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Chocolate aroma: Factors, importance and analysis

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A R T I C L E I N F O

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A B S T R A C T

Background: The quality and value of chocolate are related to its unique and fascinating flavor arisen from volatile and non-volatile compounds present in the product. The particular chocolate aroma is dependent on various factors including genotype and the agro-ecological niche (environment conditions, farming practices), post-harvest conditions and complex biochemical and chemical reactions during this period (fermentation, drying) and manufacturing stages.

Scope and approach: In this study, relationship between chemical compounds and cocoa flavors, control and management of post-harvest practices and manufacturing processing in order to obtain chocolate with differentiated characteristics and also evaluation methods especially sensory aspects of the chocolate are highlighted. For this purpose, instrumental experiments including headspace aroma extraction, simultaneous distillation extraction and sensory testing such as discrimination experiments, descriptive tests and hedonic experiments were discussed.

Key findings and conclusions: A comprehensive link between the components of cocoa flavor, sensory characteristics, human acceptability, and also the processes involved in flavor formation and formulation used, will assist the administration of a traceability system, a challenging case for quality assurance groups.

1. Introduction

Chocolate as one of the most popular foods is consumed by people of all ages. Higher consumption of chocolate was associated with significantly higher antioxidant properties, which have beneficial impact on human health (Aktar, Chen, Ettelaie, Holmes, & Henson, 2017). Unique sensory experience that chocolate creates is related with the melting profile in the mouth as well as specific odor and taste (aroma properties). For chocolate aroma, the cocoa present in the formulation and production process is very important for manufacturing the product with desired quality characteristics (Braga et al., 2018). The factors that are responsible for the aroma development in cocoa beans and chocolate are, cocoa cultivation (genetic origin, climatic conditions), post-harvest treatments (including fermentation and drying stages), chocolate processing (roasting and conching) (Da Veiga Moreira, Da Figueiredo Vilela, Santos, Lima, & Schwan, 2018).

Cocoa specific aroma can be defined as the aromatic properties that form during the cocoa processing and by the help of enzymatic reactions that mostly occur during the fermentation process of the cocoa beans. This fermentation process is complex transformation of the chemical reactions which contains: formation of organic acids, degradation of proteins, formation of insoluble compounds and hydrolization of glycosides. Fermentation is followed by drying, steam pretreatment (debacterization step) and roasting processes where Maillard reaction takes place between amino acids/peptides and reducing sugars formed during fermentation and also some organic acids are removed from the cocoa. Effective debacterization can be performed by adding water and assuring the presence of steam in the equipment. Roasting temperatures, holding times and amount of water added vary according to the applied equipment and the desired flavor profile of the product. Usually, the final roasting temperature is between 110 °C and 140 °C. Microbiological tests must be carried out for each specific roasting profile to ensure that it kills all pathogens for example *Salmonella* and reduces the total bacterial content (Beckett, 2009). Many odor substances involving pyrazines, furans, aldehydes, ketones, pyrroles and aldols are formed during Maillard reactions (taking place during drying,

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roasting and conching) which are important for the aroma characteristics of cocoa and chocolate (Crafack et al., 2014).

Type and amount of ingredients (cocoa, sugar, fat, milk powder, emulsifiers) and production process of the chocolate, especially conching are also crucial factors for chocolate aroma. Aroma is influenced by the volatile components and behavior of the continuous fat phase, affecting the liberation of volatiles into the mouth headspace and taste perception (Khairy, Saadon, Zzaman, Yang, & Easa, 2018).

Evaluation of aroma components is one of the most interesting studies in the food research area since chocolate has been commercialized. This a big challenge because significant attention has been given to chocolate and chocolate products. The use of analytical tools and sensory analysis offers interesting opportunities for quality control of cocoa-based products, enabling a great understanding of the relationship between aroma compounds and sensory attributes. Instrumental methods are needed to better characterize the levels of these important aroma compounds and understand the evolution of this parameter after harvest, according to the cultivar and the pre-and post-harvest factors. Sensory evaluation has been stated to be a good way to assess consumer preferences. Therefore, a sensory guided approach is needed to differentiate those volatiles being crucial for cocoa flavor from those having low or no impact.

In this study, factors affecting aroma composition of the chocolate and methods performed for determination of volatile compounds profile is provided.

2. Aromatic compounds related with chocolate

2.1. Main aromatic components in chocolate

Cocoa products (e.g. cocoa mass, powder, butter) and chocolate have a complex flavor (Da Veiga Moreira et al., 2018) and many researches have recognized more than 600 various volatile components in cocoa and chocolate products (Da Veiga Moreira et al., 2018; Engeseth & Pangan, 2018; Reineccius, 2006; Taylor, 2002; Taylor & Roberts, 2004) mainly aldehydes, pyrazines, alcohols, carboxylic acids, esters, ketons, furans, amines, amides, acids, phenols, terpenes and hydrocarbons (Braga et al., 2018). Important compounds that have impact in chocolate aroma are; 3-methylbutanal (chocolate note, malty), 2-methylpropanal (chocolate, malty), phenylacetaldehyde (rosy), tetramethylpyrazine (nutty), 2-ethyl-3,5-dimethylpyrazine (potato-like and popcorn), 2-acetyl-1-pyrroline (popcorn-like), trimethylpyrazine (nutty, earthy), 3-methylbutanoic acid (sweaty, cheesy), acetic acid (sour, harsh) and vanillin (vanilla-like) (Fig. 1). The rest of the components that lead to the flavor of chocolate are: 2-methylbutanal (chocolate note), 3,5-diethyl-2-methylpyrazine (chocolate, cocoa, roasted, rum) and furaneol (caramel-like) (Afoakwa, Peterson, Fowler, & Ryan, 2008; Liu et al., 2015). Key flavor components has different odor thresholds as; 3-methylbutanal (0.2–170 μg/L), methylpropanal (1–10 μg/L), 3-methylbutanoic acid (12–250 μg/L), acetic acid (22000-320000 μg/L), vanillin (25–1200 μg/L), 2-methylbutanal (3–13 μg/L), furaneol (0.3–20 μg/L), acetaldehydes (15–120 μg/L), 2,3-diethyl-5-methylpyrazine (1 μg/L). 2-Acetyl-1-pyrroline, 2,3- diethyl-5-methylpyrazine, ethyl 2- and 3-methylbutanoate, 2- heptenal, 3-hexenal, 3-isobutyl- and 3-isopropyl-2-methoxypyrazine and linalool were confirmed as very odor compounds on the basis of their low recognition thresholds (< 1 μg/L). Type and amount of these compounds specify the aroma of the end products. All of the process involved during chocolate production, from cocoa processing to manufacturing of the end product, is designed for the formation of these desired compounds and removal of the undesired ones.

2.2. Cocoa originated aroma precursors

Some of the chocolate-specific aroma compounds are evolved after the processes of cocoa and/or chocolate. However, the components and the percentage of ingredients are of importance. The main aroma precursors were determined as short chain peptides, free amino acids (Da Veiga Moreira et al., 2018), reducing sugars and cyanidin-3-galactoside. Cocoa variety is one of the primary factors that determine the variability of these aroma compounds. In addition, the same cocoa variety from different geographical origin illustrates distinct flavor characteristics (Trans et al., 2015). Apparently due to the presence of some precursors, aldehydes and pyrazines are released into cocoa beans. Because, the presence of aroma precursors formed during fermentation, such as free amino acids, short-chain peptides and reducing sugars can lead to the desired cocoa flavor development during the roasting step via the Maillard reaction (Afoakwa et al., 2008).

The intensity and efficiency of the aroma precursors in cocoa beans reveal significant differences. For example, the presence of free amino acids is the specific aroma precursors for the formation of cocoa flavor, however there are an inverse relationship between the polyphenol concentration and flavor development. Results indicated that the presence of higher concentration of polyphenol in cocoa liquor during roasting would decrease the cocoa flavor, because during roasting the polyphenols bind with aroma compounds (Misnawi, Jamilah, & Nazamid, 2004).

2.3. Effects of ingredients on aroma development

Depending on the chocolate type, it is composed of cocoa, cocoa butter, sugar, whey protein, milk powder and emulsifiers. Amount, type and quality of the ingredients and production steps of the chocolate are of importance for aroma development (Fig. 2). In this part, detailed information about the effect of these issues on aroma characteristics of the chocolate is provided.

2.3.1. The effect of cocoa origin on aroma

Raw cocoa has an astringent and unpleasant taste and aroma. The specific taste of cocoa is obtained after fermentation, drying and roasting of raw cocoa (Kumari et al., 2018). Methylxanthines, caffeine, theobromine and theophylline are the main alkaloids forming the typical bitter note of the beans. The content of alkaloids depends on the cocoa variety. The amounts of alkaloids decease gradually after fermentation, which cause the reduction of bitterness (Aprotosoaie, Luca, & Miron, 2016).

According to the geographical origin of cocoa beans, chocolate with obvious differences in flavor is generated. The genetic origin, cocoa variety and duration of the fermentation all contribute to variations in the final flavor formation (Afoakwa et al., 2008). The differences in varieties are due to quantitative differences in flavor precursors and polyphenol levels (Reineccius, 2006). Thus, formulations made with different varieties, may have considerable differences in flavor and aroma. Criollo, Forastero, Trinitario and Nacional are the main original botanical varieties of cocoa. The Criollo variety is generally known to produce mild, earthy, flowery, nutty and tea-like flavors (Ziegleder, 1990). Criollo beans are produced in the Caribbean Islands, Ecuador and Papua New Guinea and mostly used for dark chocolates (Beckett, 2008). The Forastero variety produces darker beans with a differentiable basic taste. It gives intense cocoa flavor, when compared with Criollo less fine chocolate notes are generated (Ziegleder, 2009). Trinitario, the third form, is a hybrid of Criollo and Forastero and it offers strong original chocolate flavor and wine-like character (Giacometti, Jolić, & Josić, 2015). Nacional creates a full cocoa flavor with floral and spicy flavors (Aprotosoaie et al., 2016). Fine cocoas usually show aromatic or smoother flavor, and bulk cocoa are perceived as strong flavor characters (Luna, Crouzillat, Cirou, & Bucheli, 2002).

The morphological and physiological differences between cocoa varieties have categorized them into two subspecies; T. cacao ssp. Cacao or “Criollo” (Central America) and T. cacao ssp. sphaerocarpum or “Forastero” (South America). “Forastero” is further grouped into Upper and Lower Amazon “Forastero.” Nowadays, “Criollo” is known to

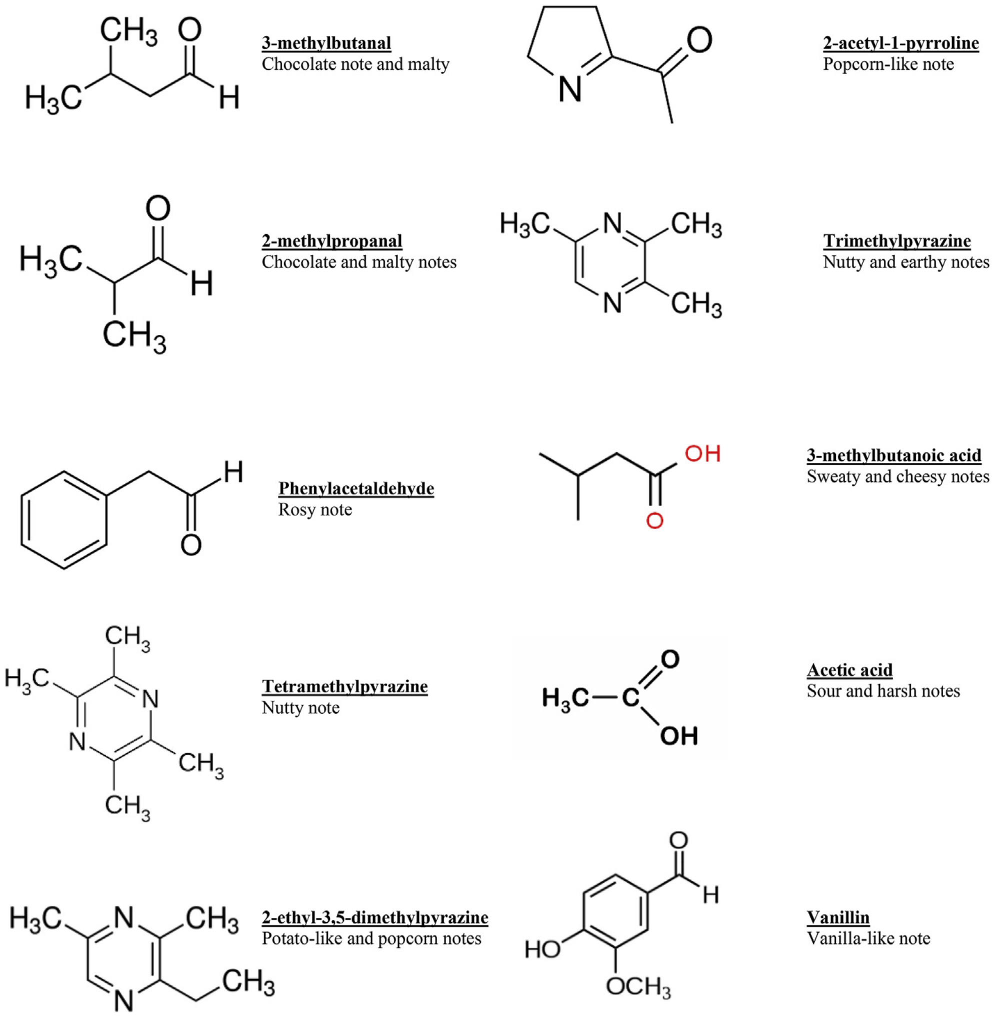

Fig. 1. Chemical structure of the major flavor compounds in chocolate and cocoa.

be a traditional cultivar. Further traditional cultivars of “Criollo” are known, the “Nacional” cacao of Ecuador, a result of transitions from the primary center of origin to the Ecuadorian highlands; the “Trinitario,” a group of “Criollo” and “Forastero” hybrids; as well as “Amelonado,” a Lower Amazon “Forastero” planted in West Africa. Under international trading aspects the “Criollo,” the “Nacional,” and the “Trinitario” are the sources of fine cocoa specified by special aroma notes (e.g., fruity and floral). The “Criollo” groups are categorized as fine or flavor cocoa; while Upper and Lower Amazon “Forastero,” is classified as bulk cocoa and do not contain a specific chocolate aroma.

Beans from Ivory Coast have low acidity and bitterness and beans originated from Brazil are entirely acidic, bitter and astringent (Urbanski, 1992). Ecuador beans are renowned for floral-spicy notes (De La Cruz, Whitkus, Gomez-Pompa, & Mota-Bravo, 1995), whereas those from America and West India for aromatic and winy notes. Bahia beans are known for their special smoked notes (Afoakwa, 2010). Cocoa beans from Venezuela, Trinidad or Ecuador possess considerable levels of terpenoids and linalool (0.5–2 mg/kg) which contributes to a tea-like and flowery aroma (Pino, 1992; Ziegleder, 1990). Bulk cocoa beans, mainly harvested in Malaysia, West Africa and Bahia, reveal a powerful intrinsic flavor and present low levels of linalool. Malaysia Cocoa nibs are defined by light chocolate flavor and high acidity. The African types are known to have the best cocoa character. These varieties contribute to bitterness, acidity, astringency, caramelized and burnt flavors (Afoakwa, 2010). Brazilian cocoa beans have a desirable level of cocoa flavor. It is more acidic than West African beans because of fermentation method. The lactic acid bacteria present in the primary stage of fermentation are the main reason for acidic notes in Brazilian beans. Arriba cocoa gives a full cocoa flavor along with floral and spicy flavors. All of those indicated that cocoa genotype, botanical and geographical origin, climate conditions used in the formulation directly influences the aroma of the end product (Engeseth & Pangan, 2018; Kumari et al., 2018).

2.3.2. *Milk fat*

Milk fat is used in all milk chocolate formulations. It is though to give better fat bloom prevention. If milk fat is added at nearly 5% of the weight of the chocolate (that contains a total of 30% fat), it makes up about 17% of the fat phase. The addition of milk fat makes it softer and slows down the transformation of form V to Form VI and produces a white coating on the surface (Beckett, 2008).

Milk fat as a flavor precursor has a functional role in chocolate. Furthermore, when the milk fat is heated, important flavor components such as, methyl ketones and lactones are generated. Dairy fats can impart different flavors due to several mechanisms such as, hydrolysis or lipolysis, dehydration and de-carboxylation that take place during the chocolate processing. Lipase which is present in fresh milk can hydrolyze the triglycerides and produce volatile favorable fatty acids comprising caproic, butyric and capric acids. These fatty acids contribute a ‘creamy’ and ‘buttery’ flavor in milk chocolate. The milk lipase is usually inactivated during pasteurization. Heating applied during chocolate processing's could be sufficient to release the mentioned fatty acids; however, this is not generally the case. Also the rate of lipolysis in milk fat should be attentively controlled to prevent the cheesy flavor,

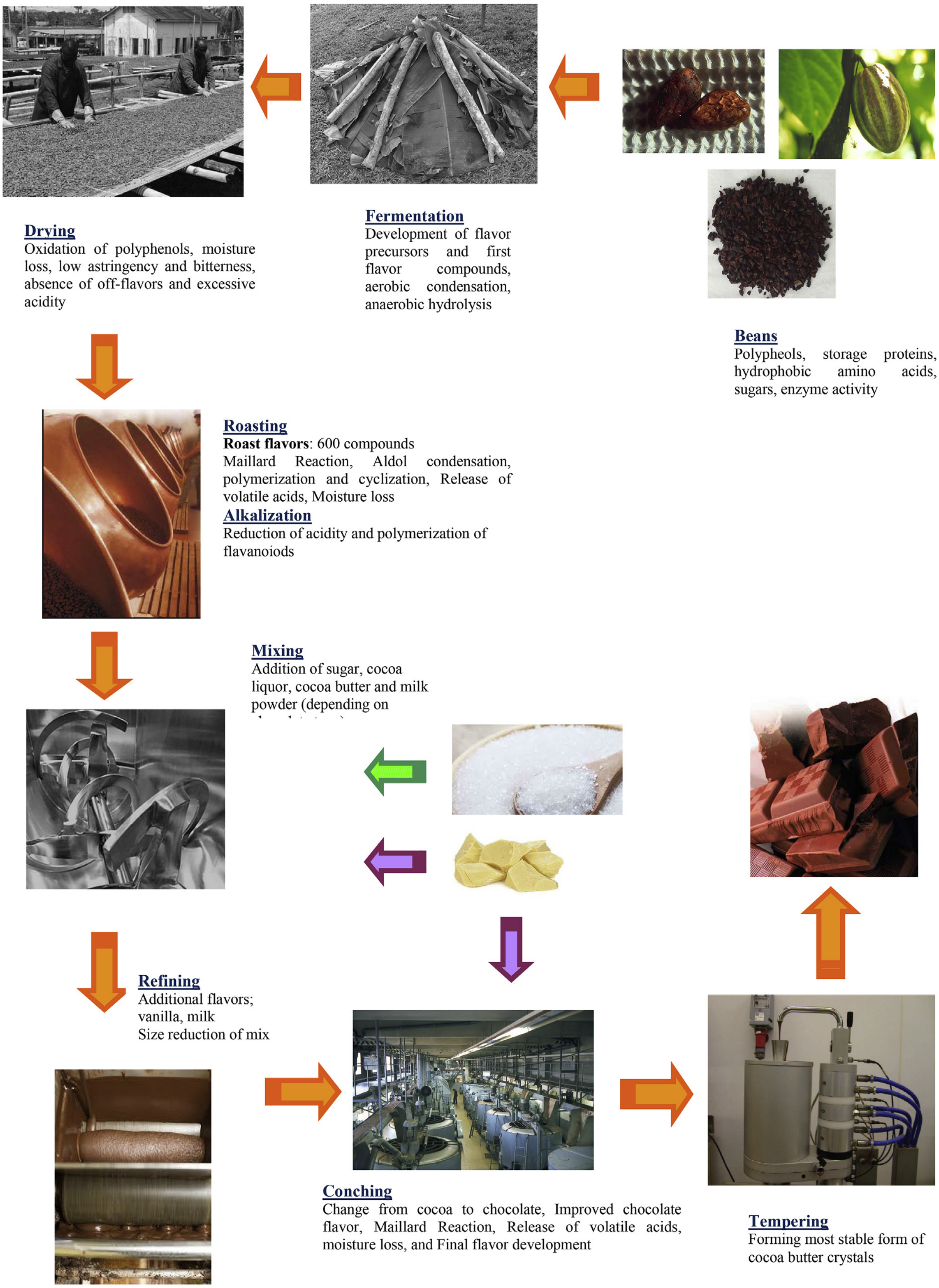

Fig. 2. Mechanism of chocolate flavor formation.

because milk fat can be oxidized by enzymes. These enzymes separate the acids into shorter chain free fatty acids, which present a rancid off-flavor. Therefore, hydrolyzed milk fats could be used to raise the buttery flavor of milk chocolate (Campbell & Pavlasek, 1987).

2.3.3. Milk proteins

Milk proteins are important in determining the chocolates flavor, texture and flow properties. The creaminess of milk chocolate depends on the balance between these proteins and cookie flavor (A major flavoring compound of cocoa bean and chocolate. It is associated with the present of acetal (1,1-Diethoxyethane)) from the beans. In the presence of water and heat, proteins can participate in the Maillard reaction, which gives cooked flavors to the chocolate.

2.3.4. Sugar

Sugar is the main ingredient used in chocolate production. It is added to chocolate to overcome the bitterness and astringent flavors. Amorphous sugar impacts the flavor and the rheological characteristics of liquid chocolate. Its surface is so reactive and absorbs any flavors that are close to it. If sugar is grinded together with cocoa, some of the volatile cocoa flavors are attracted by the amorphous sugar. This will then give a more intense flavor chocolate. In addition, the level of amorphous sugars in the structure is important due to the adsorption characteristics for some aromatic compounds (Beckett, 2008). Sugars are also crucial for the reactions such as Maillard in conching process (Crafack et al., 2014).

Bricknell and Hartel (1998) studied the effect of the sugar microstructure (either amorphous or crystalline) in bloom formation of chocolate. The results indicated that the control chocolates with amorphous sugar did not bloom and the difference in bloom formation was related to the microstructure, not the polymorphic transition. The crystalline sucrose consisted of particles with sharp edges, while the amorphous sugar indicated smooth and spherical particles. The rounded surface of the amorphous sugar influenced the formation of bloom. It let for tighter packing of the sugar crystals in the chocolate. This interfered with the migration of liquid TAG molecules to the surface and as a result diminished the development of bloom. Another possibility was the interaction of lecithin at the surface of the sugar particle that affected the formation of bloom crystals. The lecithin, which places at the surface of the sugar particles in chocolate, influenced bloom formation by affecting the migration of liquid cocoa butter TAG through the chocolate or by altering the recrystallization process at the surface.

The use of low calorie sugars can be a dominant factor in determining the aroma profile of chocolate. For example, rebaudioside A has the most acceptable flavor profile and is the most stable of the steviol glycosides (DuBois, 2000). Also, thaumatin is used as a flavor enhancer, and is approved as a sweetening agent in some countries (Kinghorn, Kaneda, Baek, Kennelly, & Soejarto, 1998). Fibers such as, inulin have no “off flavors” (Niness, 1999) and the use of inulin in chocolate include modulation of the cooling effect during melting in the mouth and improvement of the chocolate flavor.

One of the alternative sweeteners that are able to create a distinctive flavor is palm sap sugar. Saputro, Van de Walle, Hinneh, Durme, and Dewettinck (2018) evaluated aroma profile of dark chocolate formulated with palm sugar blends. The results illustrated that the chocolates containing palm sugar possessed higher levels of volatiles than the chocolates containing sucrose. These volatiles were alkyl pyrazine, such as 2,5-dimethylpyrazine, 2,6-dimethylpyrazine, 2-ethyl-6-methylpyrazine, methylpyrazine, 2,3,5-trimethylpyrazine, and 2-pyrrolidinone; alkyl furan, such as 2(3H)-dihydrofuranone and 2-furan methanol; alkyl alcohol, such as 2,3-butanediol and phenylethyl alcohol; 2-acetylpyrrole, and acetic acid. This phenomenon was related to the presence of higher concentration of amorphous phase in palm sap sugar-sweetened chocolate. In presence of amorphous phase, the more aroma volatiles of the palm sugar were trapped, producing a higher concentration of volatiles. Also, the aroma volatiles of palm sugar lead to the increase of the aroma volatile content.

2.4. Fermentation

Fermentation process of cocoa is critical for establishment of precursors that are necessary for chocolate specific aroma (Da Veiga Moreira et al., 2018). In the fermentation stage, the cocoa beans are placed in a heap or in a wooden box, for about 5–6 days. Spontaneous cocoa bean fermentation is carried out by succession microbial activities of three types of microorganisms including yeasts, acetic acid bacteria and lactic acid bacteria. The farmer's hands and equipments (knives), fermenting boxes, surfaces, dry pulp, fermenting trays and the plantain leaves used for covering the fermenting mass are the numerous sources of inoculation (Jespersen, Nielsen, Hønholt, & Jakobsen, 2005). At the primary stages of fermentation known as anaerobic hydrolytic phase, anaerobic yeasts promote. Due to anaerobic conditions, alcoholic fermentation is generated by yeasts and the pulp sugars are transformed to alcohol and carbon dioxide. The yeasts dominate the first 24–36 h of the fermentation stage, however after rising of pH it will be a limiting factor for further proliferation. The second phase is known as the oxidative condensation phase that happens under aerobic conditions and is dominated by lactic acid bacteria. After the increase in the temperature of the bean mass (45 °C) the conditions will be more appropriate for the growth of acetic acid bacteria (Afoakwa, 2010). These bacteria are responsible for the oxidation of ethanol to acetic acid.

Fermentation is crucial for flavor precursors formation and color development and also a considerable reduction in bitterness. It is a process in which flavor precursors are produced which presents the taste of cocoa following the under heating x time effect. During the primary stages of fermentation, the temperature rises, and the enzymes are released. The released enzymes break down the substances into simpler compounds. As a result, flavor precursors such as, simple sugars, peptides and amino acids are formed. Different fermentation methods cause different flavors in beans (Beckett, 2008) especially as a result of various proteolytic activities (Kumari et al., 2018). For example, in box fermentation due to movement and aeration of beans, the aerobic bacteria (Acetobacter) produce the acetic acid. Carboxylic acids display off-flavor notes such as butter, rancid and hammy. In addition, esters generated as a result of yeast metabolism present a fruity flavor. During roasting, high temperatures promote the loss of esters (Ramli, Hassan, Said, Samsudin, & Idris, 2006). The temperature and the level of acidity are the factors that determine the reaction rates.

Proteins are degraded during the fermentation phase under the action of proteases. Well and fair fermented beans can be differentiated from partially fermented and under-fermented beans by higher amounts of oligopeptides. Therefore, the peptide profile of a bean can be used as a reliable indicator for the degree of fermentation (Kumari et al., 2018). Free amino acids and hydrophobic peptides as important aroma precursors are formed during proteolytic breakdown and develop into cocoa specific aroma during roasting via Maillard reactions (Misnawi et al., 2004). Da Veiga Moreira et al. (2018) evaluated the volatile compounds and protein profiles of fermented beans from different cocoa hybrids. Cocoa beans from different geographical and genetic origins indicated different fermentation dynamics which ended in different chocolate qualities.

It has been confirmed that cocoa seed storage proteins play a critical role in flavor development since fundamental precursors of the cocoa-specific aroma components are created from their degradation during the fermentation process. These aroma precursors are released from seed proteins by the activity of the aspartic endoprotease and a carboxypeptidase. Under optimal conditions of fermentation (pH 5.2) both hydrophilic peptides and hydrophobic free amino acids are obtained. This specific mixture of hydrophilic peptides and hydrophobic free amino acids is able to produce the special cocoa flavor when roasted in the presence of reducing sugars and deodorized cocoa butter. Free amino acids alone, particularly leucine, alanine, phenylalanine, and tyrosine found in fermented cocoa seeds react with the reducing sugars fructose and glucose during the Maillard reaction (Voigt, Biehl, & Kamaruddin, 1993, 1994). Raw cocoa beans contain free sugars (sucrose, glucose, galactose, fructose, sorbose, arabinose, inositol, mannitol and xylose) and polysaccharides (starch, cellulose, pectins, pentosans and mucilage). During fermentation sucrose is transformed into reducing sugars (fructose and glucose) (Biehl & Ziegleder, 2003).

During the fermentation, some complex biochemical reactions happen which creates several flavor precursors such as reducing sugars and nitrogenous compounds. For example, the concentration of methylxanthines decreases gradually after 72 h of fermentation, which leads to a reduction of bitterness. The loss of methylxanthines is 30%. Polyphenols are responsible for astringent and bitter sensations and contribute significantly to the green and fruity flavors of cocoa liquors (Norr-Soffalina et al., 2009). During the anaerobic phase polyphenols are hydrolyzed and oxidized. The aerobic phase is characterized by oxidative and condensation reactions such as oxidation of protein-polyphenol complexes and carbonyl-amino condensation that reduce astringency (Afoakwa et al., 2008). These reactions are critical for cocoa flavor and color formation. The reactions between proteins and peptides with polyphenols give the brown color associated with cocoa. Overall the concentration of polyphenols usually decreases however there were reported cases in which their level did not change or even increased. The polymerization reactions were stated for the polyphenols increase (Rusconi & Conti, 2010). Hydrophobic amino acids exposed to Strecker degradation during the following process for generation of aromatic Strecker aldehydes and aminoketones, which are key components for pyrazine yields (Perez-Locas & Yaylayan, 2010). The Maillard reaction precursors are formed when protein and sucrose breaks up.

Ethyl-2-methylbutanoate, tetra-methylpyrazine, and certain pyrazines are the main flavor compounds that are produced during fermentation. Theobromine and caffeine along with diketopiperizines contribute to bitter notes. The latter is formed during roasting during thermal denaturation of proteins. Also flavor precursors such as, 3-methylbutanol, phenylactaldehyde, 2-ethyl-3,5-dimethyl, 2-methyl-3-(methyldithio) furan and 2,3-diethyl-5-methylpyrazine are derived from amino acids liberated through fermentations (Taylor, 2002). Less chocolate flavor and hammy flavors are developed in unfermented and excessive fermented beans respectively after roasting (Beckett, 2008; Reineccius, 2006). Comparing the volatile compounds of beginning and end of fermentation from different cocoa hybrids the results showed increase in percentage of acids and esters groups while the content of alcohols, aldehyde and ketones decreased (Da Veiga Moreira et al., 2018).

Using different fermentation techniques such as artificial methods may yield chocolates with different aroma profile in comparison to chocolates produced from conventional fermentation methods (Allison & Rohan, 1958; Owusu, Petersen, & Heimdal, 2012). The method of cocoa bean fermentation is important for determining chocolate aroma/flavor and its effect is often studied. In addition, cocoa beans from different geographical and genetic origins demonstrated different fermentation dynamics which yielded in different chocolate qualities (Da Veiga Moreira et al., 2018).

Using different starter cultures in fermentation can induce the development of aroma profiles. Therefore the appropriate yeast strains can be selected to generate desired flavor profile (Engeseth & Pangan, 2018). Crafack et al. (2014) investigated the influence of starter cultures and fermentation techniques on the chemical and sensory qualities of cocoa liquors and chocolate. Therefore the impact of mixed starter cultures, including a highly aromatic strain of *Pichia kluyveri* and a pectinolytic strain of *Kluyveromyces marxianus*, on the formation of flavor precursors, composition of volatile compounds were reported. The results compared to commercially fermented heap and tray cocoa. Fermentation method had the highest impact on the volatile aroma and sensory profile, however the utilization of starter cultures also affected the volatile aroma profile, and differences were too small to considerably alter consumer perception of the chocolates as compared to a spontaneously fermented control. For example, during the fermentation stage, the activity of various microorganisms such as *Bacillus subtilis*, *B. megatrium* could produce the formation of pyrazine compounds (Khairy et al., 2018). Furthermore, the combined effect of two cocoa fermentation techniques (heap and tray) on aroma compounds of dark chocolate were investigated by Owusu et al. (2012). The two fermentation methods had some effect on the type and number of aroma volatiles produced but also often on their concentrations. The acetic acid content (leading to sourness in cocoa products) was higher in tray fermentation technique in comparison to heap fermentation technique. The method of fermentation did not have any considerable influence on the level of 2,5-dimethylpyrazine.

In the fermentation process, mass transfer (caused by acidification and oxygen transfer) are necessary to give a more uniform treatment. It allows the interactions between seed compounds with the enzymes generating in flavor precursors (Biehl, Brunner, Passern, Quesnel, & Adomako, 1985). In terms of oxygen transfer, Lefeber, Papalexandratou, Gobert, Camu, and De Vuyst (2012) evaluated the effect of aeration on the profile dynamics of hydrophobic amino acids and methylxanthines during the transformation of cocoa by using a heap fermentation system. The results indicated that oxygen transfer to the fermentation system promoted the formation of hydrophobic amino acids (important flavor precursors) in a shorter post harvest transformation time. The oxygen acted as a substrate for acetic acid bacteria and also contributed to catalyze enzymatic reactions in cocoa seeds and enhanced the production of flavor precursors (Escobar et al., 2016). In a study performed by Hashim, Selamat, Syed Muhammad, and Ali (1998), in a rotary drum system using a small quantity of cocoa seed mass for fermentation, they found low flavor precursors content. However, increasing the seed mass level, the concentration of these compounds increased until a maximum point was reached (with a capacity of 55–60 kg). When the quantity of the cocoa seed mass was further increased, the concentrations of these compounds decreased again. The authors stated that the fermentation of a very high cocoa seed mass leads to a decrease in the oxygen transfer during the fermentation process, which results in a reduced microbiological activity, and thus, a lower temperature and proteolytic activity, which leads to low contents of flavor precursor components. The fermentation of a very small mass of seeds in the same situations generates a high oxygen transfer, which probably causes a loss of heat reducing the temperature, and therefore, the metabolic rates of microorganisms, decreases. The selection of appropriate cocoa bean fermentation technique along with optimization of the chocolate processing methods will result in chocolate with improved aroma quality.

2.5. Drying

Drying can be carried out by using various methods. Sun drying results in higher chocolate flavor development and will have less off-notes (Selamat, Thien, & Yap, 1991, pp. 71–78). Drying process continues until the moisture reduces below 8%. Sun drying has disadvantages because it is an uncontrolled process, so it depends on environmental conditions (rainy season, risk of contamination from the surroundings and from farm and wild animals), and it needs long processing times. Thus, cocoa with heterogeneous quality is produced throughout the year (Guehi, Zahouli, Ban-Koffi, Fae, & Nemlin, 2010). Therefore, artificial drying methods were investigated. In artificial drying, where wooden fires are used, an unpleasant and hammy (smoky) flavor is observed in beans. Also, due to rise in cotyledon temperature, case hardening may occur. However, this phenomenon restricts the loss of volatile acids (for example, acetic acid) and has negative effect on final flavor of the crop (Dimick & Hoskin, 1999). In very fast drying methods, the beans will taste very acidic; therefore it is necessary to dry the beans at lower temperatures for a longer time.

Within drying stage, new flavor compounds are formed due to polyphenol oxidizing reactions. Well-dried cocoa beans have brown color and less astringency and bitterness and also off-flavors for example, excessive acidity and smoky notes is not detectable. Imperfect drying or rain soaking gives high amount of strongly flavored carbonyls, leading to smoky or hammy off-flavors (Misnawi, Jamilah, & Nazamid, 2003). In smoky beans, methyl-phenols, phenol, di-methyl-phenols, 1,2-di-hydroxy-benzane, 3- methyl-gujacol and di-methoxy-phenols have been distinguished (Sandmeier, 1987). Also drying diminishes the concentration of volatile fatty acids (propionic, acetic, butyric and isobutyric acids) (Paramo, Garcia-Alamilla, Salgado-Cervantes, Robles-Olvera, & Rodriguez-Jimenes, 2010).

Furanones and pyrones are produced through drying and roasting as a result of degradation of monosaccharides (Ziegleder, 2009). They are responsible for desirable notes such as, chocolate, caramel and roasty notes. These compounds are destroyed via alkalization process. Furthermore, during drying process, due to Maillard reaction, Amadori compounds are formed in dried and un-roasted cocoa beans. These compounds are produced as a reaction of free amino acids and glucose. These intermediates are important because during roasting procedure, they will decompose to several volatile compounds. For example the generated Amadori compound of fructose-phenylalanine after heating at roasting stage, produces cocoa-like flavor compounds (Oberparleiter & Ziegleder, 1997).

2.6. Roasting

Roasting of cocoa is a fundamental stage to further develop the chocolate flavor from the precursors formed during fermentation and drying. Roasting diminishes acidity by reducing concentrations of volatile acids such as acetic acid (Ramli et al., 2006). The hydrophobic amino acids leucine, alanine, phenylalanine, and tyrosine, released by proteinase activities in fermentation, are important contributors, as are reducing sugars fructose and glucose derived from sucrose hydrolysis (Voigt et al., 1993, 1994). All these precursors participate in Maillard reaction, central to cocoa flavor development, are important in roasting. After 3 days of fermentation, the proteolytic reactions inside the beans begin. Small peptides and free amino acids are released and will influence the chocolate's flavor in the next stage of processing such as roasting (Da Veiga Moreira et al., 2018). The degree of changes is related to moisture loss during the roasting process (Engeseth & Pangan, 2018). Also, the high temperatures remove many of the volatile acids such as, acetic acid while less volatile acids especially lactic acid and oxalic acid lactic acid remain largely unchanged during the roasting process.

Un-roasted cocoa beans might taste bitter, astringent, flat, sour or musty. The aroma precursors produced from fermentation and drying will undergo transformation during roasting, therefore contributing to the aroma profile of chocolate (Engeseth & Pangan, 2018). After roasting, cocoa presents the special severe aroma with reduced acidity. Cocoa beans are usually roasted at temperatures among 120 °C–140 °C for 5–10 min. Higher temperatures (> 150 °C) and also longer times, results in 'over-roasted' beans along with burnt, bitter and coffee-like taste beans. However, the roasting parameters (temperature x time) determine the accurate conversion of the precursors. Ziegleder (1991) reported that about 25% of free amino acids and about 70% of the glucose and fructose are used up in this procedure. In addition, cocoa beans have nutty, acidic, astringent and bitter notes before roasting. Acidic notes are reduced during roasting by decreasing the volatile acid concentration. But, non-volatile acids such as lactic, tartaric, succinic, oxalic, citric acid are not influenced (Khairy et al., 2018).

The Maillard reactions between amino acids and reducing sugars during roasting cause the typical flavor of chocolate (Ho, Zhao, & Fleet, 2014). In the presence of water and heat (pH > 3), the reactions start with an amino acid, peptide or protein and reducing sugar. The main intermediates are di-carbonyl components. The reaction of leucine and glucose gives aroma notes defined as 'sweet chocolate', glutamine and threonine and glucose yield 'chocolate' notes when heated to 100 °C. The reaction of glucose and valine gives 'penetrating chocolate' note when heated to 180 °C (Dimick & Hoskin, 1999). Important flavor fractions that are formed during roasting are; pyrazines, aldehydes, alcohols, hydrocarbons and esters, ketones, sulphur compounds, phenols, pyridines, acids, pyrrols, pyrones, furanes, chinolines, lactones, thiazoles, chinoxalines, and oxazoles.

Di-merization of ketoamines to di-hydropyrazines with a subsequent oxidation process forms pyrazines, the key odor compounds in cocoa aroma. They are heterocyclic compounds and known to be valuable compounds presenting the flavor of roasted beans. They exhibit nutty, earthy, roasty and green aromas (Wagner, Czerny, Bielohradsky, & Grosch, 1999). During Maillard reaction and Strecker degradation most of the pyrazines are formed (Rodriguez-Campos et al., 2012). The formation of pyrazines during roasting is identified as reliable indicator for the Maillard reaction (Braga et al., 2018). Also some are formed during drying. Pyrazines as a volatile heterocyclic nitrogen containing compound are the main flavor compound responsible for forming of the typical cocoa butter and chocolate flavor (Khairy et al., 2018). 2,3-butanediol is one of the end products found in a high concentration (Braga et al., 2018). The variety of beans determines the total concentration of pyrazines. High temperature and time duration negatively affect the content of pyrazines. The highest concentration of tetramethylpyrazine (7 mg/kg) is reached at moderate roasting conditions (Ziegleder, 2009). However, in a recent study it has been reported that the total pyrazine concentration significantly increased as 25.94% with extending roasting time (Khairy et al., 2018). Furthermore, the reactivity of amino acids, pH and roasting procedure specify the alkyl-pyrazines quantity (Bonvehi & Coll, 2002).

Aldehydes are one of the important fractions of cocoa flavor which are produced through Strecker degradation of amino acids. However, high temperatures and long times during roasting can decrease the content of aldehydes. During secondary reactions, they might be converted. For example, acetaldehydes, 2-methyl-propanal and 3-methyl-butanal undergo aldol condensation with phenylacetaldehyde to form 2-phenyl-4-methyl-pent-2-enal, 2-phenylbut- 2-enal and 2-phenyl-5-methyl-hex-2-enal. The resulted compounds give a flowery odor (Van Praag, Stein, & Tibetts, 1968). Aldehydes and ketones confer malty, chocolate, flowery, bitter cocoa, sweet and floral notes. Also, aldehydes as intermediates can participate in the formation of heterocyclic components and pyrazines. These components dominate the cocoa flavor. As an indicator for highly volatile compounds, 2-methyl-butanal and 3-methyl-butanal (Strecker degradation yields of iso-leucine and leucine) and 2-methylpropanal (from valine) are used.

Polyphenols present fruity flavors of cocoa liquor (Norr-Soffalina et al., 2009). High temperatures of roasting influence the levels of polyphenols and the reduction of total polyphenol occurs. It is considered that the polymerization of polyphenols with low molecular weight compounds happens. Temperatures less than 140 °C can maintain the content of polyphenols (Aprotosoaie et al., 2016). Also, alkalization leads to a pronounced loss of these compounds (Jolic, Redovnikovic, Markovic, Sipusic, & Delonga, 2011), because polymerization and oxidation of polyphenols occur under alkaline situations (Giacometti et al., 2015).

In addition, proteins, peptides, polyphenols, vitamins, lipids and their oxidation products can take part in roasting reactions and affect the final flavor. Specific flavor compounds can be formed in presence of heat; thermal decomposition of catechine leads to formation of 1,2-benzendiol and thiazoles are generated by thermal decomposition of the thiamine.

By using modern equipment, cocoa can be roasted as whole beans, as nibs (produced by a fine grinding of cocoa) or as liquid cocoa mass (liquefying within its own molten fat). Particular thin-film techniques were developed for the roasting of cocoa liquor. The roasting of smaller particles has the advantage of a better controlled and homogeneous roasting level, of a reduced roasting time and of the partial removal of any excess acetic acid. Although acetic acid remains unchanged during bean roasting, it is considerably reduced during the roasting of cocoa liquor (Nuyken-Hamelmann & Maier, 1987). Roasting time for beans take nearly 30 min, nibs 12 min and liquor 2 min.

It has been stated that a pre-treatment of un-roasted cocoa nibs or liquor with water could increase flavor development. A pre-treatment of raw cocoa nibs with 15% of water for 15 min at 40 °C, followed by drying at 98 °C to 3.5% water content and roasting, indicated a more intense cocoa taste and an increased level of roast flavor compounds compared to cocoa that had been roasted without water pre-treatment. As a result of the pre-treatment with water, the consumption of amino acids and reducing sugars was increased, and an increased level of Amadori compounds was observed (Ziegleder & Oberparleiter, 1996). Likely the added water dissolves amino acids and sugars and thus supports their reaction.

As can be seen, there are many factors (starter type, temperature, period, cocoa variety in fermentation; temperature and process period in drying and roasting) influencing cocoa aroma. Therefore, all of them should be considered for producing the product with desired quality, directly affecting the consumer acceptability of the end product.

3. Marker compounds of cocoa

Pyrazines are the main volatile and the key odor compounds in cocoa and chocolate aroma (Braga et al., 2018). Pyrazines originating from Maillard reaction are the most important compounds that contribute to the final chocolate flavor. Pyrazine concentration depends on the weather conditions, varieties of cocoa, ripeness and chocolate processing (Da Veiga Moreira et al., 2018). Well-fermented cocoa from Ghana has higher levels of pyrazines (698 µg/100 g) than Mexican cocoas (142 µg/100 g) (Afoakwa et al., 2008). The Criollo cultivar contains high levels of pyrazines while Nacional/Arriba cocoa has the lowest level of pyrazines. Tetramethylpyrazine reaches high concentrations (7 mg/kg) at medium roasting conditions (Ziegleder, 2009). Pyrazines are mostly used as index components for the roasting procedure of the cocoa beans (de Brito and Narain, 2003). In addition, some of these compounds such as tetramethylpyrazine are formed during enzymatic fermentation, while others can be formed during manufacture process.

The odor threshold values of different pyrazines range from 10 to 0.000002 mg/kg depending upon the substitution. For example, Guadagni, Buttery, and Teranishi (1972) determined an odor threshold of 0.8 μg/L of water for 2-ethyl-3,6-dimethylpyrazine. After purification and re-examination of the experiments, a ten-fold higher threshold (8.6 μg/L) was reported for 2-ethyl-3,6-dimethylpyrazine. 2,3- diethyl-5-methylpyrazine and 3-isopropyl-2-methoxypyrazine were confirmed as very odor compounds on the basis of their low recognition thresholds ($<$ 1 μg/L) (Czerny et al., 2008).

Methylpyrazine contribute to nutty, musty, roasted-nuts, chocolate-like notes; dimethylpyrazine contribute to caramel, green, vanilla, nutty, roasted meat like and coffee flavor; 2,3,5-trimethylpyrazine contribute to roasted-nuts, cocoa, coffee and peanut flavor and finally 2,3,5,6-tetramethylpyrazine contribute to chocolate, coffee, cocoa and fuller vanilla flavor (Khairy et al., 2018). The concentration of 2-methylpyrazine and 2,3,5,6-tetramethylpyrazine has been illustrated as an indicator for assessment of product qualities (Perego, Fabiano, Cavicchioli, & Del Borghi, 2004). Tetra-methypyrazine is the most abundant and critical compound for flavor development of cocoa and chocolate (Engeseth & Pangan, 2018). The above compounds are responsible for sweet and strong aroma of cocoa. These substances originate from roasting process and cocoa beans attributes. Therefore, cocoa beans obtained from different regions display different flavor characteristics. The ratio of tetramethylpyrazine to trimethylpyrazine should range from 1.5 to 2.5 for a normal grade roasting (Ziegleder, 2009).

4. Relation between chocolate processing and chocolate aroma

Usage of cocoa with desired aroma profile is very important for the end product preference. In addition, processes employed for chocolate production have also great impact on the aroma characteristics of the chocolates. As known, conventional chocolate process is composed of mixing, refining, conching and tempering stages. However, the influence of applying alternative processing on flavor formation will be discussed.

4.1. Importance of refining and particle size

Chocolate refining is a size reduction stage affected by the type of product, the process and also the ingredients. The components can be blended and then ground or it may be ground then blended. The second process might not allow for the same flavor production in comparison to the first process. In the blended process, the sugar will pick up many of the aromas in the mill where it is being ground, and in the separate blending process there is cocoa in close vicinity. Fine grinding of chocolate ingredients should be carried out to generate an optimum particle size distribution which it will influence the texture, flavor and flow attributes of the end product. For chocolate of the similar ingredients that are processed under equal situations, the particle size distribution of the solids may play a substantial role in defining its flavor characteristics (Mongia & Ziegler, 2000) and sensory quality.

The sensory properties of cocoa liquor are sensed earlier than sugar or milk powder. It is assumed that with lower surface area (greater particle size) the sweetness of the sugar can be reduced. Chocolate with finer particles, tastes sweeter because small sugar crystals dissolve more quickly than greater ones. When the sugar particles are broken, the surface becomes more reactive and it could absorb with any flavor compounds. Sweeter perceptiveness was observed in chocolate brownie sample with smallest sugar particles (Richardson et al., 2018).

The shear between the rollers breaks the particles and also coats some of the newly created surfaces with fat. Moreover, as the breakage happens, the newly established surfaces, which are chemically very reactive, are capable to absorb the volatile flavor chemicals from the cocoa particles being broken nearby at the same time. This means the chocolate is likely to have a different flavor to one made using the separate grinding process.

Particle size significantly influences chocolate flavor, sweetness and the attempt required to melt (Ziegler, Mongia, & Hollender, 2001). In the study carried out by Ziegler et al. (2001) results illustrated that the time to maximum, intensity of maximum and period of attempt needed to melt, manipulate and swallow the sample all enhanced as the average particle size got finer. The intensity of chocolate flavor did not vary because the size and amount of cocoa solids were the same in all chocolate samples. The mean particle size influenced the duration of chocolate flavor. The flavor of chocolates with finer particle sizes persisted longer than samples with coarser particle sizes. This is linked to the persistence time of the sample in the mouth not to the flavor profile of the samples.

In chocolate manufacturing, two different processes are applied for grinding of solids; roller grinding and ball mill grinding. However, processing behavior of chocolate masses grounded by ball mill is not as good as obtained after roller grinding; yield value and viscosity of the molten mass are higher after ball mill grinding. Grinding transfers sucrose surfaces from crystalline to amorphous state affecting the interaction of particles with each other and surrounding cocoa butter. The differences in fat immobilization and flow behavior of ground sucrose suspensions are attributed to variations in particles surface properties.

In recent years, alternative processing techniques which need less time and energy production are highly applied in small-scale chocolate industries. For example, ball mill processing is a technique where both refining and mixing can be performed in a single production system. Studies demonstrated that the processing technique influences the aroma profile in the chocolates (Saputro et al., 2017a). One of the disadvantages of applying ball mill is the difficulty in moisture and acidity reduction. Ball mill seems to be less effective in removing moisture than the conventional techniques. Moisture remaining in the chocolate suspension would attribute to the presence of particle agglomeration. Higher degree of agglomeration can result in lower size reduction. The presence of moisture in chocolate dissolves sugar particles and creates sticky patches on the surfaces of the sugar particles, inducing agglomeration. However, as mentioned before, fineness of the chocolate particles also affects the release of volatiles. Afoakwa, Paterson, Fowler, and Ryan (2009a) reported that increasing particle size contributes to less aroma volatile release, due to increase in matrix retention via structural, rheological and textural differences. In the study of Saputro et al. (2017a) chocolate samples prepared by alternative method indicated a higher degree of agglomeration than conventional method.

The particle size of the non-fat particles stated to have an impact on fat bloom, while a smaller particle size increased migration rates and therefore, accelerated fat bloom development. Dahlenborg, Millqvist-Fureby, and Bergenstahl (2015) studied the effect of particle size on oil migration and the fat bloom development in chocolate samples with different particle size (15, 22 and 40 µm). The samples with a particle size of 15 µm had the highest occurrence of fat bloom, followed by the samples with a particle size of 22 µm, and the lowest intensity of developed fat bloom was recorded for the samples with a particle size of 40 µm. These results were supported by former studies, where Altimiras, Pyle, and Bouchon (2007) stated that the cocoa butter bars prepared with the smallest particle fraction (~5 µm) showed the highest rate of oil migration. However, in the study conducted by Choi, McCarthy, McCarthy, and Kim (2007) opposite results was obtained. Moreover, Montwani et al. (2011) reported that the interfaces of particles could be covered with liquid oil and thus oil migration increases. They offered that the non-fat particles do not support the growth of fat crystal clusters leading to a more heterogeneous crystal network ending in higher permeability and increased migration of oil. Therefore, specific surface area of the non-fat particles could play a role for possible migration pathways, where smaller particle size contributes to more surface area and thus, more passages for migration.

4.2. Flavor development during conching

Conching is a very crucial stage in chocolate production for flavor development. This process contains different phases in which the process conditions vary depending on the chocolate type. The conching conditions such as, time and temperature, technique (type of equipment, shearing forces), the moisture content are the main factors affecting the aroma profile of the chocolates.

During conching, moisture and a large amount of phenols are removed; viscosity and color are modified; oxidation of tannins takes place (Reineccius, 2006). In the later stages, interactions between disperse and continuous phase take place (Beckett, 2008). 80% reductions in volatile phenols are observed through a few hours of conching (Beckett, 2008). Oxidation and enzymatic mechanism leads the polyphenols to form a complex with amino acids, peptides and proteins (Dimick & Hoskin, 1999). During conching, polyphenols form complexes with amino acids, peptides, and proteins through oxidation and enzymatic mechanisms. The result is removal of flavor volatiles from headspaces and reductions in perceptions of astringency through irreversible phenol interactions, as well as more “mellow” final flavors (Dimick & Hoskin, 1999).

Amadori compounds that were produced in drying and roasting steps decrease via conching (Heinzler & Eichner, 1991) through evaporation or chemical reactions. However, caramelization of lactose and Maillard reactions with milk proteins occurs (Pontillon, 1995). Overall, off-flavors decrease significantly after conching (Beckett, 2003). Some flavor compounds such as, ethyl-2-methylbutanoate, 3-methyl-butanal, hexanal and dimethyl disulphide are evaporated and reduced to some extent (Schnermann & Schieberle, 1997). Besides, 2-phenyl-5-methyl-2-hexenal concentrations increase during aldol condensation of phenylacetaldehyde and 3-methylbutanal followed by dehydration (Counet, Callemien, Ouwerx, & Collin, 2002). Schnermann and Schieberle (1997) stated that furaneol and maltol formed during conching. In addition, the content of polysubstituted ethyl-, isobutyl- and iso-pentylpyrazines, tri- or tetra-methylpyrazine, furans and acetylpyrrole as hetero-cycles increased. Braga et al. (2018) stated that some compounds such as; 1-menthene, (2E)-2-heptenal, 2-ethyl-1-hexanol, trans-limonene oxide and 1,2-dihydro-5-methyl-3H-pyrazol-3-one were not detected in the nibs and liquor, but they were observed in the final chocolate. However some of these compounds contribute to the final flavor of chocolate therefore it is feasible to generate new form of aromatic compounds during conching process.

During conching physical changes such as, physical movement of the flavor molecules between the different ingredients of chocolate takes place. At the beginning of conching, the flavors are just on cocoa particles and also in the cocoa butter. The grinded sugar has sweet flavor. During conching, some cocoa flavor and fat are shifted onto the sugar surface. The outcome is a more uniform cocoa flavor with less sweetness in comparison to freshly roll-refined sugar (Beckett, 2008). Prolonged conching duration as a disadvantage results in the loss of desirable volatile aroma compounds through evaporation (Fischer, Abubaker, Hasselbarth, & Ulrich, 2010; Owusu et al., 2012). However the level and intensity of loss depends on the differences between the compounds. Fischer et al. (2010) studied the chocolate flavor changes induced by conching process and reported that the content of most aroma in the fat phase reduces during conching, but the aroma concentration in water-soluble compounds (sugar, protein) and in the insoluble material (cocoa solids) remain stable.

The content of low volatile pyrazine and pyrrole increases remarkably during conching of the chocolate. Many pyrazines namely, trimethylpyrazine, 2-ethyl-6-methylpyrazine, 2,5-dimethylpyrazine and some pyrroles increase during the manufacture of chocolate (Liu et al., 2015). In another study, it was shown that the pyrazines, which are major compound for the final aroma of chocolate along with sulphur compounds such as; methional and 2-methyl-3-(methyldithio) furan decreased in longer conching period (Fischer et al., 2010). Owusu et al. (2012) reported that short conching times results in higher amount of volatiles such as dimethyl trisulfide, 2,5- dimethylpyrazine, 2,3,4,5-tetramethylpyrazine and linalool. In another study, the effect of conching conditions on flavor attributes of dark chocolates was investigated. The results showed that the most important ingredients had highest amount in the unconched treatments (Owusu, Petersen, & Heimdal, 2013).

The complex and multi-stage Maillard reactions are divided to three main phases. The first phase that involves formation of several substances is somewhat reversible and they may react in later stages. In the next phase, the production of reactive carbonyl components occurs that determines the color and flavor development and the final phase produces heterogeneous group of compounds (e.g., melanoidins) responsible for deep-brown color. Cyclization and aldol condensation are the final steps of Maillard reactions that contribute to the establishment of heterocyclic aroma volatiles for example, pyrazines, however polymerization forms melanoidin pigments. The particular pyrazine structure is determined by side groups on dioxo components (Dimick & Hoskin, 1999).

The presence of more moisture in alternative processing techniques (ball mill) might contribute to the different aroma volatiles in the chocolates. The conching time is nearly 4 h longer that of the ball mill method that could result in more volatile and moisture evaporation.

The new coarse conching process was applied by Bolenz and Lipp (2011). This process is capable of removing water and undesirable volatiles. In the new process the conching step is performed primarily and then grinding occurs afterwards. Raw ingredients can be dried and conched before the fat addition. Water content is reduced to < 0.6%. Generally coarse crystal sugar is used that's why the novel process is named "coarse conching". Bolenz, Manske, and Langer (2014) optimized three processing parameters (percentage of lecithin at start, ball size and shear) in milk chocolates made by the new coarse conching process. The main purpose of their study was to find the best condition to obtain lowest apparent viscosity. In the second stage the flavor profile was compared with conventional roller refining and conching. In the case of sensory evaluation the results indicated that cocoa taste was more intense in chocolates prepared with the coarse conching process in comparison to the traditional process. This improvement in mouth feel perception was related to a better distribution within the particle fraction. No considerable differences were seen in attributes including nutty taste, stickiness, melting and hardness. However significant differences were recorded for the attributes such as gloss appearance, brown color, cocoa smell, cocoa taste, sweet and sandy mouth feel. All chocolates prepared with coarse conching process were notably less sweet and illustrated a more intense cocoa taste when compared to the chocolate produced traditionally.

Saputro et al. (2017a and 2017b) also assessed the quality properties of palm-sap sweetened dark chocolates by applying a 3-staged small-scale alternative process using a combination of Stephan mixing and ball milling. Particle reduction was obtained with the ball mill; mixing and liquefaction were carried out in the Stephan mixer. The alternative technique facilitated the retention of key volatiles including myrcene (spicy note), β-trans-ocimene (herbal note) and isoamyl acetate (fruity note). In the study of Hinneh et al. (2019) the effects of melanger (for chocolate refining) and Stephan mixer (for a conching-like application) on final flavor profiles were conducted. Volatiles including aldehydes, ketones, terpenes and terpenoids, indicated considerably differences due to the different refining techniques used. However, this effect was not reflected in terms of the overall volatile levels of the chocolates. Consumer preference testing showed no statistically difference preference for the chocolates.

4.3. Tempering and aroma

When evaluating the relation between tempering, aroma and the release of volatile flavor compounds; (i) effect of tempering on texturing, (ii) tempering and oil migration relationship should be taken into account.

Tempering has considerable effect on chocolate texture (Beckett, 2008). Products with different texture characteristics, can affect their residence in the mouth, oral behavior and also stimuli release (Saint-Eve et al., 2011). Perfectly tempered chocolate has a regular structure and uniform texture that preserves and protects the aroma compounds in the suspension. After the dilution by salvia the release of flavors from chocolate during consumption occurs. The three-dimensional structure of stable polymorphic form (β_V) with its regular shape spreads all the material in the suspension uniformly. Complete spreading occurs and aromas are maintained. In fact stable polymorphic form acts like a net in order to preserve all the ingredients in the suspension. This is due to their three-dimensional structure. As the structure of the cocoa butter has so much influence on the flavor and texture of the chocolate, it is essential that manufacturers know how to obtain the required and desired structure.

Chocolate flavor attributes are highly dependent on fat phase composition, consequently fat bloom impacts on the appearance attributes of chocolate products (Afoakwa, Paterson, Fowler, & Vieira, 2009b; Altimiras et al., 2007). In addition, due to the basic mechanism of the fat bloom, the intense migration of the fat to the surface of the chocolate, can lead to the loss of some oil soluble aroma compounds. This quality defect potentially considered to have an adverse effect resulting in off-flavor aroma. The main factors affecting chocolate flavor and taste changes were found to be the migration of the fat resulting in oxidation and rancidity.

5. Evaluation of aromatic compounds

Determination of aromatic compound profile of the end product is required for routine quality control and also for formulation and process developing and research studies, which is indispensable for production of the end products with desired quality characteristics. Therefore, selection of appropriate, reliable and fast test method is very important for the chocolate science and technology.

5.1. Instrumental determination of aromatic compounds

In order to determine the aromatic components instrumentally, one can follow numerous analytical methods which are; static headspace (HS) aroma isolation (using gas chromatography, GC), or detailed tedious aroma extractions and distillations (using mass spectrometry, MS or olfactometry). The method is generally determined by the sample's properties such as compound concentration or lipid content. Although each of the analytical methods has different sample preparation method with separate techniques, each method is critically appraised in terms of advantages and disadvantages.

The first method of flavor determination is static HS aroma isolation method with GC. Headspace analysis is specified as a vapor phase extraction involving the partitioning of the volatiles. The HS analyses are essentially consisting of two different techniques, static (vapor-phase extraction) and dynamic (purge and trap). Static headspace extraction (SHSE), include gas-tight vial sealed sample and after reaching the equilibrium of set temperature HS vapor sampling. The static sampling is usually done by the heated transfer line and pressurizing of the sample vial upper the capillary column head pressure in order to rapid sample transfer. On the other hand dynamic HS extraction (DHSE) involves crossing of the carrier gas through the sample solution and followed by the trapping of the purged volatiles on a sorbent and desorption on the GC. Another method of headspace aroma determination is headspace solid-phase micro extraction (HS-SPME). This technique is a fast and solvent-free method which applies fine silica fiber with polymeric coating for extracting of the organic substances from their matrix and immediately transferring to the injector of GC for thermal desorption and analyses (Braga et al., 2018). However selecting methods usually involve determining the type of fiber as well as the extraction temperature and time. The selection of various fibers and different extraction times and temperatures in several studies (Braga et al., 2018; Da Veiga Moreira et al., 2018; Khairy et al., 2018) is considerable.

In order to select a method of analyses it is necessary to notice; the sample, analysis time of target volatiles and objective. For the objective one may consider; (1) obtaining a complete aromatic properties in order to quantification of the aroma constituents in a food, (2) identification of the key aroma constituents which is usually the key aromatic component, (3) identification of the off-note in a food, (4) monitoring the changes by the time in the aroma profile, (5) determination of the food flavor adulteration and (6) predicting sensory attributes (Voilley & Etiévant, 2006).

The most challenging aroma quantification objective it the determination of the complete aroma profile. Method of flavor determination is very detailed and tiresome so sampling is critical. After selecting a sample that could represent the whole image of the chocolate sample the researcher will have to gain a precise aroma isolate where unfortunately there are still no adequate isolation method to yield an exact analytical profile. Therefore, it is vital to combine few analytical methods of aroma isolation. Following the sampling procedure, static headspace method can be used for the quantification of the most abundant volatile and non-volatile components. This method is usually combined with stir bar method to acquire information about the less volatile and numerous ingredients. Following step is the solvent extraction or simultaneous distillation/extraction (SDE) to get the least volatile components data. This procedure list usually gives the perfect qualitative view on the aroma profile of the food (Reineccius, 2006).

The explained methodology gives qualitative result about the flavor profile of the chocolate. The results can be quantified by using multiple internal standards which represents the interested compounds that have equal physico-chemical properties. By the internal standard the researcher can get comparative recovery and GC response data for all the components (Qian & Reineccius, 2002). Another option for the quantification is the using of internal standard, where an addition of known level of each aroma compound reanalyzing of them again to estimate the increase in GC peak area between the standard and added aroma component samples (Braga et al., 2018). Last method for quantification of the data is the application of isotopic dilution. In this methods the researcher adds known amount of the aromatic compound as label it isotopically to the sample (Blank, Milo, Lin, & Fey, 1999).

5.2. Sensory testing of the aromatic compounds

Sensory tests are mainly divided into three groups which are;

(i) Discrimination/difference experiments,
(ii) Descriptive experiments and,
(iii) Hedonic/affective experiments (Kilcast, 1999).

According to the test objective appropriate method should be selected. For the aroma, since it is complicated and forms as the combination of taste and odor, it is necessary to highlight important points. First task is the identification of the key components that contributes to aroma perception. Since it is not realistic to isolate a particular component on the chocolate and derived products, sensory sample is hard to be selected and prepared. Testing each component individually may sound a straight forward procedure, however recent 50 years of sensory works has still been debating with this challenge and still did not complete the task. The first step of the sensory design is the objective, where for this review we highlight that it is the aroma perception of the chocolate and chocolate derived products. For this aim we need to find a sample that represents the "chocolate" image of the consumers universally. After that point, it is necessary to isolate compound or combination of compounds which makes chocolate itself. Due to the physico-chemical properties and chemical stabilities of the compounds the isolation procedure may be an obstacle. For chocolate, the main sensory approaches are; melting character on sensory (Romanchik-Cerpovicz, Costantino, & Gunn, 2006), effect of storage conditions on sensory (Ali, Selamat, Man, & Suria, 2001), effect of compositional fat and substitution of fat on the sensory properties (Armbrister & Setser, 1994; Prindiville, Marshall, & Heymann, 2000), functionalization by adding other ingredients and its effect on the sensory attributes (Aragon-Alegro, Alegro, Cardarelli, Chiu, & Saad, 2007; Marsanasco, Márquez, Wagner, Chiaramoni, & Silvia del, 2015), effect of the compositional content and structure such as sugar (Rasouli Pirouzian, Peighambardoust, & Azadmard-Damirchi, 2016) and fat or particle size on sensory properties (Farzanmehr & Abbasi, 2009; Marsanasco et al., 2015; Romanchik-Cerpovicz et al., 2006; Ziegler et al., 2001) or effect of different sensory testing methods on the chocolate products (Romanchik-Cerpovicsz et al., 2006), designing a new formulation and etc. As mentioned sensory properties of chocolate and derived product has been widely studied and chocolate has numerous advantages on the researches since it provides multidisciplinary aspects to study with.

Perception of taste, flavor, aroma and texture in foods is a dynamic phenomenon. It means that, the perceived intensity of the sensory property alter from moment to moment. The dynamic nature of products comes from processes of chewing, salivation, breathing, tongue movements and swallowing (Dijksterhuis, 1996). Time-intensity (Tl) sensory evaluation is a useful tool to provide the panelists with the opportunity to scale their perceived sensations over time. This technique supplies the sensory specialist with potentially important temporal data about perceived sensations. Since the panelists are repeatedly monitoring their perceived sensations, from start to finish, the sensory scientist is able to quantify the continuous perceptual changes that happen in the determined attribute over time. When multiple properties are tracked, the profile of a complex food flavor or texture may indicate differences between products that change across time after ingestion. Because time-intensity analysis is a descriptive method, it can be used to get temporal profile of the flavor over time and in a special food product.

Temporal Dominance of Sensation (TDS) is a comparatively new descriptive sensory method in the sensory analysis for qualifying the temporal evolution of different sensations developed during food consumption (Labbe, Schlich, Pineau, Gilbert, & Martin, 2009). In the mentioned methodology, the panelists are asked to assess the dominant sensation during the evaluation time. Their evaluations are represented by curves that illustrate how often each sensation was considered dominant during the evaluation time. It is a fast and effective multi-attribute descriptive method when compared to other dynamic sensory tests used to assess the set of sensations induced by a special product (Pineau et al., 2009). In comparison to time–intensity, this technique offers a way to evaluate simultaneously several attributes dynamically over time. TDS prepares reliable data close to standard sensory profiling. It is useful to understand complex perceptions such as refreshing.

6. Conclusion

Flavor development in chocolate is associated to many factors, such as cacao growth conditions, the formulation and processing of the chocolate (refining and conching). There are several key compounds (nonvolatile and volatile chemical compounds) that specify the final flavor character. Several chemical, biological, and physical factors affect the formation and the development of flavor. Cocoa bean fermentation is necessary for the formation of key flavor precursors contributing to chocolate characters. Drying reduces the levels of acidity and astringency in cocoa nibs. Maillard reactions in roasting transform flavor precursors into two pyrazines and aldehydes. Conching determines the final flavor character by forming key odorants and evaporating Strecker aldehydes. Direct relationships are noticed between the primary composition and post-harvest treatments of cocoa beans and subsequent processing and technological impacts on the flavor formation and development. Good-quality sensory information along with knowledge on the chemical composition of cocoa flavor will clarify the contribution of individual components to overall flavor character. The improvement of flavor requires optimizing the post-harvest treatments, subsequent manufacturing processes during chocolate production and also the sensory strategy (human acceptability) in the evaluation of final flavor character in chocolate.

CRediT authorship contribution statement

Omer Said Toker: Conceptualization, Writing - original draft. **Ibrahim Palabiyik:** Conceptualization, Writing - original draft. **Haniyeh Rasouli Pirouzian:** Conceptualization, Writing - original draft. **Tugba Aktar:** Conceptualization, Writing - original draft. **Nevzat Konar:** Conceptualization, Writing - original draft.

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