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# Fluidized bed roasting of cocoa nibs speeds up processing and favors the formation of pyrazines

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#### ABSTRACT

Roasting is an important step in cocoa processing causing water loss and generating volatile compounds responsible for chocolate aroma like nitrogen-heterocycles. In this study, the comparison of two techniques, oven roasting, and fluidized bed roasting, in terms of effective water diffusivity (De) and activation energies of formation (Ea) of nitrogen-heterocycles was achieved with cocoa nibs. Fluidized bed roasting, recognized for its energy efficiency and low-footprint synthesis, was 16 times faster than oven roasting. The order of magnitude of De in fluidized-bed-roasted nibs was -8, while it was -9 in the oven-roasted nibs. Moreover, the  $a_w$  was 50% higher in fluidized-bed-roasted nibs than in the oven-roasted ones. The Ea of nitrogen-heterocycles ranged roughly between 40 and 80 kJ/mol. Those values were lower under fluidized bed roasting than under oven roasting. The more effortless water mobility within fluidized-bed-roasted cocoa demanded lower Ea, and favored the formation of nitrogen-heterocyclics.

Industrial relevance: This study can inspire cocoa manufacturers and equipment designers to pursue the formation of nitrogen-heterocycles during the roasting process of cocoa. It can be done either by adapting and scaling the current fluidized bed coffee roasters to cocoa beans or nibs; or by exploring other alternatives capable of leading enough water diffusivity and water activity in the cocoa nibs, as reported here. These physicochemical conditions undoubtedly boosted the formation of volatile compounds responsible for chocolate aroma, e.g., the pyrazines, without carrying the formation of typical-burn volatile compounds. This natural way of favoring the generation of pyrazines in cocoa nibs could contribute to clean labels by reducing or avoiding the subsequent use of flavorings. The implementation of efficient heat-transfer techniques during roasting, e.g., fluidized bed roasting, could reduce the processing cost and improve sustainability. Studies in the matter of sensory profile, and energy consumption/conversion are called for future research.

#### 1. Introduction

The fermented and dried seeds of *Theobroma Cacao* L., commonly known as cocoa beans, are a commodity of huge economic significance as they are the primary raw material for chocolate manufacturing. The cotyledons, also known as cocoa nibs, constitute the edible fraction of cocoa beans. They are encapsulated by testas, commonly called husks. Husks are removed either immediately before or after roasting. The first

option involves an additional step aimed to heat the surface of the cocoa beans (Gutiérrez, 2017).

Roasting is an important step that reduces the water content in cocoa nibs and produces desirable aromatic compounds (Rojas, Hommes, Heeres, & Chejne, 2022). Cocoa nibs are mainly roasted in large drum equipment at 110 to 150 °C ranging from 20 min to 2 h until the water content and water activity decrease to about 1% and 0.2 respectively (Rojas et al., 2022). This process causes a series of non-enzymatic

Abbreviations: VOC, Volatile Organic Compounds; FR, Fast Roasting/Roasted; SR, Slow Roasting/Roasted; W, Water content;  $a_w$ , Water Activity;  $L^*$ , Darkness;  $a^*$ , Redness;  $b^*$ , Yellowness; De, Effective Water Diffusivity; Ea, Activation Energy; 2,3-DMP, 2,3-Dimethylpyrazine; 2,5-DMP, 2,5-Dimethylpyrazine; 2,6-DMP, 2,6-Dimethylpyrazine; 2-Et-5-MP, 2-Ethyl-5-methylpyrazine; TtMP, Tetramethylpyrazine; TrMP, Trimethylpyrazine; 2-AP, 2-Aminopyridine; 4-MP, 4-Methylpyrimidine.  $^*$  Corresponding author.

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chemical reactions, well known as the Maillard reaction. They mainly involve reducing sugars and amino compounds to produce compounds of different molecular weights (Hodge, 1953; Martins, Jongen, & van Boekel, 2000). Some of the low-molecular-weight ones are volatile organic compounds (VOC). They are typically produced in the intermediate steps of the Maillard reaction, while the high-molecular-weight ones, known as melanoidins, are formed in the advanced stages. They exert brown color, and contribute to the texture and the antioxidant capacity of cocoa nibs (Aprotosoaie, Luca, & Miron, 2016).

Hundreds of VOC formed during roasting have been identified in cocoa beans of different origins (Diab, Hertz-Schünemann, Streibel, & Zimmermann, 2014; Marseglia, Musci, Rinaldi, Palla, & Caligiani, 2020; Mohamadi Alasti, Asefi, Maleki, & SeiiedlouHeris, 2019; Tan & Kerr, 2018) including nitrogen heterocycles like pyrazines, pyridines, and pyrimidines. Pyrazines, more specifically alkylpyrazines with different substituents (methyl-, ethyl-, propyl-), are the main class of heterocyclic volatiles and the key-odor components in cocoa derivatives by displaying cocoa, nutty, sweet, potato, coffee, chocolate, roasty, and earthy notes (Michel, Franco-Baraka, Ibañez, & Mansurova, 2021). The formation of pyrazines is enhanced with a water activity of 0.33 (Scalone, Cucu, De Kimpe, & De Meulenaer, 2015).

Heat transfer in solid foods is particularly slow, especially when surface heating techniques are applied, as in traditional oven roasting. This technique involves more conductive heat transfer from the steel of the drum or tray than convective heat transfer from the hot air sucked through the burners. In that sense, traditional oven roasting is not efficient: the temperature at the core of the roasted particles remains much lower than at the surface (Ling, Tang, Kong, Mitcham, & Wang, 2015).

There are other roasting techniques faster than oven roasting. Fluidized-bed roasting, for instance, has been successfully proven with coffee (Baggenstoss, Poisson, Kaegi, Perren, & Escher, 2008). Unlike oven-roasting, this technique is almost exclusive to convective heat transfer. In principle, fluidized beds operate by balancing the downward gravity forces of the weight of the particles to be roasted with the upward forces created by a stream of heated air (Sewel, 1995). Inside the fluidized bed's chamber, the particles are highly mobile, resulting in relatively uniform bed temperatures. Consequently, dead zones, hot spots, inhomogeneities, and variability in the quality of the products are significantly mitigated, if not completely avoided (Di Renzo, Scala, & Heinrich, 2021). Moreover, sustainable energy production/conversion and low-footprint syntheses also occur (Di Renzo et al., 2021). Even though the fluidized bed technique was introduced in the first half of the 1900s, there is no any published report on its use with cocoa beans. It could be because this technique does not resemble the industrial practice. Another reason is the weight of the whole cocoa beans, which is too high to be suspended in the air in regular fluidized-bed coffee roasters; therefore, they need to be deshelled, cracked, and sieved.

Kinetic studies are frequently applied in food science and industry to understand the relations between product and processing variables (M. A.J.S. van Boekel, 2021). Several studies have investigated the kinetics of cocoa roasting processes in terms of water loss. Domínguez-Pérez et al. (2019) found that the water loss was represented with a pseudofirst-order equation, and used the Arrhenius equation to find the temperature dependence. Hii, Menon, Chiang, and Sharif (2017) observed the typical exponential decay of cocoa's moisture content and reported the moisture diffusivities as a function of temperature. Focused on color and neoformed compounds, Sacchetti et al. (2016) found that color lightness of cocoa decreased following first-order kinetics.

However, the exploration of different roasting techniques in cocoa, e. g., fluidized bed vs. oven roasting, has not been reported in kinetic studies. Thus, this research compares the water diffusivity in cocoa nibs, and the temperature dependence of formation of some VOC during the roasting process of cocoa nibs in two different equipment, a conventional oven, and a fluidized bed roaster. Water activity and color properties were also evaluated at the final roasting time.

#### 2. Material and methods

#### 2.1. Chemicals and consumables

Fermented and dried Forastero cocoa beans (*Theobroma cacao L.*) from Ivory Coast, with a water content of  $6.25\pm0.03~w/w$ , were supplied by Barry Callebaut (Wieze, Belgium). Solid-phase microextraction fibers (75  $\mu$ m Carboxen/Polydimethylsiloxane) were purchased from Sigma Aldrich (St. Luis, USA).

#### 2.2. Preparation of cocoa nibs

Batches of 180 g of cocoa beans were heated in a pre-heated pan using an induction stove (ATAG B.V., The Netherlands) with constant stirring for 4 min. After that, they were cooled to 40  $^{\circ}$ C, and the husks were manually removed. Then, the particles adhered to the cotyledons were winnowed with an air gun. Finally, cocoa nibs were softly cracked with mortar and pestle and sieved to selectively retain only the cocoa nibs with a size between 4.0 and 7.0 mm. This size was suitable for balancing the weight of the cocoa particles with the power of the air-blower of the fluidized bed roaster. The sieved cocoa nibs were kept in vacuum bags at -20  $^{\circ}$ C until the roasting experiments.

#### 2.3. Roasting of cocoa nibs

Independent batches of 70 g of cocoa nibs with an initial water content of 4.10  $\pm$  0.18 w/w and a water activity of 0.481  $\pm$  0.05 were roasted in a pre-heated electric fluidized bed coffee roaster (Toper Optical Roaster, Izmir, Turkey) for 2'15", 2'45", 3'15", and 3'45" (min's"), at 110, 120, 130, and 140 °C. This roaster has a maximum capacity of 150 g of coffee beans ( $\approx$ 70 g of our cocoa nibs), and was provided with a fan with a constant speed of 2100 rpm. The fluidized bed roaster was programmed to cool the roasted nibs to 40 °C. These experiments were referred to as Fast Roasting (FR). Batches of 70 g of cocoa nibs were dispersed in aluminum trays and then placed in a pre-heated electric convective oven (VWR International B.V., Breda, the Netherlands) for 30', 40', 50', and 60' at 110, 120, 130 and 140 °C. These experiments are referred to as Slow Roasting (SR). A fan with a constant speed of 1400 rpm injected hot air into the oven's chamber, which inner volume was 115 L. The roasted nibs were immediately removed from the oven and cooled to 40  $^{\circ}$ C with an air gun. In both FR and SR, the temperature was measured with thermocouples located inside the roasting chambers. The two roasting techniques and the four roasting temperatures ended up with eight different roasting conditions abbreviated as FR-110 (i.e., Fast roasting at 110 °C), FR-120, FR-130, FR-140, and SR-110 (i.e., Slow Roasting at 110 °C), SR-120, SR-130, and SR-140. Each roasting condition was carried out for four different times; thus, 32 independent preparations were performed, each in duplicate. Unroasted cocoa nibs were used as control, i.e., time zero.

The second roasting times of each roasting technique, i.e., 2'15'' for FR, and 30' for SR, were the average times needed for the chambers to reach the corresponding roasting temperatures once the load was introduced. The final roasting times, i.e., 3'45'' for FR, and 60' for SR, corresponded to the average-times that the cocoa nibs needed to lose about 5% of their weight. Twenty grams of each roasting experiment, and 20 g of unroasted cocoa were ground using a screw-juicer (Vital Max Oscar 900, Hurom, Korea). Ground and non-ground cocoa nibs were vacuum-packed. The first ones were stored at -20 °C until usage, while the second ones, which were addressed to color analysis, were stored at 4 °C, and used the day after.

#### 2.4. Measurement of Water Content (W)

Approximately 1 g of ground cocoa was placed in a small aluminum cup and dehydrated in an oven (VWR International B.V., Breda, the Netherlands) at  $105\,^{\circ}\text{C}$  for  $18\,\text{h}$  in triplicate. The water content was

determined by gravimetric difference as shown in Eq. 1, with  $m_i$  being the initial mass (g) of the nibs, and  $m_d$  the dry mass (g).

$$W(\%w/w) = \frac{m_i - m_d}{m_i} x 100$$
 (1)

#### 2.5. Measurement of Water Activity (aw)

The water activity of 1.5 g of ground cocoa nibs was measured using a LabMaster-aw instrument (Novasina, Horsham, UK) at 25  $^{\circ}\text{C}.$ 

#### 2.6. Color properties

The color analysis of cocoa nibs was performed in triplicate by using an Iris Visual Analyzer 400 (Alpha M.O.S., Toulouse, France) equipped with a charge-coupled device camera. Ten grams of cocoa nibs were placed over a white background of the chamber, and high-resolution pictures (2588  $\times$  1942 pixels) were taken under identical controlled light conditions. Examples of the pictures can be seen in Fig. 2 and Fig. S1. The proportion of the pixels present in each image was obtained with the software AlphaSoft V14.1 (Alpha M.O.S., Toulouse, France). Data mining excluded the pixels whose contribution was below 0.01%. The estimation of darkness (reduction of L\*), redness (increase of a\*), and yellowness (increase of b\*) of every picture was calculated from the individual L\*a\*b\* values of every pixel (See Table S1) and their contribution to the entire picture.

#### 2.7. Volatile organic compounds (VOC)

Gas-Chromatography Mass-Spectrometry (GC-MS) measurements were performed with a Thermo Scientific<sup>TM</sup> Trace GC Ultra connected with a Thermo Scientific™ TriPlus RSH™ Autosampler (Thermo Fisher Scientific, Waltham, Massachusetts, U.S.). Vials with 1.00 g of ground cocoa were first heated for 10 min at 40 °C. A 75 µm Carboxen/Polydimethylsiloxane Solid Phase Microextraction (SPME) fiber was then inserted into the vials and exposed to the headspace for 10 min. After that, the fiber was transferred into the GC injection port for desorption of the trapped volatiles. The temperature program was carried out by heating from 40  $^{\circ}$ C to 200  $^{\circ}$ C with 10  $^{\circ}$ C/min rate. Then the temperature was kept at 200 °C for 5 min. Helium was used as carrier gas at a 2.0 mL/ min constant flow rate. The volatile compounds were separated on a Stabilwax®-DA 30 m:0.25 mm column (Restek Corporation, U.S., Bellefonte, PA, USA). The mass range was set to 33-250 m/z. The instrument setup and the data acquisition were made with the software Xcalibur 3.0 (Thermo Fisher Scientific Inc., U.S.). Finally, the retention time and the analyte peak area of each identified VOC were processed with the software Chromeleon 7.2 (Thermo Fisher Scientific Inc., U.S.)

## 2.8. Kinetics of water diffusivity and nitrogen-heterocycles formation during the roasting process of cocoa nibs

#### 2.8.1. Effective water diffusivity and temperature dependency

The rates of water loss k (s<sup>-1</sup>) during roasting time t (s) for the eight roasting conditions described in Section 2.3 were obtained with the first-order exponential model expressed in Eq. 2.

$$WR = \frac{(W - W_e)}{(W_0 - W_e)} = exp(-k')$$
 (2)

Afterward, the solution of Fick's second law of diffusion (Eq. 3) was used in determining the effective water diffusivity De  $(m^2s^{-1})$  by considering the rate of water loss calculated in Eq. 2 as the slope of Eq. 3. This calculation assumed three conditions in the cocoa nibs: their shape resembles a slab, the most widely used geometry in modeling the drying process of fruits and vegetables (Onwude, Hashim, Janius, Nawi, & Abdan, 2016); they have an average thickness of 5.5 mm, which corresponds to the arithmetic mean of the major and the minor sieve mesh

size, i.e., 4 and 7 mm; and that the samples retain their compact shape during the roasting experiment.

$$WR = \frac{8}{\pi^2} exp\left(\frac{-\pi^2 \text{De } t}{4(h^2)}\right) \tag{3}$$

*WR* stands for the water ratio; *W* is the water content (g / 100 g cocoa nibs) at any time t;  $W_0$  is the water content of unroasted cocoa (g / 100 g cocoa nibs) or initial water content;  $W_e$  is the equilibrium water content (g / 100 g cocoa nibs); and h is the half average thickness (m).

The relationship between effective water diffusivity De and temperature T (°C) is assumed to be an Arrhenius function (Onwude et al., 2016). However, the Arrhenius-like equation (Eq. 4) suits those physical phenomena that do not have activation energy, e.g., the molecular mobility of water during roasting (Martinus A.J.S. van Boekel, 2009).

$$De = De_0 \exp\left(\frac{-B}{T}\right) \tag{4}$$

where De<sub>0</sub> represents the pre-exponential factor ( $m^2s^{-1}$ ), and *B* the temperature dependency factor (°C)

#### 2.8.2. Temperature dependence in the formation of nitrogen-heterocycles

A Global fitting can be achieved to calculate the activation energy of formation of organic compounds when measurements of their concentration are taken at various temperatures (M.A.J.S. van Boekel, 2021), as is the case of the current study. Eq. 5 assumes that the temperature effect on the production of VOC can be described by Arrhenius' law:

$$C_i = C_0 + k_{ref} \exp\left(\frac{E_a}{R T_{ref}} \left(1 - \frac{T_{ref}}{T}\right)\right) t \tag{5}$$

where  $C_i$  is the relative concentration of a specific VOC at any time t (min);  $C_0$  is the initial concentration of the same VOC; Ea is the activation energy (J/mol); R is the ideal gas constant 8.3143 J·mol $^{-1}$ ·K $^{-1}$ ; T is the absolute temperature in K;  $k_{ref}$  is a reference rate of formation of the VOC; and  $T_{ref}$  is a reference temperature.

#### 2.9. Statistical analysis and mathematical models

Data were statistically analyzed by ANOVA and the Low Significant Differences (LSD) method with 95% significance was applied using the statistic software StatGraphics Centurion XVIII (StatGraphics Technologies Inc., USA). Principal Component Analysis (PCA) was performed using R commander 3.6.1 (R Foundation, Austria) and R studio (RStudio Team, USA). The aforementioned equations were executed in Microsoft Excel 365 (Microsoft Corporation, USA).

#### 3. Results and discussion

#### 3.1. Water content and water activity at the final roasting time

Expectedly, the water content and the  $a_w$  of cocoa nibs at the final roasting times (i.e., 3'45" for FR and 60' for SR) were significantly lower (p < 0.05) than that in unroasted cocoa, as given in Table 1. The water content decreased slightly with increasing roasting temperature. Interestingly, there was no significant effect of the roasting technique on the water content at the same temperature; therefore, we considered that they ended up in an "equal roasting degree." This little water interference makes them comparable from physical and chemical points of view. In other words, reaching similar water content in cocoa nibs at 110, 120, 130, or 140 °C in the fluidized bed roaster was 16 times faster than in the convective oven.

A water activity below 0.33 is desired in cocoa derivatives. It corresponds to typically crispy and brittle nibs or chocolate products (Hanselmann, 2008). This criterion was met in the eight roasting conditions with the FR cocoa nibs closer to the limit than SR cocoa. Table 1

**Table 1** Water content and  $a_w$  of cocoa nibs roasted at different temperatures at the final roasting time, i.e. 3'45" for FR, and 30" for SR.

Roasting technique	Temperature (°C)	$W \pm  ext{Std.Dev}$ (g / 100 g cocoa nibs)	$a_{ m w} \pm { m St.Dev.}$
Unroasted		$4.10\pm0.18^{a}$	$0.481 \pm 0.005^{a}$
	110	$1.94 \pm 0.28^{\mathrm{b}}$	$0.308 \pm 0.016^{\rm b}$
			0.284 $\pm$
FR	120	$1.72\pm0.28^{bc}$	$0.007^{\mathrm{bcd}}$
	130	$1.16 \pm 0.43^{d}$	$0.288 \pm 0.060^{\mathrm{bc}}$
	140	$0.89\pm0.34^{\rm d}$	$0.312 \pm 0.028^{\rm b}$
	110	$1.74\pm0.18^{bc}$	$0.206 \pm 0.010^{\rm e}$
	120	$1.47\pm0.17^{\rm c}$	$0.213 \pm 0.022^{\mathrm{de}}$
SR	130	$1.14\pm0.17^{\rm d}$	$0.186 \pm 0.020^{\rm e}$
			$0.223~\pm$
	140	$0.94\pm0.04^{d}$	0.004 <sup>cde</sup>

Values with different superscript letters within the same column are significantly different (p < 0.05).

indicates two aspects in  $a_w$ : i) roasting technique made a significant difference (p < 0.05); ii) no differences (p > 0.05) were found changing the temperature within the same roasting technique. Thus, the remaining water in FR cocoa could be more available for chemical activities than that in SR cocoa at equal roasting degrees.

Consistent with our results, Collazos-Escobar, Gutiérrez-Guzmán, Váquiro-Herrera, and Amorocho-Cruz (2020) found  $a_{\rm w}$  values of 0.20 in cocoa beans roasted in a rotatory system at 120 °C for 20 min (2% W); and Rojas, Chejne, Ciro, and Montoya (2020), who roasted cocoa nibs in an infrared moisture analyzer (100 to 200 °C) for about 20 min, reported water activity values about 0.35. Moreover, the latter found an effect of roasting temperature in reducing the  $a_{\rm w}$ . Not aligned with our results, García-Alamilla, Lagunes-Gálvez, Barajas-Fernández, and García-Alamilla (2017), reported  $a_{\rm w}$  values ranging from 0.31 to 0.54 in cocoa beans roasted in a a rotatory drum system (110 to 150 °C). In addition, some of their data were not significantly different from that of unroasted cocoa.

#### 3.2. Changes in water diffusion during roasting

Roasting is necessary for cocoa processing because it reduces the moisture content of the kernels up to optimal levels for their further processing, such as grinding and fat pressing (Minifie, 1999). During

roasting, the water present near the surface is initially evaporated; subsequently, the water from the inner layers of parenchyma cells moves toward the surface (Kashaninejad, Mortazavi, Safekordi, & Tabil, 2007). This dynamic process, which is favored when the temperature increases, can be described by Fick's Law (Crank, 1975; Onwude et al., 2016). Fig. 1 shows the decrease of the effective water diffusivity De in both roasting systems in function of the inverse of the temperature. In other words, the De increases when the temperature increases, as expected. As expressed by the *B* factor (Fig. 1), the rise of De was higher when FR was applied, meaning that the water diffusivity in FR cocoa nibs was more temperature-dependent than in SR cocoa. The order of magnitude of De in FR cocoa was higher than that of SR cocoa at the same temperature. It implies that the FR technique allowed faster mobility of water molecules in cocoa nibs than SR.

Consistent with our SR results, Domínguez-Pérez et al. (2019) reported De with orders of magnitude of -9 in whole cocoa beans  $(W_0=7\% \text{ w/w})$  roasted in a rotating cylindrical structure at different temperatures ranging from 100 to 220 °C. hii et al. (2017) found orders of magnitude of -10 roasting cocoa nibs ( $W_0$ =15% w/w) of a thickness between 3.4 and 4.0 mm in a hot air convective oven at 120, 130, and 140 °C. Sacchetti et al. (2016) also reported orders of −10 in whole cocoa nibs ( $W_0$ =6% w/w) roasted in an electric oven at 125 to 145 °C. At room temperature, the De of pure water is 1.7E-9 (Walstra, 2002), which is not distinctly different from the results of this study at roasting temperatures. The estimation of diffusion coefficients is far from simple; these differences could be due to the thickness of cocoa, the presence of the husks, the initial moisture content, the range of roasting temperatures, the equipment used for roasting, the ambient relative humidity, among other systematic factors. Moreover, the diffusivity of molecules depends quite strongly on the food matrix composition. The presence of macromolecules and networks, for instance, hinders their motion. Consequently, the diffusion coefficient can fluctuate in orders of magnitude (Martinus A.J.S. van Boekel, 2009).

The effect of the roasting technique on De is also in line with the results of water activity: in principle, the smaller the mass fraction of water, the smaller the effective diffusion coefficient (Walstra, 2002).

#### 3.3. Modification of color attributes by roasting technique

According to the color analysis, most of the 30 pixels identified in roasted and unroasted cocoa nibs correspond to brown colors.

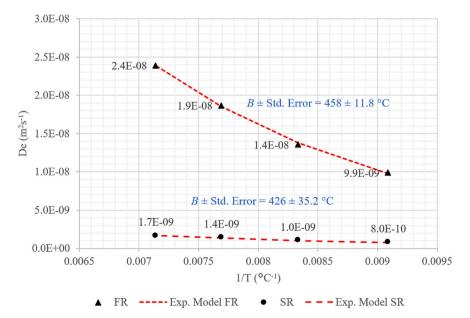


Fig. 1. Temperature dependency of the effective moisture diffusivity (De) in Fast Roasted (FR) and Slow Roasted (SR) cocoa nibs.

Nevertheless, some deep-red, deep-purple, grey, orange, deep-green, and yellow colors were present as well, and can be appreciated in Tables S1 to S4. Although no noticeable difference can be detected by naked eye among the eight different kinds of cocoa nibs roasted up to the final roasting time, the PCA analysis presented in Fig. 2 clearly differentiates the two roasting techniques. PC1 and PC2, explaining 76.8% of the data variability, show that FR cocoa nibs form a distinct cluster to the right side, while SR and unroasted nibs are mostly placed to the left and are highly overlapping.

The clusters' separation in Fig. 2 is mainly explained with the b\* color attribute, as observed in Table 2. Three relevant insights came from Table 2: (i) the FR cocoa nibs trended to have lower L\*, higher a\*, and higher b\* than SR nibs, having b\* the more distinctive differences. (ii) the samples did not turn significantly darker (reduction in L\*) upon any roasting condition. (iii) there was no significant effect of roasting temperature in any color attribute. The results reported by Zyzelewicz, Krysiak, Nebesny, and Budryn (2014) are strongly aligned with our FR findings.

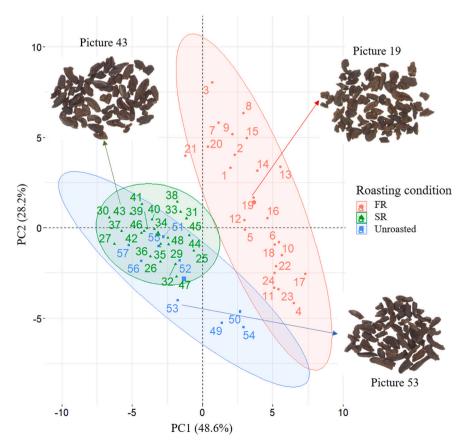
The initial color of cocoa nibs before roasting is usually deep-brown, as can be observed in Picture 53, inserted in Fig. 2 (also in Fig. S1). This condition makes cocoa a challenging product for visual color inspection. During roasting, several heat-induced chemical and physical phenomena take place in cocoa nibs, some of them working in favor of browning or darkening, and some others the other way round: (i) The hydrolysis of tannins (Perkebunan, 2009), for instance, hypothetically reduce the brownness; (ii) the formation brown color pigments via sugar caramelization and or Maillard reaction, should increase the brown color intensity; and (iii) the evaporation of water reduces the darkness of the surface of cocoa (water darkens the color of materials by increasing light absorption (Jacson, 2014)). A predominance of the second situation may explain the increase in b\* and a\*. This trend also happens when roasting cocoa at temperatures far above the most common roasting procedures (Zzaman & Yang, 2013).

#### 3.4. Kinetics of formation of volatile organic compounds (VOC)

Forty-three VOC were identified in ground cocoa by SPME GC-MS, including acetic acid, alcohols, aldehydes, fatty acids, esters, ketones, nitrogen heterocyclics, and sulphur-compounds (see Table S5). In order to have an overview of the dynamics of the eight roasting conditions in terms of VOC formation, the normalized data were grouped in chemical functions (see Table S6) and then analyzed via PCA. As shown in Fig. 3, the PC2-axis separated the roasting techniques and clustered FR and unroasted on the negative side, whereas the PC1-axis divided the lowest temperatures from the highest. Alcohols and N-heterocycles showed the most extended vectors, meaning that they strongly contributed to the formation of those clusters. Acetic acid was positively correlated with unroasted cocoa and the lowest roasting temperatures of the FR conditions. Ketones, alcohols, esters, aldehydes, and sulphur compounds were positively correlated to SR cocoa. Interestingly, the scores of both FR and SR cocoa were located along PC2 from the negative side toward the positive one in increasing order, also representing the increase in temperature. This tendency is toward the loadings of the N-heterocyclics, which suggests that their formation could depend on roasting time and temperature, especially under FR conditions.

As predicted by the PCA, the formation of the identified N-heterocyclics, e.g., 2,3-Dimethylpyrazine (2,3-DMP), 2,5-Dimethylpyrazine (2,5-DMP), 2,6-Dimethylpyrazine (2,6-DMP), 2-Ethyl-5-methylpyrazine (2-Et-5-MP), Tetramethylpyrazine (TtMP), Trimethylpyrazine (TrMP), 2-Aminopyridine (2-AP), and 4-Methylpyrimidine (4-MP) displayed temperature dependence as can be appreciated with the activation energies in Table 3. The values ranged roughly between 40 and 80 kJ/mol, which are in line with the  $\it Ea$  calculated for some Maillard reactions in model systems reviewed by Martinus A.J.S. van Boekel (2001).

In principle, reactants have to overcome an energy barrier (i.e., *Ea*) before reacting and generating new compounds (Walstra, 2002). The formation of all the N-heterocycles, except for tetramethylpyrazine,

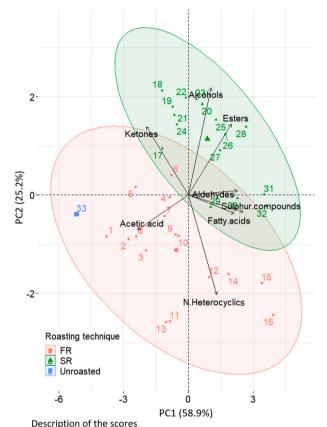


**Fig. 2.** PCA analysis of the pixel's color data of FR and SR cocoa nibs at the final roasting time (3'45" for FR and 60' for SR). Data used to plot this figure is shown in Tables S1, S2, S3, and S4. Briefly: Numbers 1–6 in the PCA correspond to 6 different pictures of Fast Roasted cocoa at 110 °C (FR-110), 7–12 to FR-120, 12–18 to FR-130, 19–24 to FR-140; 25–30 to Slow Roasted cocoa at 110 °C (SR-110), 31–36 to SR-120, 37–42 to SR-130, 43–48 to SR-140; and numbers 49 to 57 to unroasted cocoa.

**Table 2** L\*a\*b\* color attributes of cocoa beans at the final roasting time, 3'45" for fast roasting (FR), and 60' for slow roasting (SR).

Roasting condition	Temperature (°C)	L* $\pm$ St.Dev.		$a^* \pm St.Dev$	<i>I</i> .	$b^* \pm St.Dev$	·.
Unroasted		35.18	$\pm~1.37^{abc}$	5.76	$\pm~0.24^a$	5.55	$\pm~0.35^a$
FR	110	34.97	$\pm~1.47^{ m ab}$	6.54	$\pm~0.50^{ m de}$	8.29	$\pm~0.88^{\mathrm{b}}$
	120	35.10	$\pm~1.29^{abc}$	6.48	$\pm~0.38^{ m cde}$	8.33	$\pm~0.98^{\mathrm{b}}$
	130	34.40	$\pm~0.94^a$	6.63	$\pm~0.51^{\rm e}$	8.62	$\pm~0.65^{b}$
	140	34.66	$\pm 1.46^{a}$	6.17	$\pm~0.50^{abcd}$	7.91	$\pm~0.64^{b}$
SR	110	36.57	$\pm~0.82^{d}$	5.93	$\pm~0.22^{\mathrm{ab}}$	5.82	$\pm~0.26^{a}$
	120	36.24	$\pm~0.34^{bcd}$	6.05	$\pm~0.18^{ m abc}$	6.15	$\pm~0.48^{a}$
SK	130	37.05	$\pm~0.37^{ m d}$	6.08	$\pm~0.25^{ m abc}$	6.22	$\pm~0.39^a$
	140	36.41	$\pm~0.75^{cd}$	6.18	$\pm~0.14^{bcde}$	6.20	$\pm\ 0.45^a$

Values with different superscript letters within the same column are significantly different (P < 0.05).



Bescription of the	Description of the scores				
Roasting	Temperature (°C)				
technique - time	110	120	130	140	
FR - 2'15"	1	5	9	13	
FR - 2'45"	2	6	10	14	
FR - 3'15"	3	7	11	15	
FR - 3'45"	4	8	12	16	
SR - 30'	17	21	25	29	
SR - 40'	18	22	26	30	
SR - 50'	19	23	27	31	
SR - 60'	20	24	28	32	
Unroasted		3	3		

**Fig. 3.** PCA biplot of the chemical groups of VOC identified in unroasted, fast roasted (FR), and slow-roasted (SR) cocoa nibs at different roasting times and temperatures.

demanded higher *Ea* in convective-oven roasting than in fluidized bed roaster. In other words, FR allowed a more effective collision of the reactant molecules contained in unroasted cocoa nibs, such as reducing sugars and amino acids, to produce those VOC, probably due to the higher water activity and water diffusivity of FR cocoa nibs. 2-Ethyl-5-

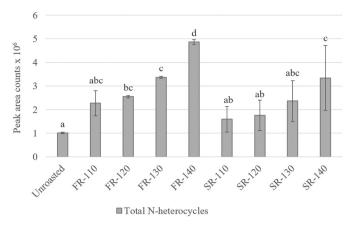
**Table 3**Activation energies of formation of N-heterocyclics in cocoa nibs under different roasting conditions.

N-heterocyclics	Fast roasting	Slow roasting	
	$Ea \pm Std.Error (kJ/mol)$	Ea ± Std.Error (kJ/mol)	
2,3-Dimethylpyrazine	$55.3 \pm 3.7$	67.7 ± 7.6	
2,5-Dimethylpyrazine	$58.5 \pm 4.8$	$89.9 \pm 35.9$	
2,6-Dimethylpyrazine	$56.5 \pm 4.6$	$87.0\pm32.9$	
2-Ethyl-5-methylpyrazine	$67.2 \pm 5.5$	$94.5 \pm 30.0$	
Tetramethylpyrazine	$43.4 \pm 5.5$	$18.3\pm10.9$	
Trimethylpyrazine	$62.1 \pm 4.3$	$76\pm8.8$	
4-Methylpyrimidine	$64.3 \pm 5.4$	$86.9 \pm 30.8$	
2-Aminopyridine	$36.6 \pm 4.3$	$43.0\pm6.0$	

methylpyrazine was the compound that showed the highest temperature dependency under both FR and SR conditions; this pyrazine can serve as an indicator compound to monitor roasting cocoa under typical roasting temperatures. The decreasing order of the other *Ea* values diverges between the roasting techniques. For instance, the formation of tetramethylpyrazine registered the lowest *Ea* in SR, but its temperature dependence was not that low in FR cocoa. The differences in *Ea* could be due to the specificity of the amino acids. For example, various amino acids can act as amino-group substrates to produce 2,3-DMP, 2,5-DMP, 2,6-DMP, 2-Et-5-MP, and TrMP. In contrast, only the amino acid Leucine can produce tetramethylpyrazine; however, Leucine is also involved in the formation of 2,5-DMP, 2-Et-5-MP, and TrMP (Arnoldi, Arnoldi, Baldi, & Griffini, 1988); therefore, there could be a higher competition for Leucine under SR than under FR.

The authors acknowledge the following limitations: i) The formation of VOC may diverge within cocoa varieties (Aprotosoaie et al., 2016) and origin (Marseglia et al., 2020); therefore, extending this investigation to other kinds of cocoa beans might provide extra support or no correlation with our findings. ii) N-heterocycles are not final products. They are intermediate products of the Maillard Reaction capable of further reacting to produce advanced products such as melanoidins. Consequently, the net amount of N-heterocycles produced during roasting was not detected; rather, the relative concentration of those, which did not follow the formation of advanced products, was measured. Notwithstanding those points, the results of this study provided valuable insights into the formation of aroma compounds under two roasting systems at regular cocoa roasting temperatures. To the best of our knowledge, this is the first study that assessed the kinetics of formation and temperature dependence of N-heterocyclics during cocoa roasting.

The high correlation of the vector "Pyrazines" with the cluster of FR cocoa (Fig. 3) is also reflected in Fig. 4. In Fig. 4, the sums of the eight N-heterocycles detected in cocoa nibs subjected to FR-120, FR-130, FR-140, and SR-140 were significantly higher (p < 0.05) than that in unroasted cocoa. At the same roasting temperatures, FR trended to produce a higher amount of N-heterocycles than SR. The boost of pyrazines under FR certainly intensified the chocolate aroma of cocoa nibs. However, a sensory analysis is needed to correlate these findings. The



**Fig. 4.** Total peak area counts of N-heterocycles detected in unroasted cocoa and cocoa roasted under different conditions: Fast Roasted at 110 °C (FR-110), Fast Roasted at 120 °C (FR-120), Fast Roasted at 130 °C (FR-130), Fast Roasted at 140 °C (FR-140), Slow Roasted at 110 °C (SR-110), Slow Roasted at 120 °C (SR-120), Slow Roasted at 130 °C (SR-130), and Slow Roasted at 140 °C (SR-140), for 3'45" in FR, and 30' in SR. Different letters above the bars represent significant differences (p < 0.05) in the sum of the N-heterocycles. The error bars correspond to the standard deviation.

presence of the N-heterocyclics in unroasted cocoa, speciallytetramethylpyrazine, was totally expected since they are also formed during the fermentation and drying processes of cocoa beans (Mohamadi Alasti et al., 2019). In addition, the surface-heating process addressed to remove the husks could have also initiated some Maillard reactions in the edges of the beans.

The concentration of VOC in cocoa during the roasting process was also reported by Huang and Barringer (2011). They also found that the concentration of 2,3-DMP, 2,5-DMP, 2,6-DMP, and TrMP increase during roasting. In addition, they reported that the higher the temperature, the higher the concentration of those pyrazines, as demonstrated in our kinetic study. Marseglia et al. (2020), Tan and Kerr (2018), and Diab et al. (2014) also found aligned results. The exploration of very high roasting temperatures (150 to 250 °C) performed by Zzaman, Bhat, Yang, and Easa (2017) demonstrated that the concentration of pyrazines peaks at the roasting time of 10 min, and then decreases.

Considering the roasting technique, Baggenstoss et al. (2008) found that the formation of pyrazines in coffee was higher in a fluidized bed roaster than in a drum roaster, as we found in cocoa; however, they did not report water activity nor water diffusivity. Aligned to our results, the effect of  $a_w$  in the formation of pyrazines in model systems was reported by Scalone et al. (2015). The system representing a water activity of 0.33 produced more pyrazines than the other systems holding aw values of

0.16, 0.38, and above 0.38.

The zero-order global model (Eq. 5) applied to the data of one of the N-heterocycles was plotted in Fig. 5. As observed in Fig. 5a and b, the model strongly fitted the data. Zero-order reactions are rather frequently reported for changes in foods, especially for formation reactions when the amount of product formed is only a small fraction of the amount of precursors present (Martinus A.J.S. van Boekel, 2009). It would be the case of intermediate Maillard Reaction products, like the aforementioned N-heterocyclics, which are typically produced by Amadori rearrangement and Strecker degradation pathways (Gibis, 2016).

#### 4. Conclusions

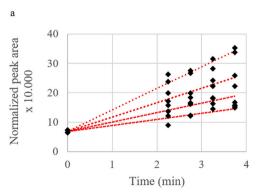
At conventional cocoa-roasting temperatures (from 110 to 140  $^{\circ}$ C), the fluidized bed roasting technique (Fast roasting) allowed faster mobility and higher availability of water molecules within cocoa nibs than oven roasting (Slow roasting) as it was expressed in the higher effective water diffusivity (De) and  $a_w$  values of its roasted cocoa nibs. The De in FR cocoa was more temperature-dependent than in SR cocoa.

The higher water diffusivity and water activity in FR cocoa certainly prompted the interaction of the reactants intricated in the formation of 2,3-Dimethylpyrazine, 2,5-Dimethylpyrazine, 2,6-Dimethylpyrazine, 2-Ethyl-5-methylpyrazine, trimethylpyrazine, 2-Aminopyridine, and 4-Methylpyrimidine. As a consequence: (i) the activation energy of those chemical reactions was lower in FR cocoa than in SR cocoa; and (ii) the concentration of those N-heterocyclics (expressed as peak area counts) was higher in FR cocoa than in SR cocoa at the same roasting temperatures.

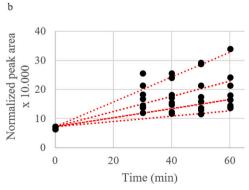
The formation of 2-Ethyl-5-methylpyrazine under both FR and SR conditions showed higher temperature dependency than the other N-heterocyclics. This temperature sensitivity could allow 2-Ethyl-5-methylpyrazine to serve as an indicator compound to monitor roasting cocoa under typical roasting temperatures.

The initial color of cocoa nibs before roasting is usually deep-brown; therefore, finding significant changes (p < 0.05) in L\* was not possible. Interestingly the b\* parameter stood out and displayed significant differences (p < 0.05), with FR cocoa higher in yellowness.

Data of this study highlighted the advantages of using fluidized bed roasting as an alternative roasting technique for cocoa nibs, being sixteen times shorter than conventional roasting. The efficiency of energy production/conversion of fluidized bed roasting and its low-footprint syntheses can undoubtedly reduce the processing cost, improve sustainability, and ensure the cocoa aroma quality with high pyrazine contents.







Data 2,3-DMP for SR ····· Arrhenius model

Fig. 5. Global fit for all temperatures using a zero-order kinetic model for 2,3-Dimethylpyrazine (2,3-DMP) under a) Fast Roasting (FR) and b) Slow Roasting (SR) conditions.

#### Authors' contributions

Ruth Fabiola Peña Correa: Conceptualization, methodology, data curation, formal analysis, writing original draft, investigation, project administration, and funding acquisition. Burçe Ataç Mogol: Methodology, validation, investigation, reviewing & editing, and supervision. Martinus van Boekel: Validation, formal analysis, reviewing & editing. Vincenzo Fogliano: Methodology, reviewing & editing, supervision.

#### **Declaration of Competing Interest**

The authors declare no conflict of interest.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at  $\frac{\text{https:}}{\text{doi.}}$  org/10.1016/j.ifset.2022.103062.

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