Physicochemical Phenomena in the Roasting of Cocoa (Theobroma cacao L.)

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Abstract

The quality of cocoa depends on both the origin of the cacao and the processing stages. The roasting process is critical because it develops the aroma and flavor, changing the beans' chemical composition significantly by chemical reactions induced by thermal energy. Aspects have been identified as the main differences between bulk cocoa and fine cocoa, the effect of time and temperature on the formation of the flavor and aroma, and the differences between conductive heating in an oven, convective with airflow, and steam flow. Thermal energy initially causes drying, then non-enzymatic browning chemical reactions (Maillard reaction, Strecker degradation, oxidation of lipids, and polyphenols), which produce volatile and non-volatile chemical compounds related to the flavor and aroma of cocoa roasted. This review identified that the effect of the heating rate on the physicochemical conversion of cocoa is still unknown, and the process has not been evaluated in inert atmospheres, which could drastically influence the avoidance of oxidation reactions. The effect of particle size on the performance of product quality is still unknown. A more in-depth explanation of energy, mass, and chemical kinetic transfer phenomena in roasting is needed to allow a deep understanding of the effect of process parameters. In order to achieve the above challenges, experimentation and modeling under kinetic control (small-scale) are proposed to allow the evaluation of the effects of the process parameters and the development of new roasting technologies in favor of product quality. Therefore, this work seeks to encourage scientists to work under a non-traditional scheme and generate new knowledge.

Keywords Cacao types · Roasting parameters · Cocoa quality · Chemical conversion · Small-scale modeling

Introduction

Cocoa Industry

Cocoa and derivatives are one of the most popular food types in the world due to their exquisite organoleptic properties (i.e., flavor, aroma, texture) and high caloric and nutritional value as it is rich in carbohydrates, fats, proteins, and minerals [118, 135]. It has even been claimed to offer health benefits, such as antioxidant capacity, improving cholesterol levels, lowering blood pressure, and antidepressant and anti-stress effects [132]. However, the excessive consumption of chocolate is generally considered unhealthy as it can affect the nervous system, raise blood sugar levels, and cause allergic reactions, constipation, and migraine [75]. Chocolate may be consumed in its pure form (i.e., white, milk, or dark) or used in bakery and confectionery products, beverages, ice cream, and cosmetic applications such as skin and hair care [141]. Cacao is the essential ingredient of chocolate and is responsible for its unique flavor and texture [44]. Cocoa is derived from beans of the cacao tree with the Latin name "*Theobroma cacao*," meaning "food of the gods" [84]. Cacao originates from the Amazon and Orinoco rainforests in South America, where the tropical climate with heavy rainfall and high temperatures creates optimal growth conditions. In premodern Latin America, cacao beans were considered so valuable that they were used as a means of payment [83]. After the Europeans' "discovery" of the Americas, chocolate became famous worldwide, which initiated cacao cultivation in other tropical areas (e.g., Africa, Asia, and Oceania).

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General Information

The total worldwide cacao production was 4,645,000 tons in 2018: 75.9% from Africa (main producer is Côte d'Ivoire with 43.06%), 17% from the Americas (main producer is Ecuador with 6.03%), and 7.1% from Asia/Oceania (with Indonesia that produces 5.8%) [65]. The processing of cacao into chocolate (and derivatives thereof) is mainly done in Germany, Belgium, and the Netherlands, with revenues of 5.4, 2.9, and 2.3 billion euro, respectively [27]. Due to the increase of world consumption of about 91% in the last 20 years, the effects due to cocoa life cycle cannot be neglected anymore. The growing demand has led to the intensification of cocoa cultivation by expanding to new lands, including forest lands, or by the use of more excessive agrochemicals, which are not yet controlled [19]. However, some Latin American farmers are applying agroforestry systems to avoid excessive agrochemicals use and reduce environmental impact [89]. These systems could represent the challenge of future cocoa production for its ecological and social benefits.

The global cocoa market size was valued at $44.35 Bn in 2019 and is projecting an increasing rate of 4.4% to reach $61.34 Bn by 2027 Bianchi et al. [19], representing a positive economic impact for the industry and producers. But it also means a need to exploit following the objectives of sustainable development, with a more equitable distribution of profits, protection of the environment, and improvement of the social conditions of the producing countries. In cocoa production, the weakness is in the poor producing countries whose communities do not receive the fair benefit. At the same time, the most promising strength for the future is the production of high-value fine cocoa and derived products.

Cacao Beans' Origin

At the age of ca. 2 years, the cacao tree produces a large pod-shaped fruit (i.e., the cacao fruit; Fig. 1a, b), which changes color during its maturation (i.e., from green to yellow, orange, and finally red or purple). Cacao beans are covered by mucilage (i.e., pulp) inside pods (Fig. 1c). Each cacao bean consists of two cotyledons (the nib) of elliptical shape (typical dimensions of 20–26 mm length, 10–14 mm width, and 6–10 mm thickness [16]) and a small embryo plant, enclosed by the skin (the shell) (Fig. 1d).

Cacao beans are typically distinguished between the bulk and fine categories. The fine cacao beans come from the "special" *Criollo* or *Trinitario* varieties, while the "ordinary" bulk cacao beans come from the *Forastero* variety. Ninety-five percent of the world cocoa market stems from bulk beans. The other 5% are fine beans, mainly exported

by Bolivia, Ecuador, Nicaragua, Colombia, Costa Rica, Peru, and Mexico [67]. However, the world demand for fine cocoa increases due to its superior aroma and flavor [26]. Fine beans are associated with a high intrinsic quality due to a more pleasant flavor and aroma and are the basis of the luxurious "gourmet" chocolate. Bulk cacao is mainly used to produce cocoa butter as it requires the addition of sugar (milk/cream and flavor enhancers) to compensate for its bitter taste to process it into high-volume common chocolate products [26, 66]. For bulk beans, the purple or red color of the interior is an indicator of good quality, as this is typically associated with a high polyphenol content, which has good antioxidant properties, but a bitter taste (which is compensated for by adding lots of sugar). In fine cacao, the color varies from white to light brown because of the low content of polyphenol therein (Fig. 1e) [133].

Cacao Beans' Composition

Freshly harvested cacao beans contain water, fats, carbohydrates, proteins, vitamins, minerals (e.g., Fe, Cu, Mg, Zn, Na, Ca, and P), active secondary metabolites (polyphenols), and methylxanthines: theobromine and caffeine [110]. Essential compounds are the reducing sugars (e.g., sucrose, glucose, and fructose) and free amino acids (e.g., leucine, alanine, phenylalanine, and tyrosine). These are essential because they are the main precursors in the formation of aroma compounds (i.e., during the cacao bean processing) and give chocolate its characteristic flavor. In fine cocoa, these precursors are typically present in higher concentrations than in bulk cocoa; the difference is about 12.5% less in the content of free amino acids in bulk cocoa [133]. Other compounds contributing to the characteristic cocoa taste/aroma are 3-methylbutanoic acid, ethyl 2-methylbutanoate, and 2-phenylethanol [46]. Polyphenol concentrations are typically higher in bulk cocoa (86.1 ± 0.73 mg g^{-1}) than in fine cocoa (66.0 ± 0.34 mg g^{-1}), which gives the prior a greater astringency (an unpleasant sensation of dry, puckering mouthfeel) [133]. However, these compounds have antioxidant properties that may benefit health [52]. The most abundant polyphenols in bulk cocoa are proanthocyanins (ca. 58%), catechins or flavan-3-ols (ca. 37%), and anthocyanins (ca. 4%) [8, 23]. The methylxanthines theobromine and caffeine increase motivation, alertness, and energy [142]. Both polyphenols and methylxanthines contribute to the bitter taste of chocolate [10]. The theobromine to caffeine weight ratio is sometimes used to identify the cacao origin. This ratio is typically 1–2 with 0.4–0.8 wt% caffeine for the *Criollo* species, whereas for the *Forastero* species, this ratio is 5–14 with 0.1–0.25 wt% caffeine. *Trinitario* has values between *Criollo* and *Forastero* [34, 134].
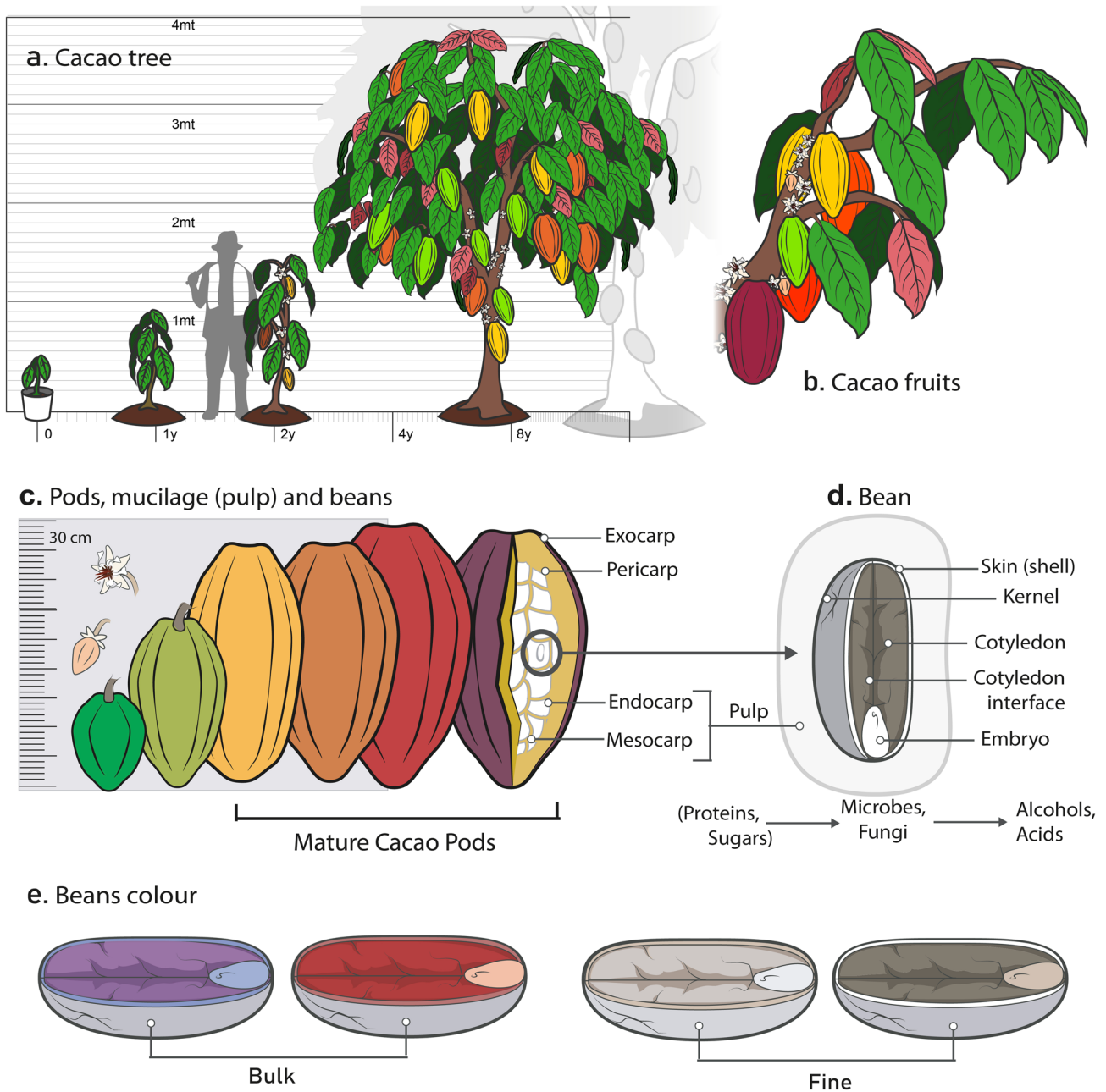
Fig. 1 Representation of (**a**) cacao tree, (**b**) cacao fruits, (**c**) cacao pods, and (**d**, **e**) bulk and fine cacao beans

It should be noted that the chemical composition, and thus chocolate flavor/aroma, of cocoa products, strongly depends on the cacao beans' genotype (variety) [54], geographical origin, agroecological conditions during growing, and the post-harvest processing techniques applied [62]. Therefore, an analysis of the influence of different processing steps in processing cacao beans into chocolate is necessary to evaluate how each step influences the cocoa flavor/aroma. This work emphasizes the roasting process.

From Cacao Beans to Chocolate

Many processing steps are required to produce chocolate and derivatives from cacao beans (Fig. 2), which may affect the final product characteristics. The mature cacao fruits are harvested manually by removing the ripe pods from the trees. These are then opened to remove the wet beans classified/sorted (i.e., by pulp color and texture and microbial contamination) and fermented before drying [86].
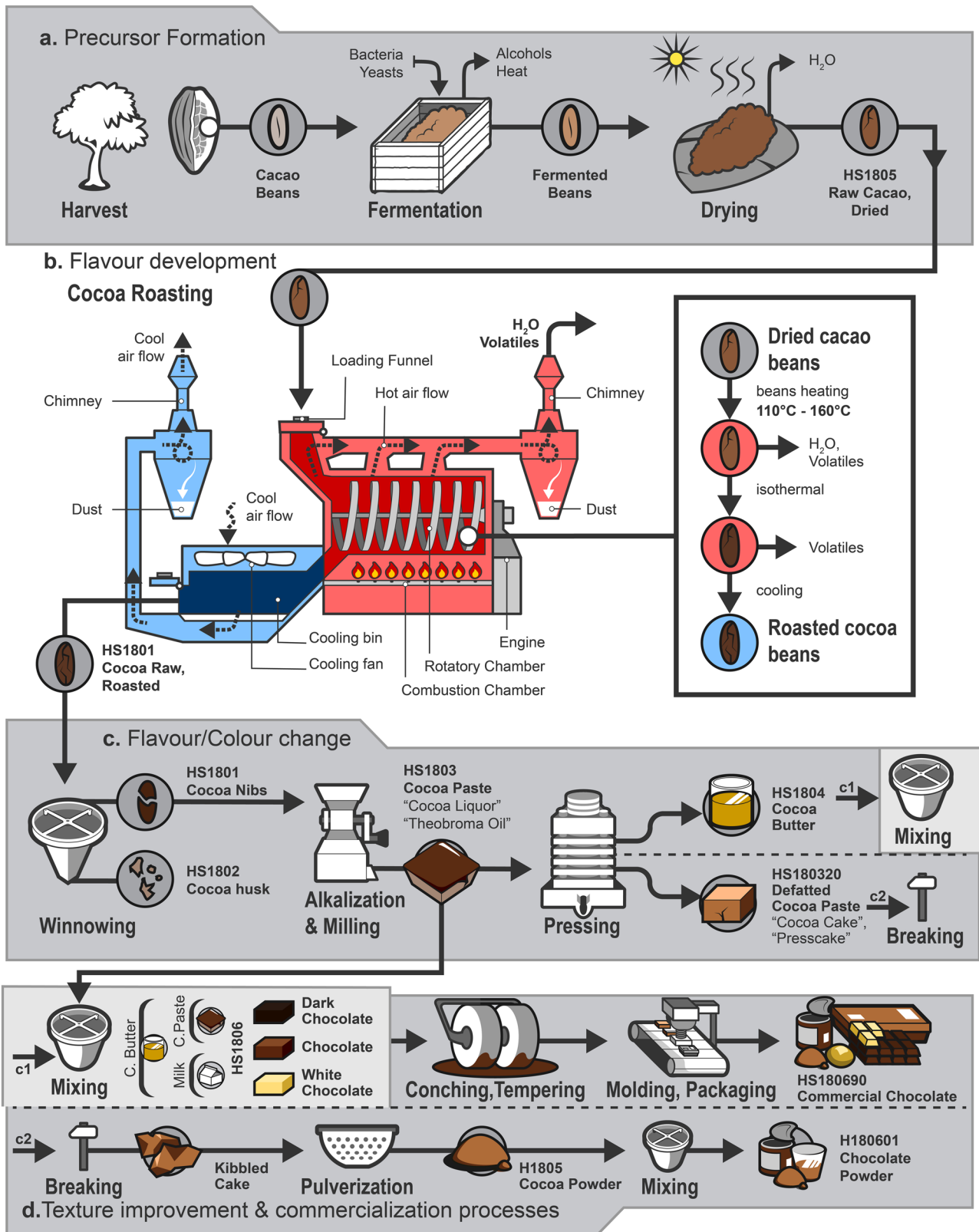
Fig. 2 Industrial processing steps from raw cacao to chocolate. (**a**) Precursor formation, (**b**) roasting, (**c**) flavor and aroma development, and (**d**) texture improvement

The fermentation is done by stacking the beans on a pile or in wooden boxes (up to 210 kg), which are protected from the rain and sun. This process takes 5 to 7 days at a temperature between 48 and 51 °C. To control the fermentation process's slight temperature increase, the beans are aerated manually [126]. The cacao bean fermentation is a microbiological process where microbiomes present in the beans (e.g., *Lactobacillus fermentum* and *Acetobacter pasteurianus*) break down sugars of the pulp (mucilage) to alcohol, lactic acid, acetic acid, and mannitol [61]. Also, other (enzymatic) reactions take place in the pulp and beans, where peptides and free amino acids are produced through proteolysis from storage proteins such as globulins [147]. Reducing sugars are formed through hydrolysis of sucrose by invertase [114, 140]. The endogenous formation of the precursors (i.e., in the beans) is influenced by exogenous processes of the pulp, where formed components may diffuse from the pulp into the cotyledon where they are retained in the drying process [33, 40].

After fermentation, the beans are dried in the sun (e.g., by spreading them out on a floor or platform) until the moisture content is reduced from ca. 55 wt% to 6.5–7 wt% [80]. Sometimes, improved methods such as direct solar drying or hot air drying (i.e., tunnel dryer and hybrid forced convection and solar dryer) are adopted [4] to accelerate the process and reduce microbial contamination in humid areas. Drying of the beans causes them to contract and decrease in density, facilitating their transport and improving shelf life due to the reduction microbial activity (water activity decreases from 0.99 to 0.72) [28, 115]. During drying polyphenols and some proteins degrade into free amino acids or denaturate completely [7, 129]. Furthermore, theobromine and caffeine contents typically decrease the drying process [35]. Additionally, drying causes the beans to shrink and increases the bean porosity, mass, and heat transfer coefficient, whereas the density decreases due to the drop in moisture content [80]. Some ranges of crude protein content in dried beans are from 15.2 to 22%, total fat 50.4 to 55.21%, ash 2.3 to 2.9%, and carbohydrates 21.0 to 24.9%; the minerals identified in mg/100 g are Fe (1.2–2.2), Cu (8.8–17.3), Mg (262.7–364), Zn (8.2–15.6), Na (2.0–3.0), Ca (143.5–170.8), P (195.8–355), and K (2070.7–2557.9) [3, 5, 11].

In Latin America, fermentation and drying are mostly done at the farms. Therefore, standardization is difficult to achieve, causing a quality decrease in the *Criollo* varieties. However, large-scale post-harvest centers are currently being built in Colombia to standardize the post-harvest processes of fine cocoa and preserve the quality [126]. Market quality standards have been established for the dried cacao beans to guarantee the quality of the chocolate [32] (Table 1). Producers supply the chocolate companies with the dried cacao beans, and the processing of the chocolate begins with roasting. The roasting of cocoa beans (see Fig. 2b) is considered the most critical step in chocolate processing because brown

Table 1 Chocolate and cocoa industry quality standards for dried cacao beans

| Parameter	Range	Reference
Moisture content	6.5–8.5% w.b.	[70]
Bean count per 100 g	Standard beans: ≤ 100 Medium beans: 101–110 Small beans: 111–120 Very small beans: > 120	[71]
Cut tests	Insect-damaged, insect-infested, or insect-germinated beans Light brown to dark brown, violet, or mix of colors Fissuring evaluation Aroma (smoke and oily taints putrid or hammy notes)	[69]
Maximum Cd content	0.5 mg/kg (0.8 mg/kg in special cases)	[27]

*w.b., wet basis

color and volatile compounds (i.e., responsible for the flavor/aroma) are generated. Also, roasting causes softening of the material essential for subsequent processing [63, 76].

The roasted beans are winnowed, where the cocoa nibs are separated from their shells (about 20% of the total weight) using gravity and airflow, i.e., the air carries away the light shell and the heavy nibs fall into the container [100]. Subsequently, the resulting cocoa nibs are ground with stone rollers (i.e., refinement) to a paste known as cocoa mass or cocoa liquor. The cocoa liquor is treated with alkali (i.e., alkalization or Dutching) to improve the color and flavor and increase dispersibility (see Fig. 2c). It also reduces astringency by complex polymerization of polyphenols, therewith decreasing the bitterness and darkening of the cocoa [3, 51]. The conching is the next step; this is a multi-day mix that contributes to the development of the final flavor and smooth texture, generally performed at temperatures above 40 °C (for dark chocolate between 70 and 82 °C) [3, 51]. Finally, the chocolate product is molded into bars, after which it is packed and ready to market. Large producers typically use continuous conveyor belts, while small manufacturers do it manually.

Cocoa Products' Characteristics

The final cocoa products' quality indicators can vary according to the consumer's requirements. The sensorial perception in cocoa and chocolate is one of the most important quality criteria in the industry and is related to the chemical composition. Currently, both the sensory evaluation by the panel of experts and the identification of the aromatic compounds through a chromatographic analysis are applied. The scores resulted define the quality profile in the Cocoa and Chocolate Flavour Wheel. For cocoa roasted and chocolate, 105 sensory attributes have been selected. These attributes
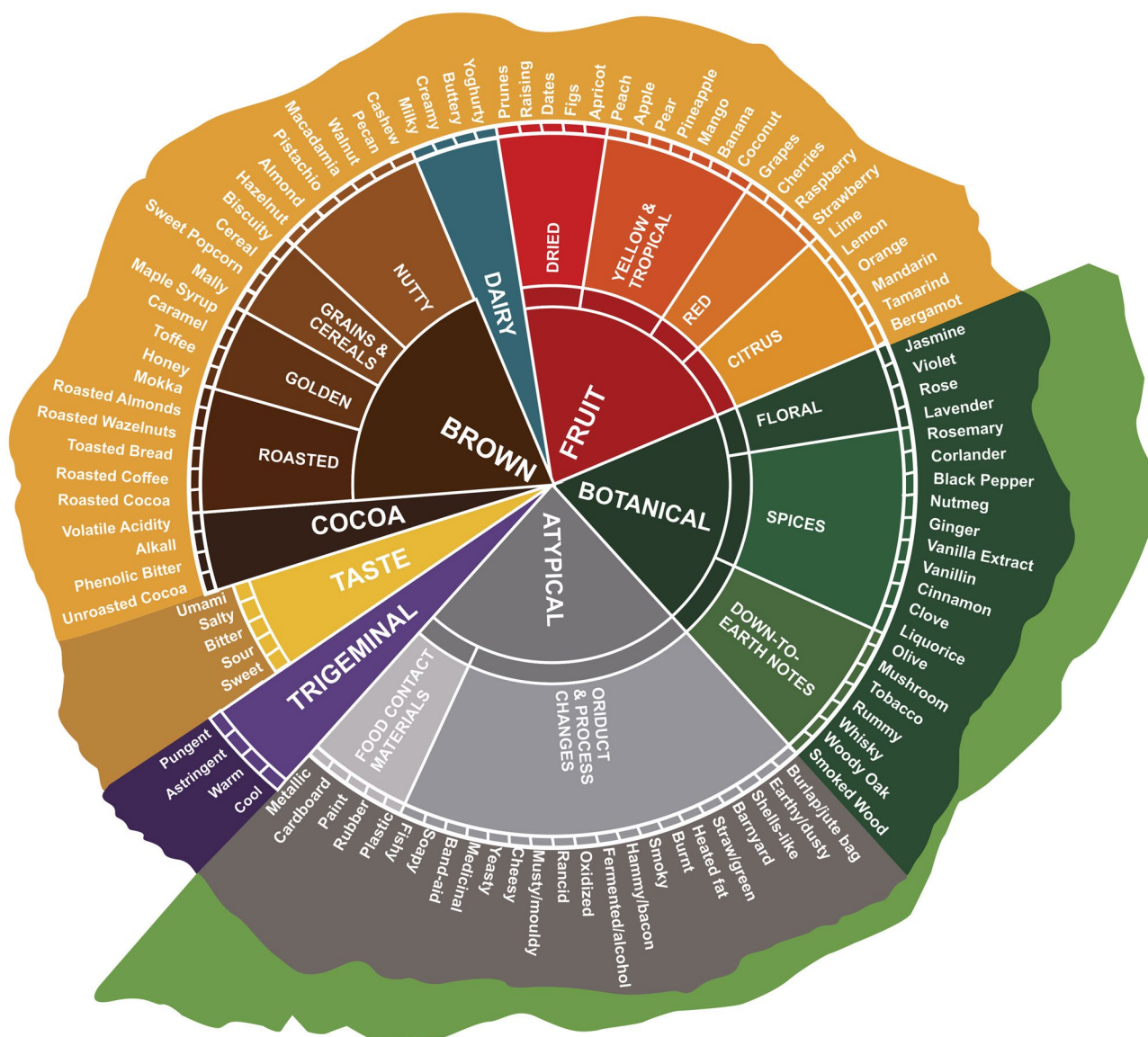
Fig. 3 Sensorial attributes for cocoa and chocolate flavor wheel by Januszewska et al [72]

are grouped into eight flavor levels, which correspond to the "Cocoa and Chocolate Flavour Wheel" shown in Fig. 3.

Making fine chocolates and candies attributes as Fruity, Floral, Sweet, and Cocoa is required, while Acidity, Bitterness, Astringency, and off-flavors are unaccepted. That is, the quality and value of chocolate are related to its unique flavor and aroma profiles [131]. However, identifying quality is a subjective issue related to the human senses and is measured by a sensory panel of experts. For example, the sound of chocolate when it is breaking it is an indicator of quality, where the high-quality has a clean, crisp, sharp snap when broken, while low-quality chocolate bends rather than breaks cleanly, has a dull sound when broken, or only crumbles [138].

High-quality or fine cocoa is characterized by a delicious taste of cacao with beautiful fruit notes. The rare, complex flavors of fine cocoa from *Criollo* varieties have an exclusive mix of complex flavors and produce fine chocolates and perfume applications [17]. Additionally, the cocoa industry has sought to highlight the quality of cocoa globally through competitions worldwide to identify where the best cocoa is produced and improve its market.

In addition, the U.S. Food and Drug Administration (FDA) has established standards of identity and quality for cacao-derived products, where the ranges of ingredients (cocoa butter, sugar, dairy products) and additives (flavorings and preservatives), the process applied, and the microbiological and chemical state as well as the testing methodologies standardized, e.g., chocolate liquor contains not less than 50% and nor more than 60% wt. of cacao fat [43].

Cocoa Roasting Process

During the roasting processes, some undesired volatile compounds (e.g., acetic acid and alcohols) are evaporated and the moisture content is reduced to about 1% w.b. with a water activity decrease from about 0.5 to about 0.2 [47, 115]. Moisture reduction minimizes the microbial activity and increases the glass transition temperature (T_g, improving the storage stability (i.e., less agglomeration of particles or texture changes. Additionally, changes in the properties of products such as texture; organoleptic, thermal, and rheological characteristics; shelf life; brown color; and functional and physicochemical properties occur [24, 120, 121].

As such, cacao roasting phenomenology and essential parameters have been researched extensively over the past decades, but roasting is a complex process of a multicomponent biomass; therefore, there are still unanswered questions and phenomena without deep explanations that are identified in this work. In the roasting process, dried cacao beans are heated from room temperature up to the roasting temperature which is commonly from 110 to 160 °C. From 34 °C, the fat reaches its melting point and goes into a liquid state within the beans' structure [115]. When the beans are further heated to temperatures above 100 °C, moisture is removed and low molecular weight compounds such as alcohols and acetic acid (formed in the fermentation process) are volatilized. Due to decreased humidity and water activity ($a_w < 0.6$), heating induces non-enzymatic browning reactions (NEB) [77]. NEB is mainly associated with the Maillard reaction. However, other chemical reactions also occur, such as Strecker degradation, lipid oxidation, and polyphenol degradation [31]. The Maillard reaction begins with the condensation of a reducing sugar and an amino acid and after can take place through different routes such as Strecker degradation, to generate aromatics such as pyrazines [48], aldehydes, esters, and ketones with a pleasant aroma to chocolate [10], and dark melanoidins [108]. NEB

reactions are responsible for forming brown compounds such as melanoidins that change the color to roasted and aromatics that give it flavor and aroma.

The roaster's technology retains the general basic design of the past and improvements have mainly focused on heating systems such as infrared heating and infrared and convection hybrids [2]. The effect of the main parameters of temperature and time on variables related to quality might be understood through modeling. This modeling must be linked to the kinetics of chemical reactions; therefore, it will make it possible to evaluate the effects of parameters not yet studied to optimize the process in terms of final quality and energy consumption.

## Technologies of the Roasting Process

Since the heating profile during cocoa roasting strongly influences the product quality, specific roaster technologies have been developed with high energy efficiency. The most common equipment is heat conduction, hot air, rotary drum roasters, or continuous roasters. The roaster technology looks to achieve uniform heating of the beans, obtain more homogeneous results, and avoid parts over-roasted or burned (Rocha et al. 2017) [112].

Technologies include the three basic zones, the come up (heating), constant targeted temperature, and the cooling zone where the product is collected (Mohos 2017) [96]. Since ancient times, technologies have been developed where new systems have been adopted, increasing heat transfer capacity and efficiency. In the beginning, a metal plate was used that contained the beans and was exposed directly to the fire, while a person moved the beans with a wooden cane (Mayer-Potschak and Kurz 1983) [191]. Today, there is continuous and batch equipment, with capacities ranging from grams (for the home) to thousands of kilograms per day according to the industry's requirements (see Table 2 and Fig. 4). High-capacity and high-performance roasters

Table 2 Roasting equipment is commonly used for cocoa

Roasting equipment	Capacity (kg/h)	Heating principle	Reference
Sirocco or ball	10–480	Convection from the hot air The beans are moved with a stirrer	[94]
Rotary drum	All shapes and sizes 0.1–3000	Conduction from direct contact with drum walls Convection from the air flowing in the drum	[37]
IR	0.4–46	Radiative heat	*Diedrich (USA)*
Continuous	1–4000	Convection from hot air passes through each permeable layer	*Bühler, Germany* *Royal Duyvis Wiener, USA* *Longer Food Machinary, China*
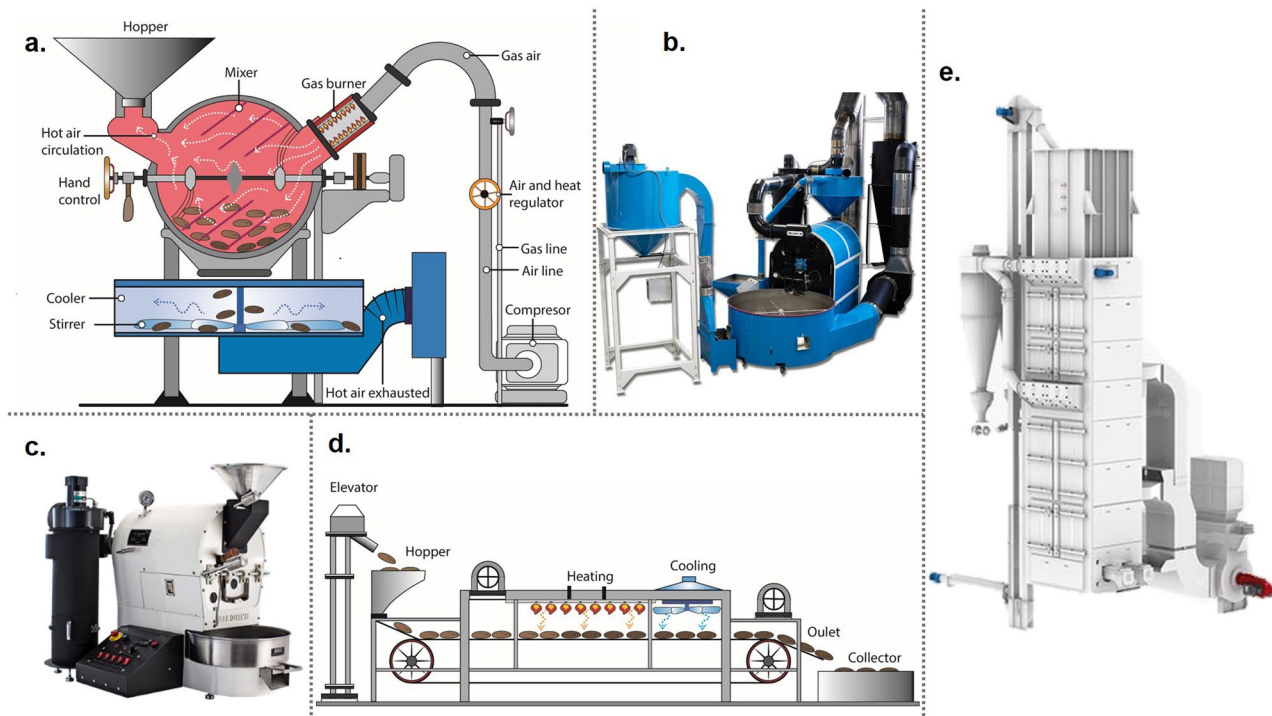
Fig. 4 Types of roasters for cocoa beans: (**a**) sirocco roaster designed and patented by G.W. Barth, Ludwisburg (1900), (**b**) industrial drum roaster up to 616 lb/h by Diedrich (USA), (**c**) infrared roaster by Die-drich (USA), (**d**) typical horizontal continuous bean roaster, and (**e**) continuous vertical roaster by Royal Duyvis Wiener (USA)

have been developed to process large volumes of bulk cocoa, while small ones are used in small companies specialized in fine chocolates. Given the cacao bean diversity and the trend of the specific demand for differentiated chocolates, cocoa roasting must specialize. Then, gourmet roasters have been developed that allow a wide range of programmable parameters, such as time, temperature, airflow, steam injection, and cooling time. In this way, it is possible to apply different operating conditions depending on the type of raw cacao and the characteristics of the product desired [58]. Additionally, the heating systems have been improved using hybrid systems (convection-infrared) and infrared (developed by Diedrich, USA) as well as the use of microwaves as a future and promising technology [128].

The cooling system that the roasters incorporate is through airflow over the cocoa beans and stirring to cool them quickly and avoid burning or over-roasting. In general, the optimal operating parameters of temperature and time depend on the type of roaster, raw material, and the roasted cocoa's characteristics, carried out by an operator who makes decisions based on his long experience.

The evolution of roasters has not been drastic, the technologies keep the same principles, and no novel developments are known, e.g., there are no roasters that use inert heating media such as N_2 or CO_2 or equipment that minimizes the processing time by shredding the beans into smaller particles. Later, emphasis will be placed on

roasting chemistry and the influence of process parameters on the formation or degradation of certain chemical compounds related to cocoa quality in the "Roasting Chemistry" section, and in the "Mathematical Modeling to Understand Thermochemical Processes" section, emphasis will be placed on kinetics and modeling of the process.

Scope of this Review

Several reported reviews have been published on agricultural topics (genotypes, harvest, and post-harvest), biochemistry and chemistry (fermentation conditions, the formation of flavor and aroma precursors) [10, 46], and health applications (antioxidant capacity, extraction, and evaluation of molecules with pharmaceutical potential) [6, 130], and also about social areas due to the importance of this product in vulnerable communities in developing countries [67, 86]. In this work, the most relevant results of cocoa roasting and technologies are grouped. It is critically evaluated how the parameters (time and temperature) improve the quality of the product related to flavor and aroma. The chemical compounds that influence the aroma and their formation reaction networks were identified. Besides, this document identified missing explanations, e.g., the effect of some parameters, such as heating rate, size particles, and reaction environment (i.e., air or inert atmosphere). Also, his work identifies the lack of experimentation and modeling that allows knowing the

true nature of the process. Finally, a way towards investigation under kinetic control (small-scale) able to describe the phenomenology present during the heating of cocoa was proposed. In this way, it would be possible to identify variations in liquid, solid, and gas fractions; temperature differentials; volatilization; and the kinetics of chemical reactions that will allow the development of new roasting technologies.

Roasting Chemistry

During cocoa roasting, the aroma, flavor, and texture characteristics of the chocolate are developed. All the chemical processes occurring during cocoa roasting are discussed in this section. In the "Aroma and Flavor Profile Related to Volatile Compounds" section, the relation between chemicals present in chocolate to its aroma and flavor profile is described, with particular attention to the differentiated characteristics of grains of the *Criollo* genotype and the main chemical reactions of roasting will be explained; in the "Maillard Reaction" section, Maillard reaction; in the "Lipid Oxidation" section, lipid oxidation; in the "Biogenic Amines' Formation" section, biogenic amines' formation; and in the "Formation of Carcinogenic Agents" section, formation of chemicals considered carcinogenic agents, and a table summary of the main chemical reactions described above, and products generated and parameters of the roasting of cocoa beans.

Aroma and Flavor Profile Related to Volatile Compounds

The flavor and aroma profile of cocoa is directly related to its chemical composition, and this determines its high or low quality. *Criollo* cacao is of the highest quality and is used in the manufacture of fine chocolates because of its high aroma and flavor to chocolate, with floral, fruity, and woody notes defined by aromatic compounds and low acidity and astringency perceptions [25]. So, this variety is more promising for future luxury applications (e.g., perfumes and fine candies) of its unique chemical composition.

The perception of the flavor and aroma of cocoa and chocolate comprises a mixture of a large amount of volatiles generated during the roasting; around 600 compounds have been identified [147], where there are alcohols, esters, amines, furans, phenols, acids, furans, furanones, pyrans, pyrones, pyrroles, pyridines, sulfur compounds, hydrocarbons, lactones, quinolines, quinoxalines, thiazoles, and oxazoles [10, 151]. With the purpose of showing the link between the chemical compound and the sensory perception, Table 3 is made. This table shows the main volatile compounds present in roasted cocoa and its sensory perception.

Among the groups of volatiles present in cocoa, the pyrazines are highlighted, because they contribute over 40% of the aroma of cocoa powder and can be used as tracers for

the flavor of cocoa [20]. These pyrazines have been found in greater numbers and higher concentrations in fine cocoa beans from the *Criollo* variety [30, 117]. About 100 pyrazines have been identified in cocoa aroma, though 2,3,5,6-tetramethyl-pyrazine (TMP) has been reported to constitute about 90% of the total pyrazines in cocoa beans [45]. Furthermore, the basic aroma of roasted beans and chocolate is attributed to TMP and TrMP (2,3,5-trimethylpyrazine), with TMP being considered the most dominant [60, 125].

In addition to pyrazines, the aroma of fine cacao is defined by aldehydes and ketones [25]. According to Voigt et al. [137], three aldehydes present in chocolate have a strong chocolate aroma (2-methylpropanal, 2-methylbutanal, and 3-methylbutanal), and the more important ketones favorable for cocoa flavor and quality are 2-heptanone, 2-pentanone, 2-nonanone, acetophenone, and acetoin [15]. The total aroma of chocolate results from the contribution of each volatile compound present in cocoa; therefore, the variation of the concentration of these results in different sensory profiles. The main desired flavors of the cocoa profile are presented in Table 3.

Considering the diverse chemical composition of roasted cocoa and its relationship with quality is essential to know the chemical reactions that govern the roasting process, as well as the influence of the main parameters, time and temperature, to look for process conditions that favor the maximum production of desirable aromatics and reduce undesirable characteristics such as astringency, acidity, and over-roasted. The above is challenging since to achieve a complete understanding of roasting chemistry, it would be necessary to initially study the kinetics of isolated principal compounds in model systems and then compare them with the cocoa matrix. The above means a time-consuming job but would generate invaluable knowledge for the cocoa industry.

The chemical reactions that govern the roasting process are Maillard reaction, Strecker degradation, lipid oxidation, and polyphenol's degradation reactions.

Maillard Reaction

Maillard reaction is complex, comprising several stages and pathways to generate volatile compounds and high molecular weight polymers (Fig. 5a). Maillard reaction begins by the condensation of amino groups with a reducing sugar to produce Schiff bases and water [57, 74]. Then, a cascade of chemical reactions that lead to the production of intermediates, aromatics, and brown polymers as melanoidins was continued [116]. The process depends on pH, temperature, type, availability, and concentration of reagents [87], as presented in Table 4. Heating accelerates the rate of the Maillard reaction, increasing the formation of aromatic compounds (showed in the previous Table 3) of cocoa [57].

Table 3 Volatile compounds present in cocoa with quantities (in mg/kg) within parentheses and their sensory perception properties

Sensory perception	Compounds	References
Aldehydes		
Sweet chocolate	3-Methylbutanal (2.69), 2-methylbutanal (0.46), 2-methylpropanal (0.23), 5-methyl-2-phenyl-2-hexenal (0.3), 4-methyl-2-phenyl-2-pentenal (0.055), 2-phenyl-2-butenal (0.39), and vanillin (9.08)	[21, 25, 60, 88, 107, 113]
Herbal, green	n-Hexanal (0.135)	[3, 60]
Fatty, waxy, pungent	Nonanal (0.063)	[88]
Bitter, grass, fruity	Benzaldehyde (2.20)	[60, 88]
Fruity, floral	Methyl p-tolyl ketone, 2-phenylpropanal, and 2-phenyl acetaldehyde (0.33)	[21, 88, 109, 136]
Alcohols		
Fruity, herbal	2-Heptanol (1.19) and 1-hexanol, 2-hexanol	[21, 60, 88]
Fruity	2-Methyl-1-butanol and 2-heptanone (0.48)	[88, 136]
Floral	1-Phenylethylethanol, 2-phenylethanol (3.68), benzyl alcohol (0.19), linalool (0.12), and 2,3-butanediol (2.68)	[60, 113, 136]
Vegetal	*Trans*-3-Hexen-1-ol and 2-pentanol (0.19)	[88, 136]
Sweet chocolate	1,3-Butanediol (2.68) and 1-propanol	[113]
Esters		
Fruity	Ethyl octanoate (0.3%), ethyl phenylacetate (0.4%), ethyl acetate (0.31), isobutyl acetate (0.14), 2-phenylethylacetate (1.5%), isoamyl acetate, ethyl butyrate, ethyl lactate, ethyl 2-methylbutanoate, ethyl valerate, ethyl hexanoate, ethyl decanoate, ethyl laurate, and methyl salicylate	[12, 21, 88, 133, 136]
Floral	Benzyl acetate, methylphenyl acetate, ethylphenyl acetate, diethyl succinate, and isoamyl benzoate	[113, 136]
Sweet chocolate	Methyl cinnamate and ethyl cinnamate	[21, 109]
Ketones		
Floral	Acetophenone (0.08)	[60]
Sweet, earthy	2-Nonanone (4.35)	[12, 60]
Floral, herbal	2-Hydroxy acetophenone	[21]
Fruity, floral	2-Phenylacetaldehyde (0.33), 2-pentanone, and 2-heptanone	[21, 88]
Furans, furanones, pyrans, pyrones, and pyrroles		
Floral	Linalool oxide (0.01), trans-linalool oxide, and 2-furfuryl propionate	[12, 21, 60]
Sweet chocolate	5-Methyl-2-furfural, 2-acetylfuran, and 2-acetylpyrrole	[21, 113]
Fruity, herbal, nutty	5-(1-Hydrohyethyl)-2-furanone and furaneol	[21, 81]
Nutty	3-Hydroxy-2-methyl-4-pyrone, pyrrole-2-carboxaldehyde, pyrrole, L-pantolactone, 2-acetyl-5-methylfuran, and 2-furfural	[21, 81, 136]
Acids		
Floral	2-Methylpropionic acid, 3-phenylpropionic acid, and cinnamic acid	[21, 81]
Amines, amides, nitriles, purines		
Nutty, floral	Benzonitrile and (2-phenylethyl)formamide	[21, 136]
Pyrazines		
Cocoa, coffee, green, mocha, roast	2,3,5,6-Tetramethylpyrazine (6.35)	[88]
Cocoa, earth, must, potato, roast	2,3,5-Trimethylpyrazine (2.49)	[88]
Nutty, chocolate, cocoa, roasted nuts	3,5-Diethyl-2-methylpyrazine (0.34) and 3,5-diethyl-2-methylpyrazine (0.019)	[25]
Peanut butter, musty nutty	2-Ethylpyrazine (0.03)	[88]
Cocoa, roasted nuts	2,6-Dimethylpyrazine (0.17), and 2,5-dimethylpyrazine (0.018),	[60, 88]
Caramel, cocoa	2,3-Dimethylpyrazine (0.48)	[88]
Nutty, hazelnut, cereal	2,3-Diethylpyrazine	[21]

Table 3 (continued)

| Sensory perception	Compounds	References
Nutty	2-Ethyl-6-methylpyrazine (0.12), 2-ethyl-5-methylpyrazine, 3-ethyl-2,5-dimethylpyrazine, and 2-ethyl-3,5-dimethylpyrazine	[60, 109]
Candy, sweet	2,3,5-Trimethyl-6-ethylpyrazine (0.43)	[88]

An important pathway of Maillard is the Strecker degradation, which leads to the initial formation of Strecker aldehydes and, subsequently through condensation, oxidation, and dehydration reactions, leads to pyrazines and other aromatic heterocyclic compounds essential in the flavor and aroma of cocoa roasted such as pyrroles, pyridines, imidazoles, thiazoles, oxazoles, hydrocarbons, ketones, esters, amines, and sulfur compounds [1113, 29, 143].

Table 4 shows that the formation of pyrazines is generated from reducing sugars, amino acids, and peptides, the contribution of peptides being greater and catalyzed by bases; also, its formation is favored at a low water activity and polyphenols can reduce pyrazines' generation (entries 1 to 3), alkaline pH produces more amount of α-dicarbonyls and less HMF and methylglyoxal (entry 4), formation of

other aromatics from same precursors as pyrazines (entry 5), and the DKPs can be assigned to a single peptide precursor (entry 6).

Lipid Oxidation

Cocoa beans have a high lipid content (32–53% by weight), and their porosity increases after drying to 24.67% [80]. Lipids can react with oxygen and produce highly reactive lipid carbonyls, which react with amino groups to produce a cascade of chemical reactions similar to the Maillard pathways and generate similar volatile products as Fig. 5b [144, 145]. In the reaction network of Fig. 5b, pathway a produces a new imine which is the precursor of the Strecker aldehyde and pathway b produces
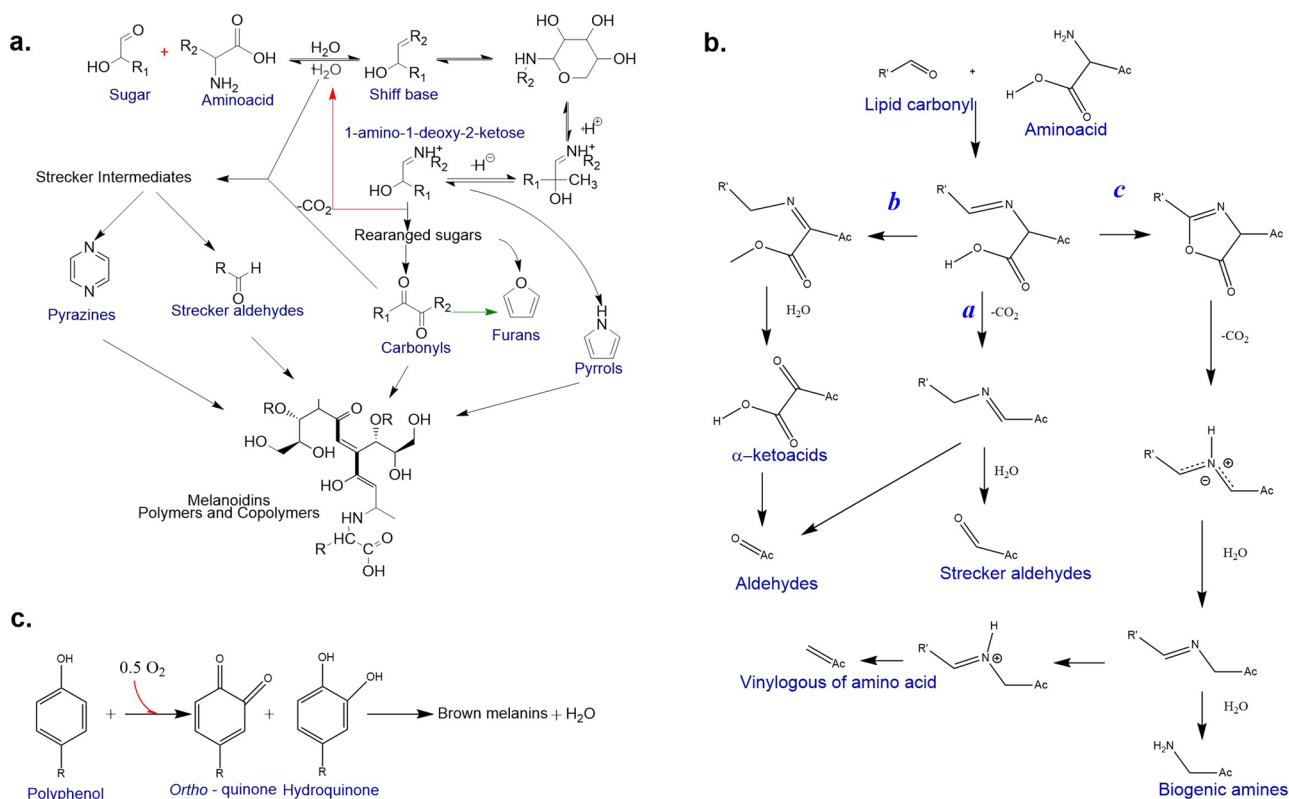
Fig. 5 (**a**) Simplified mechanism for flavor generation by the Maillard reaction by [102] with modifications, (**b**) amino acid degradation in the presence of lipid carbonyls' products of lipid oxidation [145], and (**c**) polyphenols' degradation by oxidation [92]

Table 4 Overview of chemical products and reactions during cocoa roasting

Entry	Chemical product	Precursors	Chemical reaction	Findings	Additional observations	References
1	↑ Pyrazines (Pyr)	Reducing sugars (RS) Free amino acids (AA) Peptides	Maillard and Strecker degradation	Formation is catalyzed by base (model systems)	AAs are a nitrogen source and do not provide carbon skeletons	[143]
2				The contribution of peptides is greater than AA (model systems)	The generation of pyrazines was enhanced at low aw (0.33)	[119]
3				Higher polyphenol concentration reduced pyrazines formation	Polyphenol molecules may bind part of the pyrazine formed	[95]
4	↑ HMF ↑ N-ε-Carboxymethyllysine (CML)	Reducing sugars (RS) Free amino acids (AA)	Maillard and associated pathways	Alkaline cocoa had higher concentrations of α-dicarbonyls and less of HMF and methylglyoxal	In slightly acidic conditions, 3-DG was further dehydrated to form HMF while in alkaline conditions its fragmentation was predominant	[127, 102]
5	↑ Aromatics	Reducing sugars (RS) Amino acids (AA)	Maillard and Strecker degradation	Roasting activates reactions between reducing sugars and free amino acids or short-chain peptides to generate aromatics	Reduction in the concentration of free amino acids and reducing sugars	[88]
6	↑ 2,5-Diketopiperazines (DKP)	Peptides	Maillard and associated pathways	DKPs can be assigned to a single peptide precursor	DKPs are essential for a balanced cocoa bitter flavor	[9, 124]
7	↓ Fatty acids ↓ Essential amino acids	Fats Amino acids (AA)	Lipid oxidation	Degradation of essential fatty acids, amino acids	Decreasing nutritional value	[38]
8	↑ Melanoidins	Sugars Proteins Amino acids Lipids	Maillard, lipid oxidation, polyphenols' degradation	Higher content of fat and polyphenols increases the formation of melanoidins	Glu and Fruc react with proteins and amino acids to form melanoidins	[103, 108]
9	↑ Acrylamide	Strecker degradation	Reducing sugars Amino acids	Aasparagine react with a reducing sugar	Asparagine provides the acrylamide skeleton	[42]

*↑ Increasing or formation, ↓ Decreasing or loss, aromatics (aldehydes, ketones, pyrazines, pyrroles, furanes, pyranes, and hydrocarbons), Glu (glucose), Fruc (fructose), HMF (5-hydroxymethyl-furfural)

α-keto acids and the pathway c leads to the formation of biogenic amines and Strecker aldehydes. Additionally, because of lipid carbonyl's ability to decarboxylate and deaminate amino acids, diverse studies have pointed to lipid carbonyls as alternative compounds contributing to acrylamide formation in fat-rich food products [53]. Also, by oxidation of lipids, nutritional compounds such as essential fatty acids and amino acids are degraded (Table 4, entry 7). During heating, the remaining water evaporates and leaves more porosity in the cocoa beans; then, the oxygen comes into contact with the lipids and causes oxidation reactions because always the process is done in non-insulated roasters or using hot air as a heating medium [115]. Thus, it has been determined that roasting causes a decrease in fat content especially using high temperatures and times [82]. Roasting causes a significant increase in the primary oxidation state (peroxide index) and secondary oxidation state of fats (Thiobarbituric acid value) [38]. Therefore, it is essential to evaluate inert atmospheres in the roaster chamber to identify differences in the quality of the product. Above is a research challenge that has not yet been done. That shows the need for further research, e.g., evaluating the effect of CO_2 and other compounds released and accumulated in the roaster chamber, which could influence chemical reactions in the surface and porosity of the grains.

Polyphenols' Degradation

Polyphenols are thermolabile components; therefore, roasting temperature lowers the final concentration of polyphenols by thermal degradation [1]. The thermal degradation of polyphenols occurs by epimerization and oxidation/autooxidation reactions. Usually, the epimerization reactions occur from (−)-epicatechin to (−)-catechin, and from (+)-catechin to (+)-epicatechin [79]. Figure 5c shows the general mechanism of polyphenol degradation in cocoa given by heating in oxidizing environments.

Astringency is due to the presence of high concentrations of polyphenols common in bulk cocoa beans. Various studies have been conducted to explain the degradation of polyphenols during cocoa roasting looking to preserve them because these have antioxidant activity [68, 139, 150]. Then, in roasted cocoa, it is necessary to obtain a balance of polyphenol content that gives it antioxidant capacity but does not affect the taste of the chocolate. In addition, the darkening due to the formation of melanoidins is favored by a high initial content of fats and polyphenols because they are products of oxidation reactions of lipids and polyphenols as well as Maillard (Table 4, entry 8).

Biogenic Amines' Formation

On the other hand, biogenic amines are non-volatile compounds, without taste and aroma, with biological activity on the central nervous system that can be risky if excessive concentrations are consumed [14]. The main biogenic amines found in cocoa and chocolate are 2-phenylethylamine, tyramine, tryptamine, serotonin, dopamine, and histamine [56]. The presence of these substances in high non-dangerous quantities do not represent the negative effect on quality; on contrast, this means cocoa can be the source of these components that are of high value in the pharmaceutical industry. These biogenic amines are related to lipid oxidation reactions during heating in oxidizing atmospheres such as air (Fig. 5b), in the same way as some volatiles similar to the products of the Maillard reaction (Strecker aldehydes).

Formation of Carcinogenic Agents

However, the excellent quality of roasted cocoa can be affected by the presence of furans, HMF, and acrylamide [149], which have been classified as carcinogens and are controlled by the WHO (World Health Organization). Both acrylamide and HMF are products of the Maillard and lipid oxidation reactions; the amino acid asparagine is the precursor of acrylamide formation because it provides the basic molecular structure of acrylamide (see Table 4, entry 9) [15]. In this way, both aromatic compounds that provide desirable flavor and aroma to cocoa and undesirable components can also be generated during roasting. However, roasting is a fundamental stage in the cocoa transformation that deserves further attention and research for optimization purposes.

Roasting Process Parameters and Configuration

The main parameters of the cocoa roasting process are temperature and time; then, its influence on the formation of chemical components that are relevant to the quality of roasted cocoa is described below.

Considering that the process is divided into three basic zones as Fig. 6: (i) come up (heating), (ii) constant targeted temperature (isothermal), and (iii) cooling. Roasting begins with heating the beans from room temperature to the set process temperature. The heating rate is slow due to conductive heat transport within large beans (Biot > 0.1) that offer significant resistance to energy flow. Therefore, in equipment that roasts large amounts of cacao and is heated from the outside without adequate bean movement and bean gas contact, this heating rate ends up being much slower because it is a cluster of particles with bigger dimensions than an individual bean. In the second step to maintain the process temperature for a set time, time is between 5 and 120 min,

Fig. 6 Illustrative diagram of the stages of roasting cocoa in a roaster
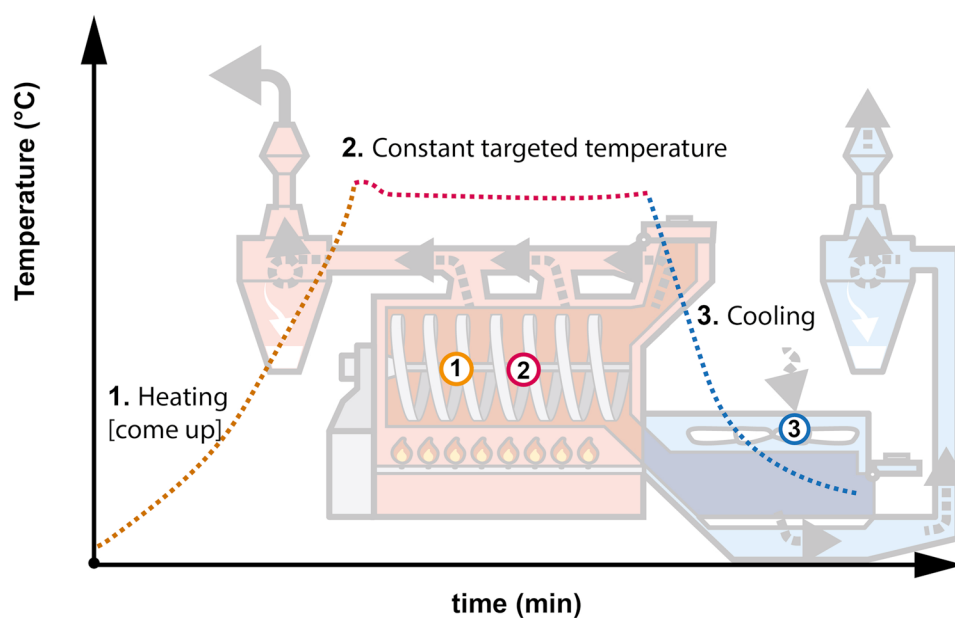
usually 10 to 60 min, and temperature is between 110 and 160 °C, usually 120 to 140 °C [42, 68, 79, 106]. However, high temperatures, 170 and 190 °C, have also been studied, resulting in good catechin content using short residence times [122]. Finally, the third step is the cooling of beans, which is intended to be quick to avoid overcooking and loss of aroma, depending on the technology of the roaster.

Table 5 shows the effect of temperature and time of roasting on roasted cocoa's main physicochemical changes found in the literature. The rate of formation of pyrazines (entry 2) is higher at high temperatures during the first 10 min of the process after the remaining concentration decreases [115, 151]. These results suggest that short roasting times < 15 min favor the maximum content of pyrazines in the cocoa beans, which represents a good quality of aroma given by these compounds. Most volatiles, including pyrazines, aldehydes, alcohols, acids, esters, and ketones (entry 2), were generated and reached maximum concentrations within the first 15 min of roasting [64]. In addition, high temperatures during short times cause less generation of HMF (entry 3), i.e., shorter times achieve lower thermal damage than low temperature and long time [116]. Lower HMF contents are positive factors of quality because they have cytotoxic effects at high concentrations. However, it should be considered that the volatile compounds mentioned above, measured using solid-phase microextraction (SPME–GC–MS), were generated during roasting and remained trapped within the cocoa beans. So, when finding that the highest concentrations are during the first minutes of heating, it is evident that there is a lack of knowledge about any low molecular weight compound lost by volatilization (the gas fraction) or degradation when heating to longer residence times. Likewise, the distribution of these compounds within cocoa bean

is unknown since, due to the low conductivity, temperature differentials can be generated and consequently difference in the performance of chemical reactions. Therefore, it is recommended to do small-scale experimentation under kinetic control to determine the rate of compound formation, and process modeling to identify the evolution of thermal and mass differentials in cocoa.

In the same way, as for volatile compounds, it has been found that the generation of acrylamide (entry 4) tends to decrease when using high temperatures (> 150 °C); this is because acrylamide is not thermally stable. Therefore, the use of high temperatures is recommended to minimize the acrylamide concentration as a carcinogen and HMF, which affect the quality of chocolate [42]. However, due to the risk of excessive browning or thermal differentials when heated faster at high temperatures, it is advisable to evaluate more efficient heating technologies such as microwaves, IR, or hybrid systems, which could represent the future of roasters. On the other hand, since current research has been done under typical conditions and conventional equipment, it is necessary to leave this vision and dare to change conditions such as the use of inert atmospheres and reduction of cocoa size to improve heat transfer and track the chemical variation over time.

Roasting causes decreasing natural products with biological activity such as theobromine, caffeine, and polyphenols (entries 5 and 6). For example, roasting for 40 min at 100 caused a decrease in total polyphenols of 9.7% while at 190 °C it decreased to 39.9% [123]. It is desirable to optimize roasting conditions that maximize the desired compounds' production while preserving a desirable sensory profile. Nevertheless, roasting increases the content of biogenic amines (entry 7), resulting in *Trinitario* beans the highest final content [104]. The main biogenic amines found are 2-phenylethylamine,

Table 5 Effect of the main roasting parameters on physicochemical changes in roasted cocoa

Entry	Influence of roasting	Experimental conditions	Variety	Effect	References
1	Formation of volatile compounds	HA vs SHS from 150 to 250 °C (15 min)	*Forastero* (pH = 5.6)	↑ Rate < 15 min (150 °C) ↑ Rate < 10 min (200 °C)	[151] [64]
2	Formation of pyrazines	IR heating from 100 to 200 °C (15 min)	*Criollo*	↑ Content at 150 °C ↓ Content at 100 and 200 °C	[115]
3	Formation of HMF	HA from 125 (74 min) to 145 °C (40 min)	*Criollo*	↓ Content at ↑ temperatures (0.1–0.8 g kg^{-1})	[116]
4	Formation of acrylamide	HA from 110 to 160 °C (15 to 40 min)	*Forastero*	↓ Content (> 150 °C) ↑ Content (< 150 °C)	[42]
5	Decreasing of methylxanthines	C at 180 °C (10 min)	*Forastero*	↓ Content of theobromine (28 to 70% lost) ↓ Content caffeine (around 60% lost)	[146] [41]
6	Polyphenols' degradation	CO from 100 to 190 °C (10 to 40 min)	*Trinitario*	↓ Content at ↑ temperatures and ↑ time 9.17% lost (100 °C) to 39.9% lost (190 °C)	[123] [122]
7	Formation of biogenic amines	HA from 110 °C to 150 °C (25 to 85 min) with RH (0.3% to 5.0%)	*Trinitario*	↑ Rate at ↑ T and (18.67 to 33.46 mg/kg ff-dw)	[104]
8	Decreasing of moisture (X_w) and water activity (a_w)	HA vs SHS from 150 to 250 °C (15 min) IR from 100 to 200 °C (15 min) C at 110 to 170 °C (5 to 65 min)	*Trinitario* and *Criollo*	↓ Rate at ↑ temperatures (~ 1%) a_w from 0.4 to 0.6 ↑ Maillard reaction	[151] [85] [115]
9	Formation of melanoidins	HA from 125 (74 min) to 145 °C (40 min)	*Criollo*	↑ Rate at ↑ temperatures	[116]
10	Darkening	HA from 125 (74 min) to 145 °C (40 min)	*Criollo*	↑ Rate at ↑ temperatures (E_a: 132 kJ mol^{-1})	[116]
11	Diminution of surface area, specific internal volume, and the average pore size	IR from 100 to 200 °C (15 min)	*Criollo*	Melted fat and solidified after heating accumulate in the pore walls affecting microporosity	[115]

*HA (hot air), SHS (superheated steam), IR (infrared heating), CO (convection oven), C (conduction), RH (relative air humidity), ↑ (higher), ↓ (lower), and kg ff-dw (fat-free dry weight basis)

tyramine, tryptamine, serotonin, dopamine, and histamine [78, 105]. Biogenic amines have physiological roles in humans, acting as local hormones and neurotransmitters in low concentrations, but they can cause a range of toxicological effects if are consumed in excess [130].

On the other hand, roasting also produces high molecular weight polymers such as melanoidins (entries 9 and 10); they are responsible for darkening and involved in sensory properties (i.e., taste, flavor and texture) of foods [98] and antioxidant activity [36]. Both the darkening and the formation of melanoidins are greater when using high temperatures and longer times. Finally, in addition to the softening of the cocoa beans, the heating causes the fat's fusion and mobility, which transports substances and obstructs empty spaces, causing a diminution of surface area, specific internal volume, and the average pore size [115].

Consistent with the above discussion and table, there is evidence that the analysis of the main physicochemical changes caused by roasting, mainly the generation and volatilization of aromatic compounds, is valuable but has not yet been explored

in depth. For example, the effect of heating rate, particle size, and environment of reaction conditions (inert or oxidant) is still missing, opening a world of exciting science possibilities that deserve to be explored. For this purpose, an efficient tool for analyzing and understanding the cocoa roasting process are kinetics and phenomenological modeling explained in the next chapter.

Mathematical Modeling to Understand Thermochemical Processes

In order to improve the technological processes of cocoa roasting and obtain a high-quality product in line with consumer trends, it is essential to have a thorough knowledge of the chemical, physical, and thermal phenomena in cocoa beans during roasting. In this way, the kinetic analysis of the formation of volatile compounds, the degradation of natural cocoa products, and the mathematical modeling of the process (i.e., mass and energy balances of the system) are handy tools for a deep understanding of the roasting. With

these theoretical and experimental methodologies, it is possible to predict results accurately and reliably and optimize the process.

Modeling allows drawing, interpreting, and understanding a particular process's phenomenology by applying phenomenological laws of nature. With these models, it is possible to identify and describe events that, through experimentation, are not possible for any reason (e.g., times too short or too long to track the phenomenon). In engineering sciences, modeling is performed to predict results, design and optimize processes, minimize the costs of experimentation and validation, and characterize and generate knowledge of any process. For example, with modeling, it would be possible to understand the physicochemical and thermal changes that occur within cocoa beans during heating, and it would be possible to predict the evolution of phenomena that cannot be observed experimentally, such as heat transport through the solid, porosity, and gas generation over time, among others.

Mathematical models can be empirically based if the expressions between the different quantities that are modeled (temperature, concentration, moment vs input quantities) are determined based on a statistical analysis of the experimental results. In this sense, they are mathematical expressions that allow predicting the magnitude at different times, and conditions are valid for the equipment where the experimentation was carried out; they cannot be considered general models. Also, the models can have a combination of respecting the balances of matter, energy, and moment that include terms based on constitutive relations of transport mechanism that can be determined experimentally and therefore are considered semi-empirical models. Finally, the models can be phenomenological in nature, including balance equations and theoretical models for constitutive equations or relationships. Also, the models can be made at different scales macroscopic (bulk and particle) and microscopic (molecular); both are a useful emerging tool to analyze the thermochemical process as roasting.

Some mathematical models describe the evolution over time of variables such as density, momentum, and energy at the macroscopic level. At this macro-scale, the variation in time and physical space of these variables can be followed due to the macroscopic movement of the continuous system and the transport phenomena that occur within the system due to the microscopic world. In this way, both empirical models and Fick, Fourier, Newton, and Ohm's laws can be applied.

In heterogeneous systems such as cocoa and other biomasses (see Fig. 7c), it is necessary to consider the volume variation and the interactions between the present phases; this applies to processes as drying, roasting, torrefaction pyrolysis, combustion, and gasification. Also, the models

must consider the different scales, which can be understood, taking into account the concept of volume fraction (ε_j) for each j-phase. In this way, the cocoa roasting process can be modeled on different scales (Fig. 7d). The bulk scale (i.e., several beans or in a roaster), then on a smaller scale, is the particle models. A particle is like a small, heterogeneous cocoa bean that preserves all the phases present in the original system (a group of cells or an individual cell). Going on a smaller scale, there is modeling at the molecular level that could explain specific phenomena such as forming a certain compound, the mechanisms, and interactions present at the micro-scale.

Depending on the particle size and heating rate, both drying and devolatilization processes may occur simultaneously inside the particle, and thus, one could expect wet biomass, dry biomass, and char at the same time. This is observed in case of large particles, within which large temperature gradients are present, but for very small particles, such gradients are unlikely, and in such cases, only one of these phases can be found inside the particle. For example, [55] developed and validated a torrefaction model of large biomass particles by coupling the material balance and energy to a kinetic model in two steps, drying and devolatilization. This model predicted the variation of gas, water, and solid fractions over time, as well as variations in pressure and density within the particle.

Alean et al. [7] considered a thin layer of spherical cocoa beans (bulk scale), dried by hot air at temperature "T," absolute gas moisture, with velocity "V" and the phases gas "g" and solid "g." The material balance considered the convection, diffusion of water, and degradation of polyphenols (Y) (Eq. 1). The energy balance in the gas is considered the convection and phase change (Eq. 2) and the conduction in the solid (Eq. 3).

$$\varepsilon \rho_g \frac{\partial Y}{\partial t} = -\varepsilon \rho_g v_g \frac{\partial Y}{\partial x} + \frac{\partial}{\partial x}\left(\rho_g D_{eff} \frac{\partial Y}{\partial x}\right) + \rho_s \dot{m}_w''' \qquad (1)$$

$$\varepsilon \rho_g C_{p,g} \frac{\partial T_g}{\partial t} = -\rho_g v_g C_{p,g} \frac{\partial T_g}{\partial x} - Ua(T_g - T_s) - \dot{m}_w'''\left[C_v(T_g - T_s) + \lambda\right] \qquad (2)$$

$$(1-\varepsilon)\rho_s C_{p,s} \frac{\partial T_s}{\partial t} = -\frac{\partial}{\partial x}\left(K_{eff} \frac{\partial T_s}{\partial x}\right) + Ua(T_g - T_s) - \dot{m}_w'''[\lambda] \qquad (3)$$

where the bed porosity ε, i.e., the void fraction between beans and intra-beans. It is determined from the volume fraction ρ_s occupied by the solid. Besides, Borda-Yepes et al. [22] proposed a drying model with volume variation $\left(\frac{1}{V}\frac{\partial V}{\partial t}\right)$. This consideration of the volume variation is a great contribution because it is helpful to apply in cocoa roasting, where
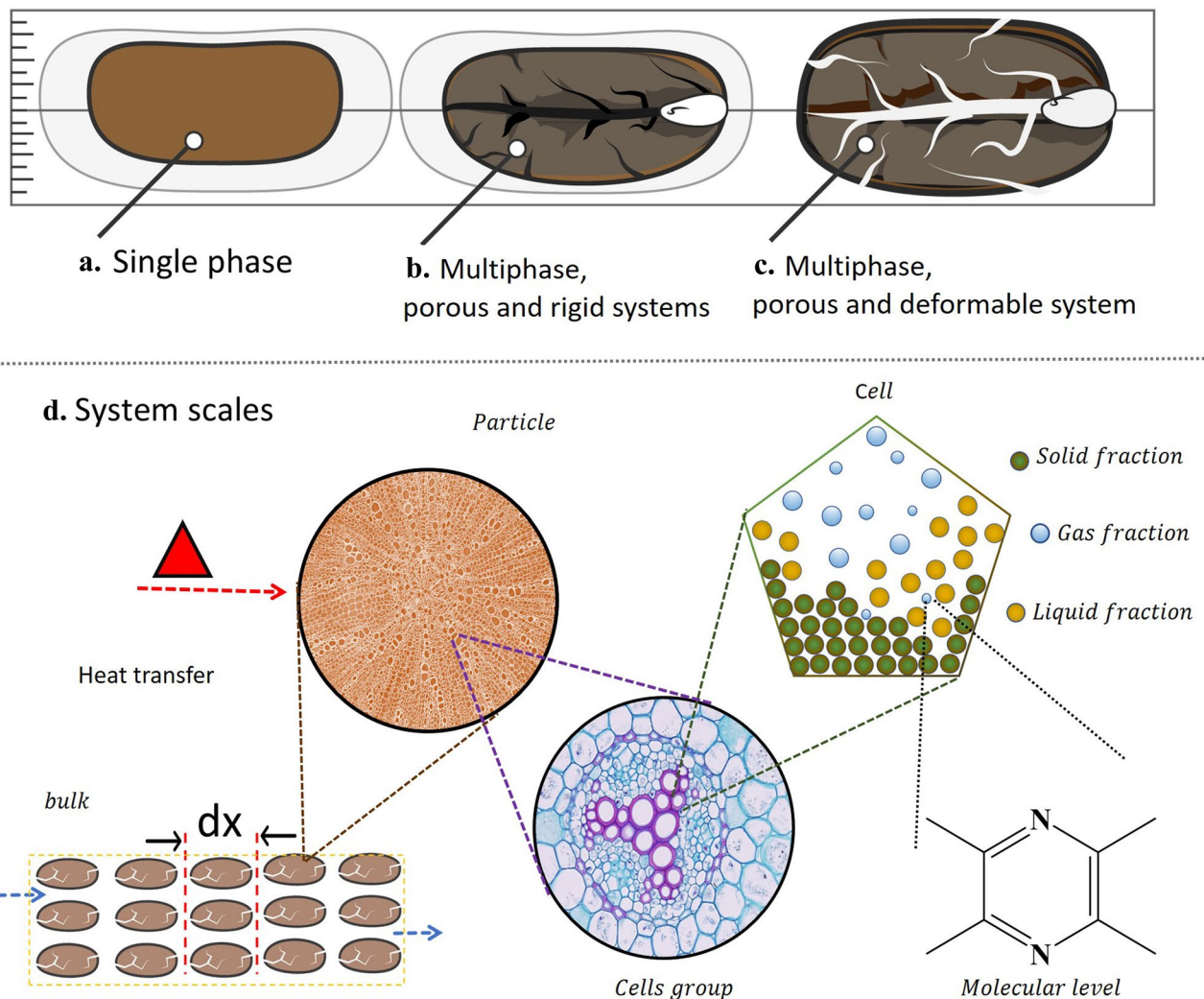
Fig. 7 Illustrative scheme of (**a**) types of systems single and multiphase and (**b**) heterogeneous system at different scales and different phases useful for the mathematical modeling of thermochemical processes

the swelling of the beans occurs during heating due to the strong internal pressures of gasses generated (Fig. 7c).

Particle Mathematical Modeling

At the particle level, the mass and energy transfer phenomena especially alter the behavior of the released products (distribution and quantity). During the heating, many gaseous species are released, which, depending on the type of biomass and operating conditions of the reactors, can favor the production of tars, the loss of valuable aromatics, or heat release.

Many authors have established that the main factors affecting the particles' mass transfer processes are size and pressure. Niksiar and Rahimi [101] considered that for small particles (< 900 μm, there is a kinetic control

scale; therefore, the restrictions on the transfer of mass and energy are negligible. In these cases, it is enough to use zero-dimension models to present the conversion during the reaction. In VRM models (Fig. 8), it is assumed that the particle is consumed uniformly throughout the volume at constant volume expressed as $\frac{d\alpha}{dt} = k(1 - \alpha)$, where k is the kinetic coefficient of the reaction and α is the conversion.

The decreasing nucleus models (SUCM and SUPM) describe a particle dense and non-porous one, where the reaction occurs at an interface, which moves to the center. SUCM is associated with the ash production, where the ashes cover the unreacted nucleus of the particle. In this model, the size of the nucleus decreases, but the total volume of the particle remains constant. The above models can be represented by the same previous mathematical expression with an order of $\left(\frac{2}{3}\right)$.
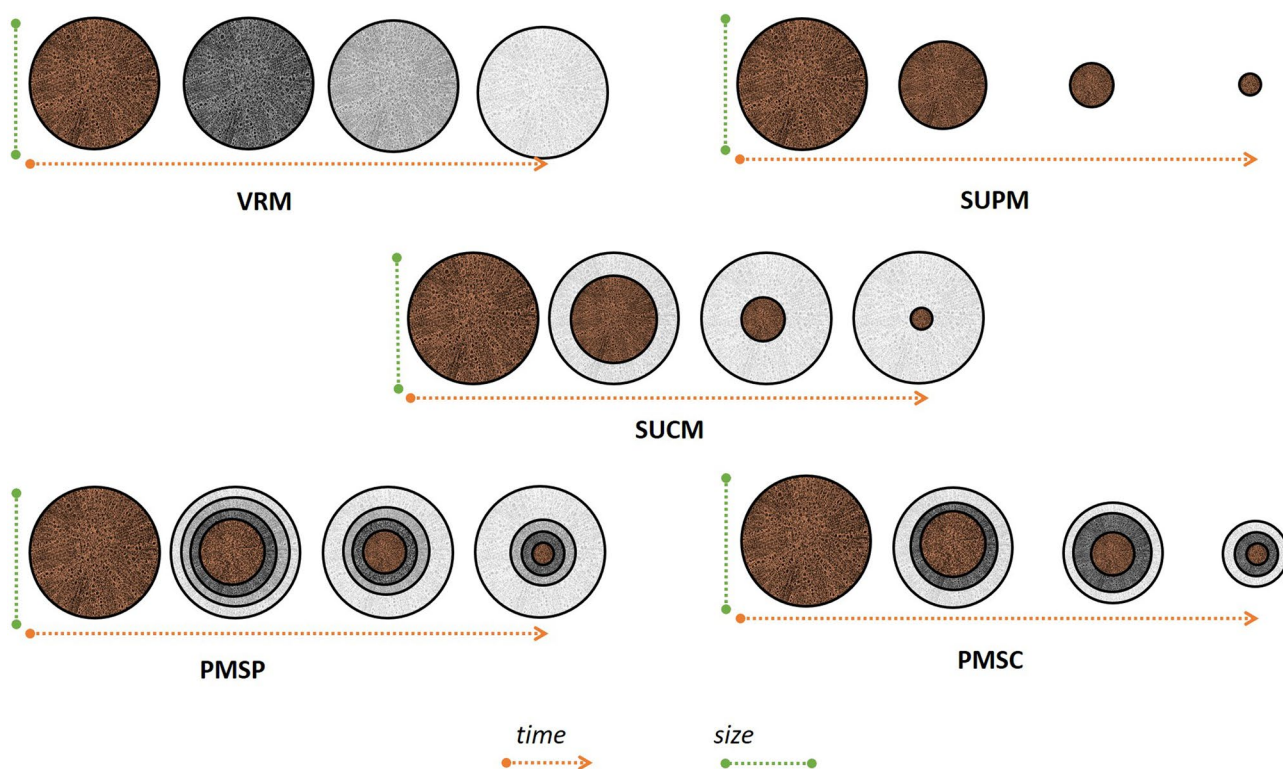
Fig. 8 Type of models based on the conversion of the particle: volume reaction model (VRM), shrinking unreacted particle model (SUPM), shrinking unreacted core model (SUCM), progressive model with shrinking reacting particle (PMSP), and progressive model with shrinking reacting core (PMSC) [148]

The progressive models (PMSP and PMSC) are extensions of the previous models, where the reaction occurs in the entire volume, but intermediate conversion states appear. The RPM (Ramdom Pore Model) has normally been used to represent progressive models. The RPM describes the behavior of a porous particle, whose internal surface area changes depending on the conversion as (Eq. 6)

$$\frac{d\alpha}{dt} = k(1 - \alpha) \cdot \left[1 - \varphi \log(1 - \alpha)\right]^{1/2} \tag{4}$$

where φ is a parameter associated with the internal structure of the porous. A high value of φ means that the initial porosity is small and that any change in the internal surface area greatly affects the degree of conversion.

Solid–Gas Reaction Models

Gas–solid reaction systems are useful to know the dynamics of gas interactions with the solid surface. Thus, in gas–solid reactions, the diffusivity and the kinetics depend largely on the solid's microstructure, which can vary due to the chemical reaction and sintering, among others. So, grain size distribution and sintering affect the microstructure's development during solid–gas reactions, a problem of interest in classical grain models [49, 50]. To study this effect, a model based on population balances was developed by [90], to consider the distribution of grain size inside the pellet and at the same time consider sintering through the terms of death and birth in the population balance. In this way, as the chemical reaction proceeds, the initial grain radius (r_0) increases or decreases (r_p) depending on the molar volume of the solid product and the sintering process. In contrast, the unreacted core (r_c) radius decreases (see Fig. 9). It is considered that the particle is composed of a large number of grains with an initial radius distribution (see Fig. 9b); then, each grain changes from size due to chemical reaction and sintering.

The material balance for the gas is based on the reaction system: (gas) $+ bB$(solid) $\rightarrow cC$(solid) $+ dD$(gas) only with the diffusive term: $J_j = \frac{1}{R^2} \frac{\partial}{\partial R}\left(D_e R^2 \frac{\partial C}{\partial R}\right)$, where C is the molar density of the specie j, D_e is the effective diffusion, R is the spatial variable, and the generation term is related to the chemical reactions (r) (Eq. 5).
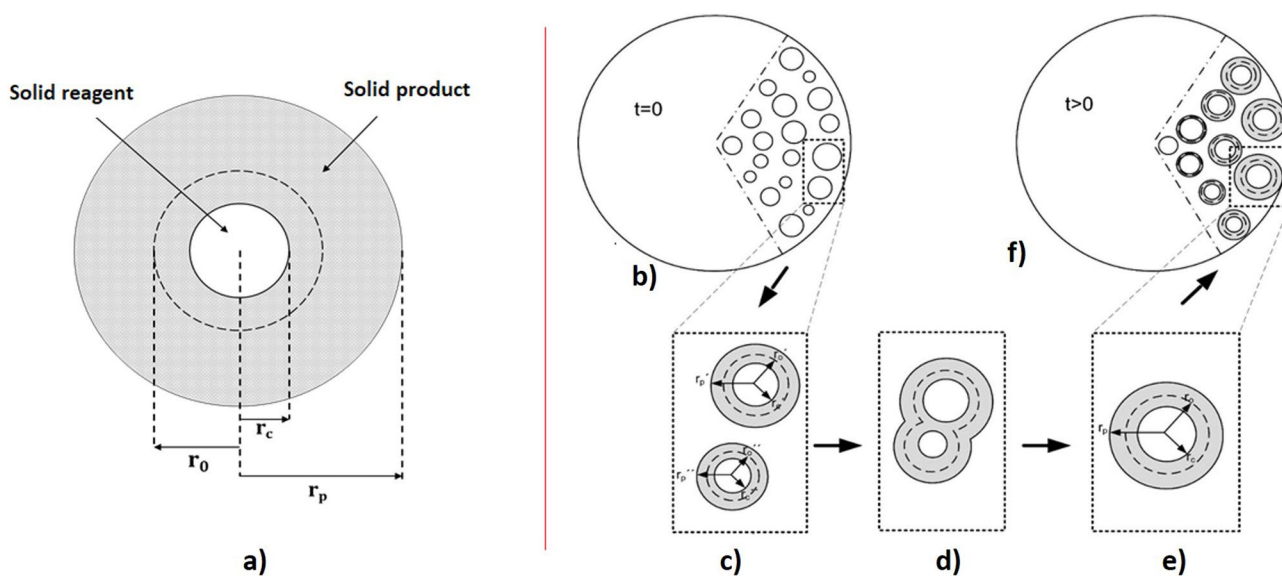
Fig. 9 Graphic illustration of (**a**) grain size change and (**b**–**f**) evolution of the change in the size of each grain due to chemical reaction and sintering [90]

$$\varepsilon \frac{\partial C}{\partial t} = \frac{1}{R^2} \frac{\partial}{\partial R} \left(D_e R^2 \frac{\partial C}{\partial R} \right) - \dot{r}''' \tag{5}$$

On the other hand, other authors have developed models to understand and predict the behavior of the small-scale pyrolysis process, so Montoya [97] developed a mathematical model in fast pyrolysis (1200 °C s^{-1}) considering that phases solid, liquid, and gaseous coexist in the particle (equations not shown). Likewise, this model considered the consumption and formation of species (reagents and products) and bubble dynamics generation with a population balance.

Modeling of the Cocoa Roasting Process

Cocoa roasting modeling is complex because it is necessary to include some quality attributes as dependent variables [18]; these variables are subjective to the perception of human senses so it is difficult to predict them. However, these variables are correlated with roasted cocoa's chemical composition, so a model able to predict the most relevant chemical compounds is a current challenge for engineering. On the modeling of cocoa roasting, there is little bibliographic information; an approach towards kinetics was primarily found where both semi-empirical and empirical models have been used all of them on bulk scale.

The main phenomenon that has been studied is the loss of water. In this way, the kinetics of moisture loss follows an exponential decay very similar to the drying processes; such behavior was similar for all the models shown Table 6.

That is, the mass transfer process is dominated by internal diffusion [73, 99]. The loss of moisture resulted up to a final value between 1.9 and 2.3% d.b. [116]. Furthermore, water loss depends strictly on the temperature used with an activation energy of 59.6 ± 0.8 kJ mol^{-1}, which indicates that it is a coupled process where the phenomena of mass and energy transfer are closely related.

Likewise, the kinetics of HMF generation by the exponential model [116], the formation of 2,5-diketopiperazines (DKPs) was correlated positively with their peptide precursor and was analyzed using a solid-state reaction of zero-order (sigmoidal) [9].

Darkening has been evaluated with first- and zero-order models finding activation energy of 59 ± 8 kJ mol^{-1} that is similar to that of the oxidation of polyphenols [68]; therefore, it was concluded that non-enzymatic browning during roasting is initially induced by the oxidation of polyphenols [116]. The dependence of melanoidin formation on the roasting temperature was also determined by the asymptotic model, and the degradation kinetics of polyphenols during the roasting of cocoa beans was evaluated with the Weibull probabilistic cumulative model [68]. All the model equations are in Table 6.

On the cocoa roasting process, there are several specific points where the modeling, on a smaller scale, is necessary to explain this process's phenomenology better. Although it is known that there are important differences directly related to factors such as temperature and process time, there are no studies conducted where the influence of the heating rate is analyzed; therefore, its effect on the final

Table 6 Kinetics and phenomenological models used for the cocoa roasting process

Type	Phenomena	Model	Equation	Reference
Kinetics	Moisture loss	Newton	$MR = exp^{-kt}$	[59,39, 116]
		Page	$MR = exp^{-kt^n}$	
		Two-term	$MR = exp^{-kt} + bexp^{gt}$ b, k, g (constants), MR (moisture ratio)	
		Weibull	$MR = 1 - exp^{-(t/\beta)^\alpha}$ α, β (shape and rate parameters)	
	HMF formation	Exponential	$C_t = C_0 + k_0 exp^{k_t}$ k_0 (pre-exponential factor, k_t (rate of formation)	[116]
	Formation of 2,5-diketopiperazines (DKPs)	Zero order and solid-state reaction	$P = A_0 + kt$ P (DKPs concentration), A_0 (initial concentration), k (rate constant)	[9]
	Malanoidins generation	Asymptotic	$C_t = C_0 \dfrac{t}{\frac{1}{K_{in}} + \frac{t}{C_e - C_0}}$ k_{in} (initial rate melanoidin formation), C_0, C_e, and C_t (initial, equilibrium and time t concentrations)	[116]
	Darkening	First order	$L^* = \dfrac{1}{k_L t + \frac{1}{L_0^*}}$ L_0^*, L^* (initial and time t lightness), k_L, (reaction rate)	
		Zero order	$h° = h° + k_h t$ $h°_0$, $h°$ (hue angle value), k_h (reaction rate)	
	Polyphenols' degradation	Weibull probabilistic cumulative	$\dfrac{C_o - C_t}{C_o - C_e} = 1 - exp^{-(t/\beta)^\alpha}$ C_0, C_e, C_t (initial, equilibrium and time t concentrations), α (shape parameter), β (rate parameter)	[68]
Phenomenological	Effective diffusivity of water (D_e)	Arrhenius equation	$D_e = D_o exp^{-\frac{E}{RT}}$ D_o (diffusivity constant), E (activation energy), R (universal gas constant)	[5913]
	Diffusion of moisture from inside the bean to the surface	Fick's second law	$MR = \dfrac{6}{\pi^2} \sum\limits_{n=1}^{\infty} \dfrac{1}{n^2} exp^{-\left(\frac{D_e n^2 \pi^2 t}{r_0^2}\right)}$ MR (initial, equilibrium and time t moisture), D_e (effective diffusion), r (radius), n (integer number)	[39, 116]
	Thermal diffusivity (α_e)	Fourier law	$TR = \dfrac{8}{\pi^2} \sum\limits_{n=1}^{\infty} \dfrac{1}{2n-1} exp^{(2n-1)\frac{x^2}{4L^2}t}$ $TR = \dfrac{T_i - T_s}{T_0 - T_s}$ T_R, T_0, T_s (temperature ratios, initial, and surrounding)	[9359]

chemical composition and volatilization is still unknown and physical properties.

The heating rate can determine the residence time of the process; the efficiency of heat transfer will also depend directly on being a thermal gradient which can be generated and consequently, some areas over-roasted and other partially raw areas if very large particles as cacao beans are used. So, another important factor that has not been explained is the effect of particle size. Considering that in the thermochemical processes, there are coupled phenomena of mass and energy transfer, so the particle size can determine these; therefore, it is necessary to study this factor. Thus, particle scale modeling would be a helpful tool to analyze the cocoa roasting process.

Mathematical modeling of thermochemical processes from biomass for energy applications is more advanced than thermochemical processes for food and flavoring applications. These latest applications include quality attributes and various variables to make them viable for human consumption, making them a great challenge for the engineering sciences.

Concluding Remarks

The quality of chocolate and cocoa derivatives is conditioned by the origin of the cacao beans and the processing stages during their transformation; therefore, the traceability of these products is decisive to guarantee a uniform final quality as well as knowing the origin of the raw material.

The roasting process has been evaluated on a bulk scale (beans) using traditional hot air toasters and ovens, while the small-scale study has been neglected, and consequently, the explanations of all the phenomenology present during heating are still missing.

The characteristics of quality highly appreciated in the cocoa and chocolate market are related to the chemical composition (i.e., aromatic components generated in roasting). However, the effect of variables such as heating rate, particle size, and reactor atmosphere (i.e., oxidant vs inert gasses) is still unknown.

The literature showed that the researchers identified the chemical compounds present in roasted cocoa, that is, the chemical compounds of the solid fraction, while the chemical compounds released during heating in the gas fraction are still unknown. Consequently, there is a potential for processing cocoa that is not evaluated, representing a great economic value in the industry.

Declarations

Ethics Approval Ethics approval was not required for this research.

Consent to Participate Not applicable.

Consent for Publication All permissions for this document are available.

Conflict of Interest The authors declare no competing interests.

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