by a multifactorial analysis of variance (ANOVA), with a confidence level of 95% LSD ($p < 0.05$). Data were analysed by the STATGRAPHICS Centurion XVI v. 17.2.04 statistical software (Manugistics Inc., Rockville, MD, USA).

A principal component analysis (PCA) was performed with all the evaluated physico-chemical parameters, which meant that the statistical study used 18 variables. All the variables were mean-centred and scaled to unit variance prior to the analysis. For all the PCA components, a score for each sample was calculated as a linear combination of the initial data for the variables. The contribution for each parameter to the PCA score was deduced from the loadings for that factor. PCA was performed by the XLSTAT 2020 software (New York, USA).

3. Results and Discussion

3.1 Composition

The fat, moisture content, cocoa solids and pH values of the three principal ingredients are shown in Table 2. These values were used to calculate the equivalent amounts of cocoa butter and cocoa powder to a certain amount of cocoa liquor and to, thus, establish the composition of the different formulations. With these calculations, the different recipes were followed (100 g of cocoa liquor was the equivalent to approximately 51.68 g of cocoa powder and 48.32 g of cocoa butter).

Table 2. Chocolate composition.

	Fat (g/100g)	Cocoa solids	pH	Moisture (g/100g)
Cocoa liquor	54.00 ± 0.70	46.00 ± 0.30	5.60 ± 0.03	0.80 ± 0.08
Cocoa powder	11.00 ± 0.24	89.00 ± 0.50	5.42 ± 0.05	3.30 ± 0.12
Cocoa butter	100	-	-	-

3.2 Colour

The L * coordinate values of the different chocolate samples ranged from 13.2±0.5 (F1-95) to 14.7±0.3 (F2-70). As seen in Fig. 1a, lightness values were slightly higher in the samples prepared with cocoa powder and cocoa butter (F2), but these differences were not statistically significant ($p>0.05$). What was statistically significant for both formulations was the effect of cocoa percentage on the formulation. For both formulations, the L* value lowered as the percentage of cocoa increased and, therefore, the samples with 95% cocoa solids were darker.

Figure 1b illustrates how the colour purity (C*) values range from 15.29±0.16 (F1-95) to 17.74±0.16 (F2-70). Once again, samples F2 had the highest colour purity values. However, these differences were only statistically significant when using 90% and 95% of cocoa. In contrast, the C* values (less pure colour) statistically and significantly lowered as the cocoa percentage rose.

Finally, the hue values (h*) of both formulations are represented in Figure 1c. These values ranged from 48.4±0.3 (F1-95) to 50.5±0.2 (F2-80). Once again, the samples prepared following the formulation F2 type presented higher h* coordinate values (less reddish), but these differences were only statistically significant when the highest cocoa percentages were used. In this case, the cocoa percentage affected only the hue of chocolate when high cocoa concentrations were applied.

After considering all the colour coordinates, we conclude that formulation type (liquor or reconstituted liquor) did not significantly affect the colour of the obtained chocolate. As expected, however, chocolates became darker, had a less pure colour and were more reddish when increasing the cocoa percentage.

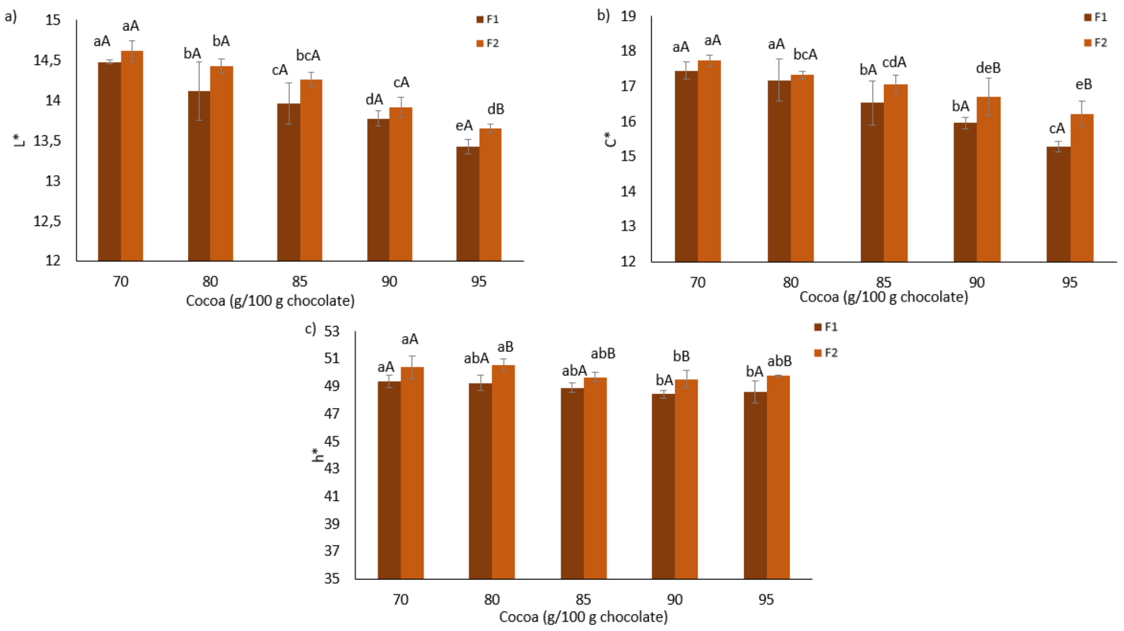

Fig. 1 Values (average ± sd, n = 3) of a) lightness, b) chroma and c) hue for both formulations and cocoa percentages. Different lowercase letters denote statistically significant differences between cocoa percentages ($p < 0.05$).

Different capital letters within groups with the same cocoa percentage denote statistically significant differences ($p < 0.05$) between formulations. F1- traditional chocolate formulation; F2- new chocolate formulation.

3.3 Particle size distribution

The particle size distribution (PSD) parameters from the samples are presented in Table 3. When comparing the chocolate with growing cocoa percentages, no significant differences between the different formulations ($p > 0.05$) were found in C90 (measured value of which 90% of particles were smaller), mean (length width) or % >75 (% of particles whose diameter was longer than 75 µm). As particle size is considered to influence sensory perception, these results indicated that consumer acceptance should not change between consuming traditional or the newly formulated chocolate.

Table 3. PSD values for the different chocolate samples.

	C90	**Mean**	**% >75**
F1-70	33.53 ± 0.90^{abA}	16.28 ± 0.17^{aA}	0.54 ± 0.05^{aA}
F1-80	32.52 ± 0.90^{aA}	16.17 ± 0.15^{aA}	0.51 ± 0.07^{abA}
F1-85	28.79 ± 0.46^{cA}	15.73 ± 0.27^{bA}	0.47 ± 0.04^{abcdA}
F1-90	29.22 ± 1.12^{cA}	15.40 ± 0.10^{bA}	0.43 ± 0.03^{cdA}
F1-95	29.89 ± 0.62^{cA}	14.38 ± 0.31^{cA}	0.42 ± 0.06^{cA}
F2-70	33.83 ± 0.41^{aA}	16.34 ± 0.14^{aA}	0.50 ± 0.06^{abcA}
F2-80	32.70 ± 0.40^{aA}	16.47 ± 0.37^{aA}	0.49 ± 0.03^{abcdA}
F2-85	30.59 ± 0.89^{bB}	15.35 ± 0.38^{dA}	0.43 ± 0.06^{cdA}
F2-90	29.92 ± 0.82^{cA}	15.77 ± 0.20^{bB}	0.44 ± 0.05^{bcdA}
F2-95	28.73 ± 0.89^{dA}	14.06 ± 0.56^{cdA}	0.43 ± 0.05^{cdA}

Different lowercase letters denote statistically significant differences between cocoa percentages ($p < 0.05$). Different capital letters within group with the same cocoa percentage denote statistically significant differences ($p < 0.05$) between formulations. (F1-traditional chocolate formulation (liquor + powder); F2-new chocolate formulation (butter + powder)).

Regarding the PSD of samples differing in cocoa percentages, the results showed that the C90 values dropped as the percentage of cocoa increased. As the PSD values are the consequence of cocoa solids and sugar being present (T.-A.L. Do et.al, 2010), these results suggest that a drop in sugar content, as it is substituted for cocoa powder, caused the sample's better fineness. Moreover, smaller particle sizes are known to improve sensory properties (Ziegler, et al., 2001). The same trend was found for the mean size and percentage of particles, with size exceeding 75 microns. In both cases, the increase in cocoa powder statistically and significantly ($p<0.05$) lowered the values.

3.4 Rheology

Based on the rheological behaviour described by the flow curves, all the samples displayed plastic Bingham behaviour and were time-dependent (thixotropy). Such behaviour coincides with previous studies carried out into chocolate and semisolid chocolate-flavoured products (Beckett, 2009; Glicerina et al., 2013).

The flow curves of the second down cycle of samples were adjusted to the Herschel-Buckley model, and R^2 adjustment values higher than 0.99 were obtained in all the samples, which confirmed the method's adequacy to model this rheological behaviour.

All the samples exhibited yield stress (□0), which suggests that they all presented initial resistance to flow (Fig. 2). The yield stress values were statistically and significantly higher ($p<0.05$) in F1 (prepared with cocoa liquor) than in F2 (prepared with reconstituted liquor). Moreover for both chocolate formulation types (F1 and F2), the □0 values significantly increased ($p < 0.05$) when the amount of cocoa in the recipe did. This increase in yield stress has been associated with the smaller particle size of suspended solids (Chevalley, 1994), which occurs when the amount of cocoa solids increases (see Section 3.3). It has been also linked with a better connection of cocoa solid particles' surface with cocoa butter, which is expected to be higher in the F1 samples as the microstructure of liquor is conserved and, thus, cocoa solids remain closely connected to fat (Mongia et. al., 2000).

The consistency index reflects the overall thickness of samples. In general, this parameter was higher in the F1 chocolate than in the F2 one for the same cocoa percentage. So using the traditional chocolate recipe made thicker and less fluent products. These differences among formulations could be due to the distinct interaction between cocoa particles and cocoa fat in both liquor and reconstituted liquor, which coincides with the report of T.-Al. Do et al., (2011), which compared chocolate prepared with different fat percentages. Despite the observed differences, they were only statistically significant for certain cocoa percentages. Once again for all the formulation types, k increased significantly when the amount of cocoa powder rose because PSD decreased when sugar was replaced with cocoa powder.

Regarding the flow index (n), values lower than 1 indicate that the behaviour of all the formulations is pseudoplastic. The flow index was statistically and significantly higher for the formulations prepared with liquor (F1) than for those prepared with the reconstituted one from its two components: cocoa fat and cocoa powder (F2). Moreover, differences were found among the chocolate made with different cocoa percentages, which means that all the factors which affected $\square_0$ and k also affected the flow index in the same way.

These changes observed in chocolate rheology may not only affect the mouth feel perception, but also taste because the time that chocolate solid particles need to arrive at sensory receptors depends on viscosity (Beckett, 2001). According to Jeffery (1993), the removal of particles below 12-15 μm can significantly reduce chocolate viscosity. As the chocolate prepared with the new formulation (F2) exhibited lower viscosity values than those prepared following the traditional formulation (F1), the opposite strategy should be followed. However, during the sensory evaluation (section 3.10), no significant differences were found in the mouthfeel attribute evaluation made between chocolate F1 and chocolate F2 for the same cocoa content. These results indicate that, despite the chocolate formulation having an influence on chocolate rheology, it did not affect consumer preferences.

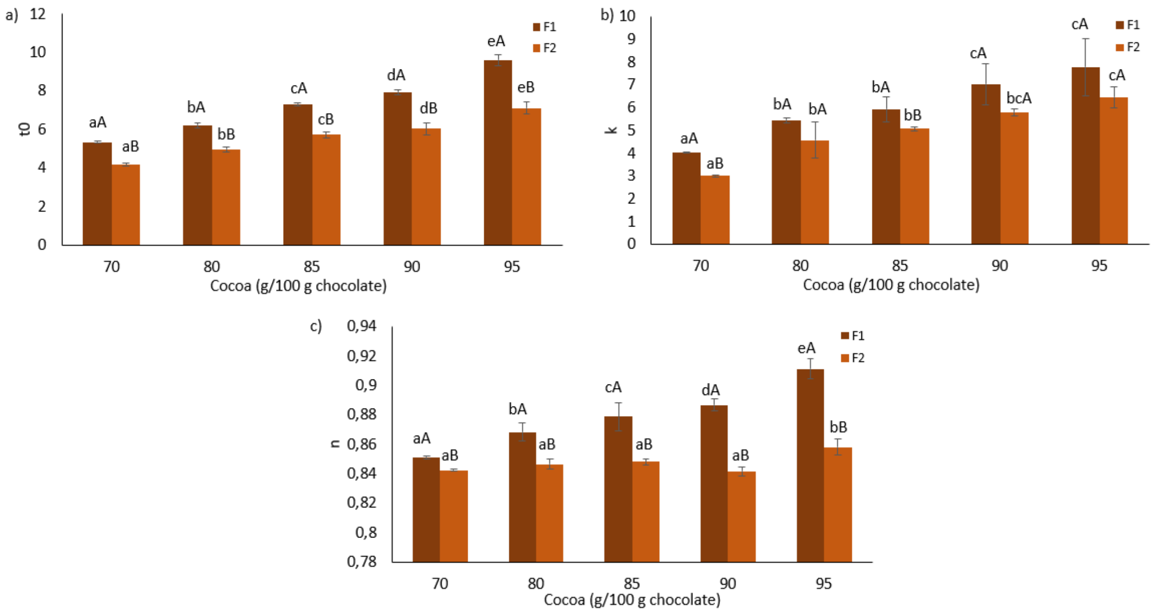

Fig. 2 Values (average ± sd) of the rheological parameters obtained using the Herschel-Bulkley model for different chocolate formulations. a) Yield stress; b) Consistency; c) Flow index.

Different lowercase letters denote statistically significant differences between cocoa percentages ($p < 0.05$). Different capital letters within groups with the same cocoa percentage denote statistically significant differences ($p < 0.05$) between formulations. F1-traditional chocolate formulation; F2- new chocolate formulation.

3.1 Differential scanning calorimeter

The T onset (temperature at which a specific crystal form starts to melt), T end (temperature of complete melting), T peak (temperature at which the melting rate is the highest) and T index (T end – T onset) values of the dark chocolate samples are reported in Table 4. As we can see, the T onset values ranged from ca. 28ºC to ca. 30ºC, while the T end value fell with a range from ca. 35ºC to ca 37ºC. The T peak values went from ca. 33ºC to ca. 34ºC, and the T index values from ca. 6ºC to ca. 7ºC. These values are similar to those reported by other authors for dark chocolate (Walter and Cornillon, 2002; Afoakwa et al., 2008b; Afoakwa et al., 2009). Moreover, despite the statistically significant differences found, the minimal differences in absolute terms and the fact that no behaviour pattern appeared among the samples in any of the studied parameters would mean that the melting properties of the different formulations were equivalents.

Table 4. DSC values for the different chocolate samples.

	T onset (ºC)	**T end (ºC)**	**T index (ºC)**	**T peak (ºC)**
F1-70	29.69±0.11^{ab}	37.07±0.45^{a}	6.95±0.70^{c}	34.04±0.55^{ab}
F1-80	30.10±0.78^{a}	36.75±0.69^{ab}	6.90±0.50^{bc}	34.13±0.56^{a}
F1-85	28.90±0.52^{bc}	35.65±0.23^{bcd}	6.28±0.60^{abc}	33.22±0.39^{ab}
F1-90	29.68±0.39^{ab}	36.47±0.98^{abc}	5.86±0.18^{abc}	33.57±0.66^{ab}
F1-95	28.19±0.97^{c}	36.11±0.40^{abcd}	6.49±0.64^{abc}	34.12±0.53^{a}
F2-70	29.44±0.31^{ab}	36.39±0.39^{abc}	7.38±0.33^{bc}	33.61±0.16^{ab}
F2-80	29.25±0.13^{ab}	36.12±0.63^{abcd}	7.25±0.64^{bc}	33.33±0.54^{ab}
F2-85	29.03±0.49^{bc}	35.31±0.19^{c}	6.75±0.29^{ab}	33.16±0.34^{b}
F2-90	29.59±0.32^{ab}	35.44±0.49^{cd}	6.79±0.59^{a}	33.26±0.23^{ab}
F2-95	29.35±0.09^{ab}	35.84±0.55^{bcd}	6.83±0.18^{abc}	33.54±0.72^{ab}

Different lowercase letters denote statistically significant differences between cocoa percentages ($p < 0.05$). (F1-traditional chocolate formulation (liquor + powder); F2- new chocolate formulation (butter + powder)).

3.2 Polyphenol content and antioxidant capacity

Regarding the functional properties of the prepared chocolate, Figure 3 shows the total polyphenol content of the different formulations. The total polyphenol content of the samples prepared with the lowest cocoa percentage was around 6-8 g GAE/100 g ffd. These values are comparable to those of green tea (4.6 g GAE/100 g) and are 10-fold higher than those for apple (0.4-0.5 g GAE/100 g), pear (0.3-0.5 g GAE/100 g) and kiwi (0.3 g GAE/100 g) (Perea-Villamil et al., 2009).

When comparing the different formulations at the same cocoa percentage (70 the phenolic content of F1-70 was 25% higher than that of F2-70. This means that, although both formulations were based on ingredients obtained from the same raw material (cocoa beans from Ivory Coast), the polyphenol content of the reconstituted liquor was lower than that of the original liquor. It makes sense because to obtain cocoa butter and cocoa cake from cocoa liquor, high temperatures and pressures are applied, which are conditions that have been reported to alter cocoa functional compounds (Redovnikovic et., 2009; Tamrin et al. (2012). The same behaviour was observed when comparing the chocolate samples prepared with all the different cocoa percentages.

As expected, Figure 3 also depicts that when the cocoa percentage increased, so did the total polyphenol content, which confirms that increasing cocoa solids in a recipe is a good strategy to enhance chocolate functionality (Urbańska, et. al (2019). Indeed polyphenol content was 10.66±2.24 g GAE/100 g ffd in sample F1-95, which denotes that if the chocolate with the 70% cocoa content can already be considered to be functional foods, then those with 95% would be perceived as being even more meaningful.

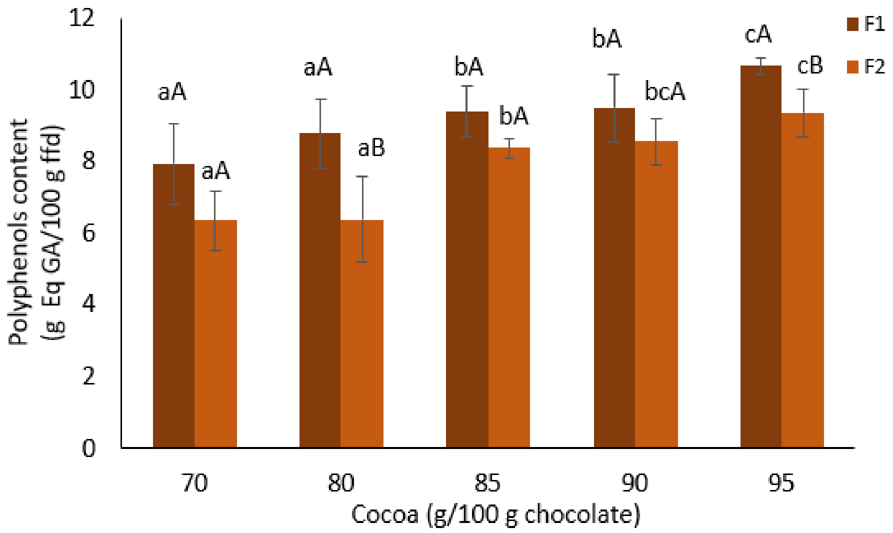

Fig. 3 Values (average ± sd, n = 3) of total polyphenol content in the chocolate formulation. Different lowercase letters denote statistically significant differences between cocoa percentages ($p < 0.05$).

Different capital letters within groups with the same cocoa percentage denote statistically significant differences ($p < 0.05$) between formulations. F1- traditional chocolate formulation; F2- new chocolate formulation.

In parallel, Figure 4 shows the antioxidant capacity values obtained for the analysed chocolate samples. These values ranged between 2.34 (F2-70) and 4.45 (F1-95) g TE/100 g ffd. Once more when comparing formulations, F1 (prepared with cocoa liquor) obtained the highest values of all the cocoa percentages. Besides, when the cocoa percentage increased, antioxidant capacity also increased.

Finally, when comparing Figs. 3 and 4, we see that antioxidant capacity was closely related to total polyphenol content. This correlation between both parameters (total polyphenols and antioxidant capacity) has been previously described by Nazario et al., 2014, who indicated that the high values of both parameters were due to the ability of polyphenols to yield electrons in order to generate an antioxidant response.

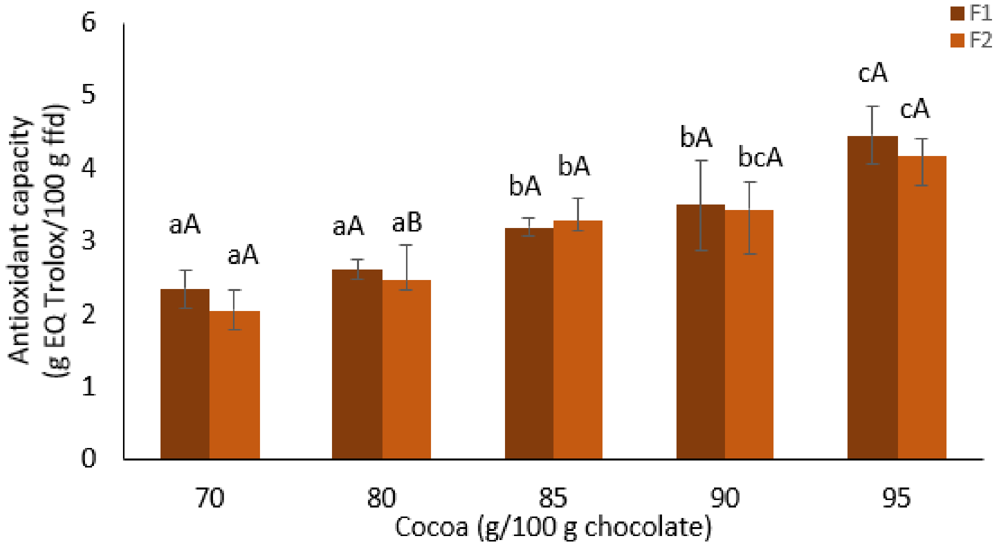

Fig. 4 Values (average ± sd) of antioxidant capacity in the chocolate formulation. Different lowercase letters denote statistically significant differences between cocoa percentages ($p < 0.05$).

Different capital letters within groups with the same cocoa percentage denote statistically significant differences ($p < 0.05$) between formulations. F1- traditional chocolate formulation; F2- new chocolate formulation.

3.3 Catechin and epicatechin content

Fig. 5 shows the results of the catechin and epicatechin contents for the chocolate prepared with different recipes. Regarding catechin values, significant differences ($p < 0.05$) were found when comparing recipes with varying cocoa content percentages. Including 70% of cocoa in the recipe provides a catechin content of 47.37 mg/100g ffd chocolate. However when adding 25% cocoa content (95% of final cocoa content), the catechin content increased to 68.1 mg/100g ffd chocolate (when comparing standard chocolate recipe F1), so catechin content had increased 30%. Therefore, high catechin values appeared when cocoa content rose. For the same cocoa content, higher catechin values were always found in the cocoas prepared using F1 (liquor and powder). These values are in accordance with polyphenol content.

A similar trend, but with higher contents (130-170 mg/100g ffd chocolate), was found for epicatechin, a flavonoid whose content in chocolate is higher than that of catechin (Gottumukkala, et. Al., 2014). Regardless of formulation, these data were higher than those reported by Arts et al. (2000) for dark chocolate: 61 mg/100 g chocolate. This means that, despite the chocolate prepared with F2 having lower phenolic content, their average values came similar to those of commercial samples, and all the prepared chocolates should be considered a good source of dietary flavonoids (Urbańska, et. al., 2019).

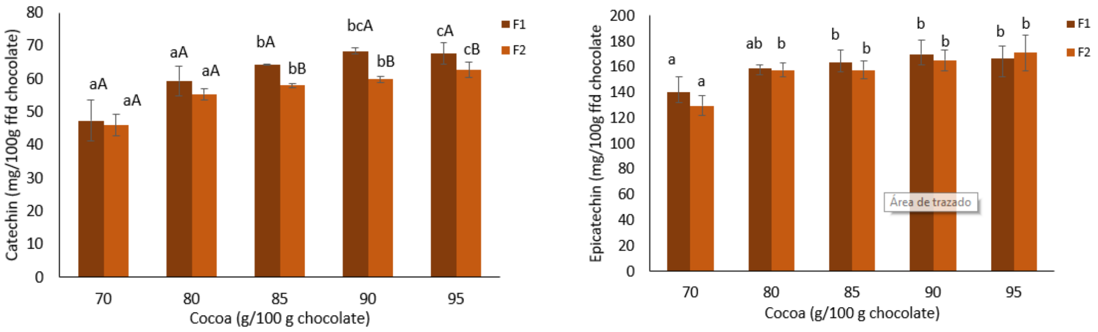

Fig. 5 Values (average ± sd, n = 3) of catechin and epicatechin. Different lowercase letters denote statistically significant differences between cocoa percentages ($p < 0.05$).

Different capital letters within group with the same cocoa percentage denote statistically significant differences ($p < 0.05$) between formulations. F1- traditional chocolate formulation; F2- new chocolate formulation.

3.4 Global variability among formulations

Due to the large number of parameters included in the physico-chemical characterization of chocolates, the global variability among the samples herein used was analysed by a PCA. Fig. 6 shows the combination of the loading plot and the score plot. The most important principal component (PC1) explained 50.91% of total variation and allowed the separation of samples in relation to their cocoa percentage. For both formulations, negative scores were related to a lower cocoa content, whose value rose as the cocoa percentage did. The second principal component (PC2) explained 17.30% of total variation and allowed the separation of samples regarding the formulation. In general, negative scores were found in the samples belonging to F1 (prepared with liquor) and positive scores in the samples belonging to the F2 (prepared with reconstituted liquor). This analysis allowed us to conclude that both cocoa percentage and chocolate formulation clearly influenced chocolate physico-chemical properties. However, the effect of using different cocoa percentages (from 70% to 95%) provoked more variability than using liquor or reconstituted liquor. Finally, the analysis of the square cosine of the variables indicated that the most influential ones in PC1 were colour coordinates L* and C*, followed by τ_0 and k of rheology and functional properties (total polyphenols and antioxidant capacity). Likewise, the most influential variables in PC2 were T_{peak} and T_{end}, both related to the DSC analysis. However, as the differences in melting properties between the samples formulated with real and reconstituted liquor were minimal, these data reinforce the idea that cocoa percentage has a stronger impact than formulation type. Hence preparing chocolate from cocoa butter and cocoa powder, instead of from cocoa liquor, might be a real alternative to reduce processing costs without affecting the essential physico-chemical parameters that define chocolate quality.

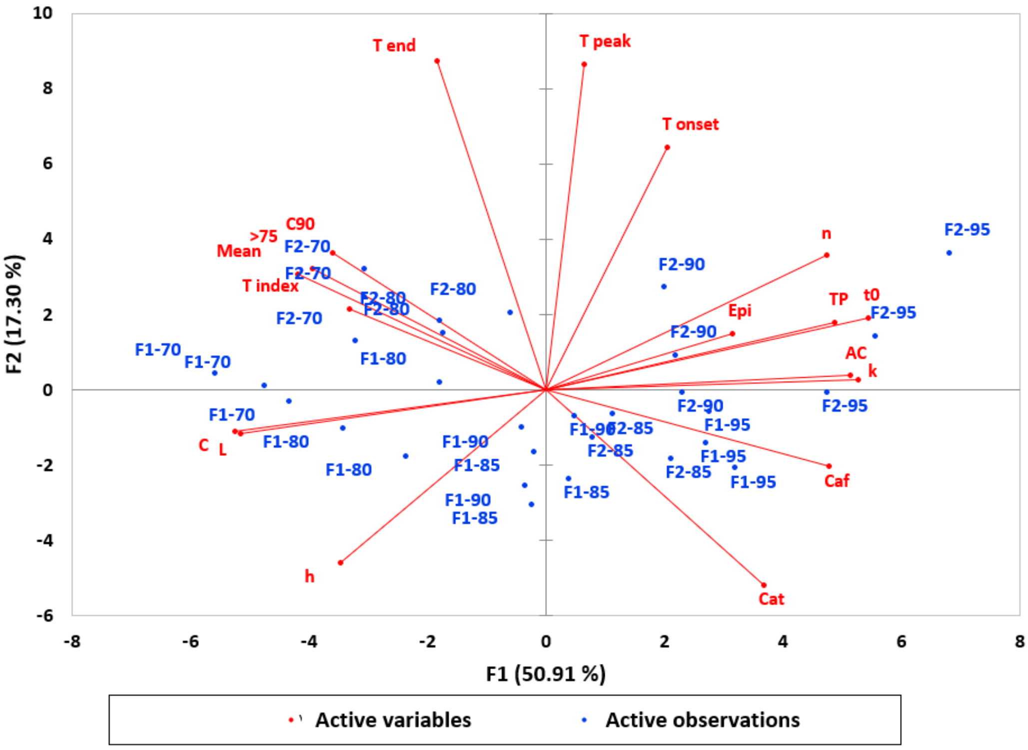

Fig. 6 Principal components analysis (PCA) for chocolates prepared with the traditional (F1) and the new formulation (F2) and different cocoa percentages (70–95%). Figure shows the overlap of the loading plot and the score plots.

3.5 Sensory evaluation

In parallel to the instrumental evaluation, samples F1-70, F2-70, F1-95 and F2-95% were sensory-evaluated by a panel of untrained consumers (n=40). Samples were presented in pairs of cocoa percentages in random order. Consumers were asked to evaluate six attributes of the samples on to a 7-point hedonic scale. The sensory test results are shown in Fig. 7. The statistical analysis revealed no statistically significant differences (P > 0.05) in colour terms, which demonstrates the degree of similarity between the samples of both formulations for the 70% and 95% cocoa contents. For the colour, flavour, fatty taste, mouthfeel, sweetness and global appreciations, the samples made with 70% cocoa content were appreciated the most. However, the chocolate with 95% also received good scores from many tasters, especially from those who reported frequently eating chocolate with a high cocoa content. These data indicate that habits and personal preferences are very important when assessing black chocolate.

Finally in the global scores, no statistically significant differences ($p > 0.05$) were found between the scores given to samples F1 and F2 for the same percentage of cocoa content. These results indicate that, despite the newly proposed formulation from cocoa butter and reconstituted powder affecting the rheology of products, it did not affect consumers' final sensory preference at all, regardless of cocoa content.

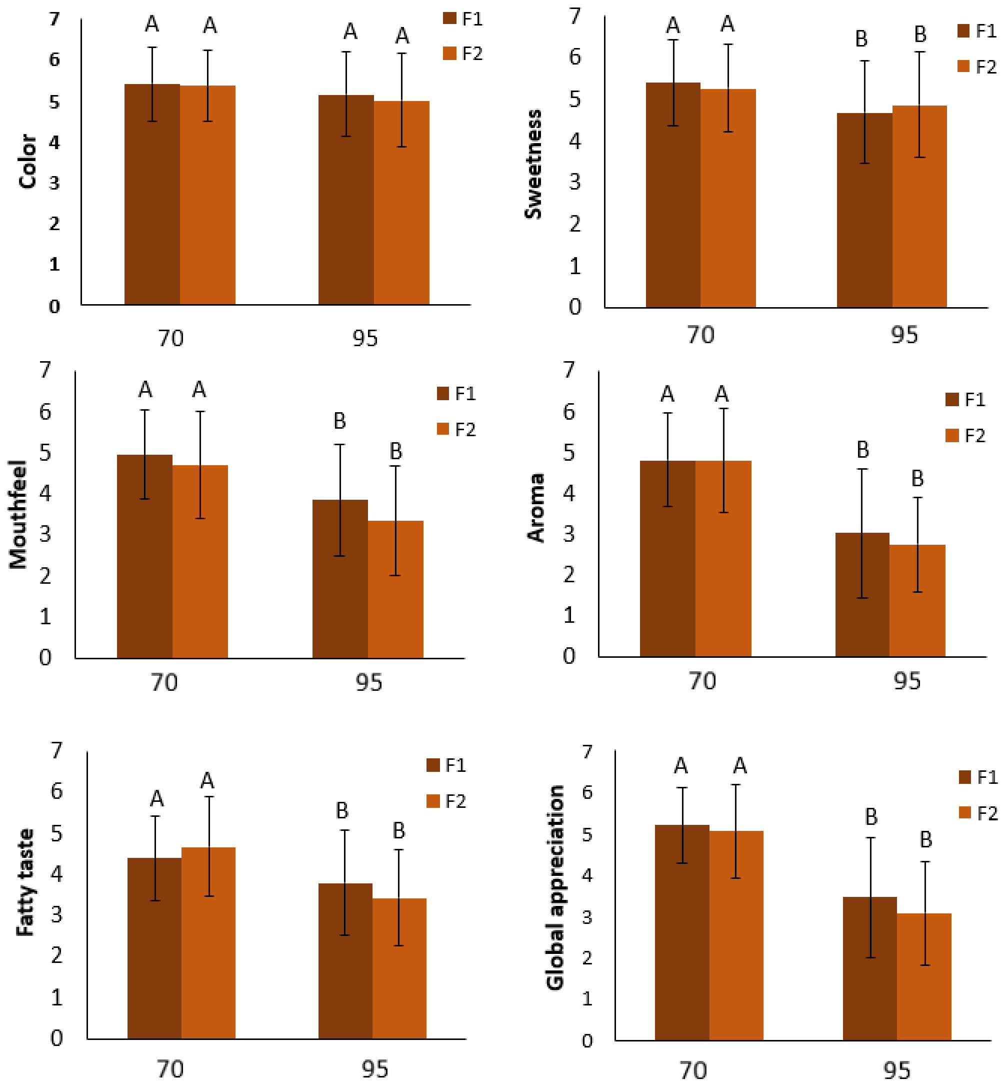

Fig. 7 Values (average ±sd, n = 40) given to each of the sensory attributes for each of the formulas with different percentages of cocoa. Different capital letters within groups with the same cocoa percentage denote statistically significant differences ($p < 0.05$) between formulations.

4. Conclusions

Our results showed that the preparation method affected mainly chocolate rheology and its functional properties, insofar as the samples prepared with the alternative chocolate manufacturing method were statistically less thick in consistency terms and had a lower polyphenol content. Moreover, increasing cocoa solids in the chocolate prepared with both formulations led to a darker, less pure and reddish colour, higher consistency and a better functional profile. With those factors, a PCA analysis built up with all the data collected during the physico-chemical characterisation revealed that cocoa percentage was the technical variable that most influenced the differences observed between samples. This observation was corroborated by a sensory analysis performed by a panel of consumers, which did not find statistical differences between both chocolate preparation methods for a same cocoa solid percentage. Consequently, the effect of cocoa percentage is more decisive in defining chocolate characteristics than the preparation method alone.

Bearing this in mind, it can be concluded that the reconstitution of cocoa liquor from its main two components has a lower impact on the physico-chemical and sensory properties of chocolate than increasing the cocoa solid content, which is an increasingly common trend in product innovation for brands. Thus avoiding the use of cocoa liquor to prepare chocolate preparation might offer better prices for cocoa producers at certain times of the year (when powder or fat demand lowers) or in some countries where import duties for cocoa liquor are higher than those for cocoa butter and cocoa powder separately. This would modify the way by which chocolate is prepared and would, consequently, lower the price of chocolate, which would allow more people to consume it. Finally, the percentage of maximum cocoa solid conditions should be adjusted to meet consumer preferences because not all consumers sensorially tolerate chocolate made with 95% cocoa.

Acknowledgements

The authors wish to acknowledge the financial assistance provided by Ministerio de Economía, Industria y Competitividad (Spanish Government) and the European Regional Development Fund (Project RTC-2016-5241-2).

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7. General discussion

In the present thesis, different problems in the cocoa industry are described and analysed. This thesis aims to develop and find solutions for cocoa problems, mainly sustainability, shortage of raw materials, clean labels, and consumer trends and demands.

Given growing cocoa and chocolate demands worldwide in recent years, the cocoa and chocolate industries have been focal points due to unsustainable and unethical production practices. Bearing all this in mind, **Chapter I** studies sustainability problems associated with the cocoa industry on the one hand, and sustainability labelling in consumers' perception of sensory quality and purchase intention of both cocoa and chocolate on the other hand. The problems identified in the sector can be classified into four groups: bad labour conditions for farmers (two main problems: low salary for cocoa farmers and child labour); unstable profit margins (price fluctuations and low profits); problems in cocoa plantations (low yields, high pest and disease rates, old cocoa tree age, etc.); the supply chain's environmental impact during cocoa manufacturing.

In order to improve farmers' labour conditions, cocoa sustainability and the stability of the cocoa industry-related economy, different certification programmes have been created in the last few years. These certification programmes can be divided into three groups: internationally accepted certification, sustainability programmes from cocoa industries and other initiatives from network, association and platform initiatives.

There are three internationally accepted certifications: Fair Trade Labelling Organisations International, Rainforest Alliance (emerged with UTZ in 2018) and International Federation of Organic Agriculture Movements (IFOAM). These certifications focus on farmers' conditions and livelihoods, but each has its own principles.

For the sustainability projects owned by manufacturing companies, the principal objectives are farmers' conditions and consumer awareness of sustainable cocoa production. Each company has its own strategy. Some examples are: the Nestlé Cocoa plan, Cocoa for Generation (Mars), the Cocoa life program (Mondelez), Cocoa Compass (Olam), among others.

The last group of certifications is managed by networks, associations and platforms. The most important ones are the actions taken by the International Cocoa Organization (ICCO), the World Cocoa Foundation (WCF), the European Associations cocoa (ECA) and the Association of Chocolate, Biscuit and Confectionery Industries (CAOBISCO).

The labelling of these initiatives has been a challenge for consumers, who are now more aware about problems on cocoa farms. However, four different approaches can be analysed: are consumers able to identify the sustainable labels associated with cocoa and chocolate production?; do consumers trust cocoa and chocolate sustainability labels?; are sustainably produced products perceived as more desirable than traditional ones?; does sustainable production affect the sensory perception of cocoa and chocolate?

Some sustainability labelling issues include consumers not being able to identify the commonly used sustainability labels. It can be stated that customers decide to buy sustainable products based on four different reasons: a purely altruistic environmental reason; a warm-glow effect satisfying consumers' ego; a selfish reason, when a green characteristic correlates positively with other characteristics; a positional effect that indicates purchasers' high income. Another reason is that the sustainability label affects the sensory perception of cocoa. On the one hand, farmers' practices affect the quality of chocolate and cacao. Thus the incorporation of standards and certifications helps to increase the traceability and control of cocoa flavour. On the other hand, different studies conclude that the consumers who buy sustainable products have higher expectations.

To make consumers aware of the impact that sustainability has on food (price increases, quality improvements in the final product, and also in farmers' lives), cocoa companies should create awareness campaigns. Consumers need more reasons to select this more expensive option than the traditional product when shopping.

The main objective of **Chapter II** is to study different cocoa processing parameters to prepare the cocoa industry to face shortage of raw materials (e.g.

stock differences between nib and cake) and price fluctuations (alkalising agents). To evaluate these parameters, the impact of alkalisation type (nib vs. cake), alkalising agent (K_2CO_3, $NaHCO_3$ and KOH) and process intensity (mild and strong) on the physico-chemical and sensory properties of sponge cakes is studied. To do so, eight different alkalised cocoa powders were produced and used in a standard sponge cake recipe.

On pH, the data confirm that cake dough pH is generally established by the main ingredient to have a buffering effect, and is merely affected by the employed cocoa. Regarding colour, the darkest and reddish powder was that prepared with KOH and the lightest was that made with $NaHCO_3$. In consistency terms, the dough and cake made with these cocoa powers exhibited the same colour behaviour. When comparing the nib- and cake-alkalised powders with K_2CO_3, colour differences were not significant for most parameters in both cocoa powders and corresponding cakes.

Regarding dough rheology, different water-holding capacities were observed depending on the alkalisation type. The doughs prepared with cocoa powders under mild conditions and nib-alkalised K_2CO_3 had a more dominating elastic and viscous modulus than the dough prepared with cake. More elasticity appeared for the dough prepared with K_2CO_3. Under the strong conditions, alkalisation type did not affect either elastic or viscous modulus. Thus it can be concluded that alkalisation type (nib or cake) affects dough rheology.

As regards texture, the cakes prepared with mild-alkalised cocoa powders had higher hardness and lower elasticity values than strong alkaline. When comparing alkalising agents, the cocoa cake made using the cocoa powder with K_2CO_3 presented greater hardness, and lower cohesiveness and resilience.

Despite the described differences, the sensory evaluation was similar for all the samples despite the darker samples being perceived as tastier. The results revealed no statistically significant differences in colour, sponginess, taste, chocolate flavour and mouthfeel, nor in overall appreciation terms.

To summarise, the principal differences were found for rheology and colour. The best conditions for processing cocoa if used to prepare sponge sakes would be alkalisation in cake because it is a more economical process (butter not affected) and does not reduce consumers' perceived sensory quality. Moreover, KOH and strong-alkalising conditions should be preferred to develop darker products for consumers to perceive an intenser cocoa flavour.

Chapter III studies a new strategy of *in situ* cocoa alkalisation while baking, whose aim is a clean label. This chapter describes cocoa cake recipes containing cocoa powder and different amounts of sodium bicarbonate (alkalisation during food processing). The focus of this chapter lies in helping the bakery industry in two different ways to avoid: the labelling of "alkali-treated cocoa (liquor)" and the labelling of cocoa powder containing more than 7% alkali. For this study, two different phases were studied and compared to the control cocoa powders (N, LA, MA and SA): Phase I: a standard cake recipe with natural cocoa powder (N) and different bicarbonate levels (used as a leavening agent; 1.5-, 1.8-, 2-, 3- and 4-fold the amount of the control recipe); Phase II: a standard cake recipe with medium-alkaline cocoa powder (MA) and different bicarbonate levels (used as a leavening agent; 1.5-, 1.8- and 2-fold the amount of the control recipe). The effect of the different amounts of sodium bicarbonate was evaluated by measuring water loss, moisture, specific volume, colour measurement, texture, and image and sensory analysis.

For moisture and water loss, statistically significant differences appeared between the control samples in Phase II, but not in Phase I. For specific volume, there were statistical differences for the control samples, but not for Phases I and II.

According to the colour measurements, the colour of crust and crumb was analysed. On both surfaces, colour parameters L*, C* and h* progressively decreased when increasing the degree of alkalisation (control) or with increasing amounts of bicarbonate (Phases I and II). For the control, minimum values were obtained for the sample made with cocoa SA. In Phases I and II, the drop in the L*, C* and h* values was related to increasing the amount of bicarbonate. The colour check showed that it is possible to obtain a similar colour for the SA cakes using the 4N (4-fold the level of bicarbonate and natural cocoa powder) and 2MA (twice the level of bicarbonate and medium-alkalised cocoa powder) recipes.

Hardness, elasticity, cohesiveness and resilience were studied for texture. One of the most important conclusions to be drawn was that the structure of samples 3MA and 4MA could not be measured due to a weakened gluten network. The study of the influence of degrees of alkalisation (control) demonstrated that by rising the degree of alkalisation, the hardness and elasticity of cakes were lower, but their cohesiveness and resilience were higher. From Phases I and II, it was concluded that it is possible to replace the MA control with cakes made using cocoa N and bicarbonate between 1.5 and 1.8 to avoid using alkalising agents in cocoa powder. Another conclusion is the possibility of obtaining SA texture with MA and bicarbonate contents from 1.5 to 1.8.

However, the image analysis concluded that with intermediate levels of the number of bubbles and their size, optimal textural characteristics can be obtained, and it is important for them to have high distribution and circularity values. This can be achieved by working with intermediate bicarbonate levels.

Regarding the sensory analysis, one conclusion was the possibility of using natural cocoa powder with a bicarbonate level of 1.8 and obtaining similar results as when medium alkaline cocoa was employed. However, it is also possible to employ medium-alkalised cocoa powder with 1.8 and 2 bicarbonate levels and to obtain a similar result as when applying strong-alkalised cocoa powder.

So the general conclusion is the possibility of obtaining sponge cakes with similar colour and textural properties to those obtained with alkaline cocoa starting from natural cocoa and increasing the proportion of sodium bicarbonate to 4-fold higher levels. However in sensory terms, the cakes prepared with a bicarbonate level over 2-fold the amount in the control recipe would be unacceptable. This is a very important conclusion for the bakery industry because: firstly, it is possible to achieve similar colour, flavour and texture as the medium- or strong-alkalised one using natural cocoa powders and avoiding the “treated with alkali labelling that is mandatory in some countries; secondly, with medium-alkalised cocoa powder, similar colour and flavour can be obtained as when strong-alkalised cocoa is used, with less than 7% alkali in the recipe.

The aim of **Chapter IV** is to develop a new transformation process to ensure chocolate demand on new markets. There are two reasons for this project. The first reason is because in Indian countries, the import duties for the cocoa liquor imported from ASEAN countries is 33%, but is 0% for liquor and butter. The other reason is having an option available on the market for cocoa product price and stock fluctuations.

To carry out the studies, two different dark chocolate formulations were compared: the traditional (blending cocoa liquor with cocoa butter and the necessary number of solids (cocoa powder)) and the new formulation (using cocoa powder and cocoa butter). To study the influence of solid cocoa on the recipe, cocoa recipes with different amounts of solid were followed (80, 85 and 95 g/100 g).

Regarding colour coordinates (L*, C* and h*), the applied formulation (standard chocolate or reconstituted recipe) did not significantly affect the colour of the obtained chocolate. However, the cocoa content percentage had an influence: chocolate became darker, its colour was less pure and more reddish when increasing cocoa content.

On PSD, when comparing the chocolate with growing cocoa percentages, no significant differences between different formulations ($p > 0.05$) were found in C90 (measured value of which 90% of particles were smaller), mean (length/idth) or % >75 (% of particles whose diameter was bigger than 75 µm). Regarding the PSD of samples differing in cocoa percentages, the results showed that the C90 values dropped as the percentage of cocoa increased.

More differences were found in rheology. All the samples displayed plastic Bingham behaviour and thixotropy. Yield stress, flow index and consistency values were statistically and significantly higher in F1 than in F2. These values also increased when the amount of cocoa content did. This can have an influence on both mouthfeel perception and taste.

However with the results obtained from the DSC, it can be concluded that the melting properties of the different formulations were equivalents given the minimal differences obtained in absolute terms.

Antioxidant capacity, and polyphenol, catechin and epicatechin contents rose with increasing amounts of cocoa content. This confirmed that increasing cocoa solids in a recipe is a good strategy to enhance chocolate functionality. This as higher for formulation F1 than for F2.

In sensory terms, it was concluded that no statistical differences were found between F1 and F2 for the same percentage of cocoa content. Another finding was that, depending on tasters, the chocolates prepared with 70% or 95% cocoa content were preferred. Generally speaking, the tasters who frequently eat chocolate prefer high cocoa content.

So the general conclusion drawn from this article was that is it possible to make chocolate from reconstituted cocoa liquor because it has a lower impact on the physico-chemical and sensory properties of chocolate. However, increasing the amounts of cocoa content leads to a darker, less pure and reddish colour, higher consistency and a better functional profile. Therefore, the effect of cocoa percentage is more decisive for defining chocolate characteristics than the preparation method alone. The advantage for the chocolate industry is that if using cocoa liquor to prepare chocolate is avoided, it can result in better prices for cocoa producers at certain times or in some countries, and is also another option when stocks fluctuate.

8. Conclusions and perspectives

Conclusions

This thesis includes four research lines to develop new uses and processing methods for the cocoa industry. The main conclusions are:

- On sustainability in the cocoa world, the main conclusion is that, although consumers are more aware about the impact of cocoa and chocolate production on the environment and producing communities, they need more information about these programmes and how they can be identified and affect the final product's price. This fact should be considered in forthcoming years to design products and packaging, and for effective awareness-raising campaigns that imply an actual change in consumer habits
- To be prepared to face shortages of raw materials and price fluctuations of alkalising salts, the study on sponge cake evidences that even K_2CO_3 is the most widely used alkalising agent, KOH provides the darkest, the most reddish and the least saturated cocoa, while $NaHCO_3$ yields the lightest one. When comparing nib-and cake-alkalised powders with K_2CO_3, colour differences are not significant for most parameters. The same applies to texture, but not to rheology, where the doughs prepared with the nib-alkalised powders under mild conditions exhibit a higher elastic modulus. Despite these differences, consumer satisfaction with different cakes is similar, although darker products are perceived as tastier
- To fulfil the new "Clean label" trend when preparing dark cocoa cakes, the study of replacing alkalised cocoa powders by increasing $NaHCO_3$ levels concludes that it is possible to obtain sponge cakes with similar colour, textural and sensory properties to those obtained by employing alkaline cocoa starting with natural cocoa, but by increasing the proportion of sodium bicarbonate to 2-fold higher levels. To achieve properties to the cakes made with similar strong alkaline cocoas to using medium-alkalised cocoa powders, similar properties are obtained when applying levels of sodium bicarbonate and medium-alkalised cocoa powder from 1.5- to 1.8-fold

- Studying new transformation processes to ensure chocolate demands concludes that the reconstitution of cocoa liquor from cocoa butter and cocoa powder has a lower impact on the physico-chemical and sensory properties of chocolate than increasing the cocoa solid content, which is an increasingly common trend in product innovation for brands. However, avoiding the use of cocoa liquor to prepare chocolate might offer better prices for cocoa producers at certain times of the year or in some countries with higher import duties for cocoa liquor

These four strategies are expected to contribute to find responses to many of the challenges faced by the cocoa processing industry as a result of growing social demands and recent legislative changes.

Future perspectives

To make consumers aware of the impact that sustainability has on food (price increases, quality improvements for the final product and farmers' lives, cocoa companies should create awareness campaigns. Consumers need more reasons to select this more expensive option than the traditional product when shopping.

In view of the scarcity of materials and alkalinising agents, the industry must go ahead and look for options to continue processing. After the recent COVID-19 pandemic, some elements include having stock problems, for example potassium. So industries should find new ways to continue producing with new alkalising agents

Regarding chocolate composition, consumers are always looking for indulgent and healthy products. Hence new research works should focus on this trend: create healthy products, but are indulgent. As an idea, cupuaçu is one of the products with similar properties to cocoa powder and can be a good option to be included in recipes

Although consumer concerns about clean labels have grown in recent years, their concerns are expected to further increase in forthcoming years. These studies make Spanish companies more competitive and prepared to make the most of this trend and to adapt more quickly to the change in consumer behaviour. We will have to continue to work on this guide and to provide consumers with solutions.

9. Scientific contributions

List of scientific papers

Puchol-Miquel, M., Perez-Esteve, É., Palomares, C., Barat, J.M., (2020). Formulation and physico-chemical and sensory characterization of chocolate made from reconstituted cocoa liquor and high cocoa content. Food science and technology (LWT). https://doi.org/10.1016/j.lwt.2020.110492

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Poster communications

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