Analysis of cocoa particle roasting process in a μ-reactor

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ABSTRACT

Thermal energy changes the chemical composition of cocoa, which is related to its quality, during roasting. The effect of the heating rate on the physicochemical changes of cocoa, and the dynamics of generation and degradation of volatile compounds during heating are still unknown. Therefore, the weight loss of cocoa and the chemical composition of the released gases released at temperatures from 40 to 350 °C were identified in using a μ-reactor (PTV-GC-MS) with heating rates of 2 (β1), 4 (β2), and 8 °C sec⁻¹ (β3). The thermal process was divided into three stages (raw, dry, roasted, and over-roasted). Higher heating rates cause lower volatilization at the same temperature due to shorter residence times. Likewise, more compounds were identified in the gas-fraction at β1 than at β2 and β3 with the same temperatures. Also, a 2D phenomenological model coupled to kinetics was made to predict phenomena such as thermal differentials, water and gas content, solid fractions, conversion, pressure, and gas outlet rate.

1. Introduction

Chocolate is one of the most commercialized food products globally, it has led to develop a large industry that includes agricultural production, transformation, and commercialization (ICCO, 2019). The product quality depends on the origin of the beans and their processing. Roasting plays a key role among the processes that take place outside the production, transformation, and commercialization (ICCO, 2019). The commercialization of cocoa has led to develop a large industry that includes agricultural processes to obtain the desired characteristics of cocoa beans and chocolate, including sensory ones.

It is a thermochemical process that changes the chemical composition of food products such as cocoa beans, coffee, and cereals and it is essential to acquire organoleptic characteristics like texture, color, flavor, and aroma (Krysiak et al., 2013; Redwell et al., 2003). In the first stage, cocoa fats melt around 34 °C (Rojas et al., 2020); then, some low molecular weight compounds of the raw cacao are dried and volatilized. During heating, chemical reactions generate volatile compounds like aldehydes, ketones, alkenes, esters, pyrazines, esters, and phenols (Castro-Alayo et al., 2019; Utrilla-Vázquez et al., 2020); and physical structure changes such as bean swelling, pore plugging, darkening, density decrease, and softening (Krysiak et al., 2013; Rojas et al., 2020; Sukrisno et al., 2006). Darkening and early gas formation are attributed to Maillard’s reaction; the chemical compounds released at this stage are related to flavor and aroma (Steinhart, 2005). This reaction includes three consecutive stages: in the first stage (colorless products), the sugar–amine condensation and Amadori rearrangement take place; the intermediate stage (colorless or yellow products) involves sugar dehydration, sugar fragmentation, and amino acid degradation (Strecker degradation); and the final stage (products highly colored) are the aldol condensation, aldehyde–amine condensation, and formation of heterocyclic nitrogen compounds (Rchavarria et al., 2012; Steinhart, 2005). Hence, roasting favors the formation of biogenic amines such as serotonin, phenylethylamine, tryptamine, and tyramine (Dijkeng et al., 2018; Nehlig, 2013).

It also reduces the content of natural products such as polyphenols and (-)-epicatechin (Stanley et al., 2018), and alkaloids (theobromine, caffeine) (Zapata et al., 2015). Sugars, proteins, and vitamins can also be affected by heating (Moreira et al., 2018). Therefore, research has focused on studying the effect of process parameters such as temperature and residence time on the quality of the final product (Jolic et al., 2011; Missawi et al., 2005; Zyżelewicz et al., 2015; Zzaman et al., 2014).

Understanding the roasting process in depth is a challenging task; however, modeling is a valuable tool for describing non-perceptible phenomena during experimentation analyzed by phenomenological laws. Roasting modeling has been based on the laws of conservation of...
mass and energy, and in some cases, it involves terms of reaction kinetics (Bhattacharya, 2014). Kinetic and semi-empirical models about cocoa roasting to analyze water loss were found in the literature. These models (12) (Sacchetti et al., 2016). The polyphenols degradation was analyzed by the Weibull probabilistic cumulative model (12) (Ioannone et al., 2015); the color lightness (L*) and Hue angle (h) changes (darkening) using first (7) and zero-order models (8); and the formation of Maillard reaction products as melanoidins and HMF, through an asymptotic (11) and exponential models (12) (Sacchetti et al., 2016).

However, according to Scopus (2021), there is a significant deficiency in literature on modeling cocoa roasting; only 8.3% of the total papers on cocoa roasting and 0.15% of the total publications on cocoa.

Water loss kinetics follows an exponential decay remarkably similar to the drying processes, such behavior is typical of the models presented previously. The mass transfer process is dominated by internal diffusion (Jayas Digvri et al., 1991; Morales and Van Boekel, 1997). It was determined that water loss during bean roasting achieves a final moisture content between 1.9 and 2.3% db (Sacchetti et al., 2016). The formation of DKPs was more accurate than the Prout-Tompkins model, which describes quasi-auto-catalytic reactions with an average activation energy of 85 kJ/mol and a distribution close to normal when evaluated at 120 and 150 °C for 70 min (Andruszkiewicz et al., 2019). In the same way, the darkening kinetics has been evaluated with a zero-order model, thus finding an activation energy of 59 ± 8 kJ mol⁻¹ — similar to oxidation of polyphenols—; HMP formation was between 0.1 and 0.8 mg kg⁻¹ (Ioannone et al., 2015; Sacchetti et al., 2016). Also, the concentration of peptides in 2,5-diketopiperazines (DKP) stagnates and decreases at a longer heating time, probably due to polymerization reactions at non-neutral pH at 120 °C and 150 °C (Andruszkiewicz et al., 2019).

There are differences related to temperature and time; however, no studies analyzing the heating rate effect were found, thus, their impact on volatilization, chemical composition, and physical properties is still unknown (Rojas et al., 2022). The heating rate can determine the residence time. The heat transfer efficiency will also influence the presence of a thermal gradient in the beans; consequently, some areas are over-roasted and others remain partially raw if large particles as cocoa beans are used. It is also necessary to study the particle size —also of interest— since it can help determine mass and energy transfer, which are coupled in thermal processes.

In roasting, volatilization explains weight loss during heating. Thus, to better understand thermochemical reactions, it is necessary to know both the final composition achieved in the solid and the composition of the gases released in heating. This would allow monitoring the volatile compounds responsible for the final aroma of products to determine which process conditions favor their formation and make the remain solid or volatilized. Nevertheless, small-scale studies (small samples under kinetic control), the heating rate effect, and the gas-fraction chemical composition are still unknown. This work aims to explain the roasting phenomenology through small-scale experiments under non-isothermal conditions, including typical and higher roast temperature ranges, to understand chemical degradation, and a mathematical model coupled with three-stage kinetics was proposed. The programmable temperature vaporization injector (PTV-GC-MS) was used as a μ-reactor together with a new experimental methodology able to identify the effect of the heating rate (2, 4, and 8 °C sec⁻¹) on the gas fraction and its chemical composition. The model was a valuable complementary tool for a better understanding of the roasting thermochemical phenomena. It allowed us to accurately predict phenomena not perceptible during the experimentation but which can be analyzed through phenomenological laws. In this case, the variation of the solid and gaseous fractions, temperature differentials within the sample, density, pressure, formation, and gas release rate were predicted. Hence, new scientific bases to make recommendations for redesigning and optimizing the roasting technology in the cocoa industry were obtained.

### Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Name</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Newton</td>
<td>[MR = exp(-\alpha t)]</td>
<td>Baghdadi and Hii (2017); Hii et al., 2017</td>
</tr>
<tr>
<td>2</td>
<td>Page</td>
<td>[MR = exp(-\beta t)]</td>
<td>(2017); Hii et al., 2017</td>
</tr>
<tr>
<td>3</td>
<td>Two-term</td>
<td>[MR = exp(-\alpha t + \beta t^2)]</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Arrhenius</td>
<td>[D_t = D_0 \exp \left(\frac{E}{RT}\right)]</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Fourier law</td>
<td>[TR = \frac{T_t - T_i}{T_s - T_i}]</td>
<td>McCabe (2005)</td>
</tr>
<tr>
<td>6</td>
<td>Fick’s second law</td>
<td>[M_f - M_t = \frac{M_s - M_r}{r} - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(-\frac{D_n^2 \pi^2 t}{r^2}\right)]</td>
<td>(2016)</td>
</tr>
<tr>
<td>7</td>
<td>Zero-order</td>
<td>[C = C_0 + kt]</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Prout-Tompkins</td>
<td>[E = \frac{1}{\alpha} - \frac{1}{\beta}]</td>
<td>(2019)</td>
</tr>
<tr>
<td>9</td>
<td>First-order</td>
<td>[L^* = \frac{1}{K_1 + \frac{t}{T_0}}]</td>
<td>(2016)</td>
</tr>
<tr>
<td>10</td>
<td>Weibull</td>
<td>[\frac{C_0 - C_f}{C_0 - C_\infty} = 1 - \exp(-\beta t^\gamma)]</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Asymptotic</td>
<td>[C_t = C_0 - \frac{t}{K_0 - C_0}]</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Exponential</td>
<td>[C_t = C_0 + k_{\text{conv}} \exp(-\beta t)]</td>
<td></td>
</tr>
</tbody>
</table>

* a, b, k, g = constants, T_R, T_0, T_s = temperature ratios, E = activation energy, k_1 and k_2 = rate constant at the temperatures evaluated (T_1 and T_2 for Prout-Tompkins model), R = universal gas constant, C_0, C_e, C_t = initial, equilibrium and time t concentrations, \(\beta\) = rate parameter, and k = rate constant.
2.2. Physicochemical characterization

Moisture content ($X_w$) and elemental analysis (C, H, N, and S). The moisture was measured in an Hal. Moisture Analyzer HC103 with an accuracy of 0.0001 g (Mettler Toledo GmbH, Greifensee, Switzerland). Elemental analyses were performed using an Euro Vector 3400 CHN-S analyzer (Foggia, Italy). The difference determined the oxygen content. All experiments were made in triplicate, and the average value was obtained.

Identification of thermal phenomena. The enthalpy of reactions and heat capacity ($C_p$) were measured by modulated differential scanning calorimetry (MDSC). Around 5 mg of sample were placed in a sealed aluminum sample pan and heated using a DSC Q2000 (TA Instruments, Lindon, UT USA). The thermal changes were tracked in modulated mode (MDSC), ±0.50 °C every 40 s, starting with an isothermal process at 90 °C for 3 min, followed by heating at 10 °C min$^{-1}$ from −90 °C to 400 °C.

2.3. Roasting in programmable temperature vaporizing (PTV) injector

An Atas Optic 2 Programmable Injector (Veldhoven, The Netherlands) coupled directly to the Hewlett Packard 5972 GC/MS gas chromatograph with mass detector (Waldbronn, Germany) was used as μ-reactor to roast particles of raw cacao. This instrument is a particular injection system of GC-MS; the samples are put into a μ-vial (borosilicate) with a diameter of 2.9 mm and a volume of 60 μL. This μ-vial is introduced into a liner (internal diameter of 3.4 mm). The PTV inlet’s programmable temperature control system consists of a heating coil and a coolant jacket with airflow, as shown in Fig. 1a. The heating coil allows heating both the liner and an μ-vial with the sample. In this way, roasting starts when the sample is heated and produces the gas fraction injected directly into the GC-MS column. The oven was programmed at 40 °C (1 min), heating to 120 °C (4 °C min$^{-1}$), to 180 °C (5 °C min$^{-1}$), and up to 310 °C (10 °C min$^{-1}$) with a Restek Rxiv®-5Sil MS (30 m × 0.25 mm I.D. × 0.1 μm). Split Mode injection (ratio 1:50), a mobile phase of helium at 1 ml min$^{-1}$, and MS detector in scan mode (30–500 m/z).

The remaining solid (solid fraction) was analyzed by SPME/GC-MS using a CAR/PDMS) fiber with volatiles adsorption of 50 min (60 °C) and desorption of 6 min (260 °C) in a manual Holder sampling Supelco (Milan, Italy) in split less mode. The gas and solid fractions compounds were identified using the NIST05a mass spectral library. The experiments were made duplicate and the average is obtained.

Experiments were performed with samples of 5–15 mg, temperatures from 40 °C ($T_1$) to 100 ($T_2$), 125 ($T_3$), 150 ($T_4$), 175 ($T_5$), 200 ($T_6$), 250 ($T_7$) and 350 °C ($T_8$), with heating rates of 2 ($\beta_1$), 4 ($\beta_2$), and 8 °C sec$^{-1}$ ($\beta_3$).

Fig. 1. Illustrative scheme of a) PTV injector diagram, and b) scheme of the μ-reactor system for modeling.

Fig. 2. Kinetics scheme of the cocoa roasting process.
(βm). The wall temperature in the µ-vial empty wall and the sample were measured using a Type K Thermocouple with 0.5 mm of diameter (accuracy of 1.1 °C and response time 0.3–1.5 s). Additionally, the weight was recorded before and after heating on an analytical balance with an accuracy of 0.01 mg. The weight loss was obtained by \( m_i/m_0 \), and the volatilized gas fraction by \((1 - \text{weight loss})\). This volatilized weight was related to the components profile identified by GC-MS.

A transversal section of the µ-vial center with length x (radius) and height were assumed for the modeling. Thus, it was made in Cartesian coordinates in 2 dimensions (x and y) for the bed of cacao powder in the µ-vial, as shown in Fig. 1b.

### 2.4. Modeling

**Material balance.** The raw cacao first loses free water, and some low molecular weight compounds are present in it (stage 1). Subsequently, it starts the formation of new volatile compounds and their release due to the higher temperature in stages 2 and 3. It was found that from 150 °C the products of chemical reactions begin to be released into the gas fraction (pyrazines and CO\(_2\)). Then, for kinetic studies, the following process scheme was proposed (Fig. 2).

The first stage is the drying and volatilization of the compounds present in the raw cacao, like acetic acid and alcohols, and the obtention of dry cacao (Eq. (1)). Water variation is defined in Eq. (2), and dry cacao in Eq. (3):

\[
dm_c = \frac{dm_c}{dt} = -m_c(k_w + k_d) \\
\]

(1)

\[
dm_w = \frac{dm_w}{dt} = m_c(k_v) \\
\]

(2)

\[
dm_o = \frac{dm_o}{dt} = k_w m_c - m_o(k_w + k_v) \\
\]

(3)

where, \( m_c \) is the mass of raw cacao, \( m_D \) is the mass of dry cacao (pre-roasted) obtained until 150 °C, and \( m_w \) is the mass of water and low molecular weight compounds of the sample. In the next stage, volatile compounds appear as products of solid-state reactions due to heating, then the roasted and over-roasted cacao are produced as shown in Eq. (4), Eq. (5), and Eq. (6):

\[
dm_{v1} = \frac{dm_{v1}}{dt} = k_w m_D \\
\]

(4)

\[
dm_{v2} = \frac{dm_{v2}}{dt} = k_v m_D - (k_w + k_v) m_R \\
\]

(5)

\[
dm_o = \frac{dm_o}{dt} = k_w m_R \\
\]

(6)

where \( m_R \) is the mass of roasted cocoa, \( m_O \) is the mass of over-roasted cocoa, \( m_{v1} \) and \( m_{v2} \) the volatiles loss at 250 and 350 °C, respectively. The balance of the gas fraction, composed of the water vapor and the volatiles generated in the following two steps, is defined as Eq. (8):

\[
\frac{dn_v}{dt} = -\text{div}(m_v \bar{\nu}_v) + k_w m_c + k_{v1} m_D + k_{v2} m_R \\
\]

(8)

where \( \bar{\nu}_v \) is the velocity vector of the volatiles within the sample. A gas flow through a porous medium governed by Darcy’s law was considered. Then, the gas velocity in the particle x and y-axis was defined as Eq. (9):

\[
\theta_{xy} = \frac{B_{xy} \Delta P}{\mu} \\
\]

(9)

where B represents the sample permeability, P the pressure, and \( \mu \) the viscosity of the gas. All kinetic constants are used according to Fig. 2 (i.e., \( k_w, k_v, k_{v1}, k_r, k_{v2}, \text{and } k_o \)) for the formation/destruction rate of different phases and are defined by the Arrhenius equation for non-isothermal heating Eq. (10):

\[
k_i = \frac{dt}{d\beta} = A_i \exp \left( -\frac{E_i}{R_T} \right) (1 - \alpha)^n \\
\]

(10)

\[
\beta = \frac{dT}{dt} \\
\]

(11)

\( A_i \) is the pre-exponential factor for each reaction, \( n \) is the reaction order, \( \alpha \) is the conversion (zero, 1, or 2), and \( \beta \) is the heating rate Eq. (11) in °C sec\(^{-1}\). The conversion is given by the mass variation with temperature Eq. (12):

\[
\alpha = \frac{m_i - m(T)}{m_i} \\
\]

(12)

where \( m_0 \) is the initial mass, \( m(T) \) is the mass in the temperature T, and \( m_f \) was the final mass obtained at 350 °C. Finally, the residual mass fraction \( M_f \) at any instant in time is expressed as the sum of all possible fractions present as Eq. (13):

\[
M_f = \sum_{i=1}^{N} m_i \\
\]

(13)

\[
M_f = m_c + m_v + m_D + m_R \\
\]

(14)

The initial conditions for \( t = 0 \) are: \( m_i = 0 \) and \( m_f = m_o = m_R = m_i = 0 \).

\[
t = 0; m_c = 1 \\
\]

(15)

\[
m_o = X_{o,w} m_c \\
\]

(16)

\[
m_D, m_v, \text{ and } m_R = 0 \\
\]

(17)

where \( X_{o,w} \) is the moisture content (wet basis) of raw cacao powder.

**Energy balance.** The heat transfer in the solid sample is given by conduction mechanism. In the boundary conditions, the heat is transferred by conduction and radiation through the µ-vial walls. Within the biomass, it was considered that the heat is transferred from the walls of the µ-vial by the external heat source, and part of this heat is absorbed in the solid-state chemical reactions, thus generating and volatilizing chemical compounds. These reactions can be endothermic or exothermic. The energy balance is shown in Eq. (18):

\[
\frac{\rho C_p d T}{d t} + \text{div} \left( \rho C_v \bar{\nu}_v, \bar{\nu}_v \right) = \text{div} (\lambda_{eff} \nabla T) + \dot{Q}_{\text{reactions}} \\
\]

(18)

where \( C_p \) and \( C_v \) are the heat capacities of solid and gas fractions, \( \bar{\nu}_v \) is the gas velocity, and \( \lambda_{eff} \) represents the effective thermal conductivity in the solid. The fractions of each phase \( \gamma_l \) present in the particle are defined as the ratio of the volume of the phase \( V_l \) and the total volume of the particle \( V_P \).

\( \dot{Q}_{\text{reactions}} \) represents the consumption or generation of energy in the cacao during the drying and roasting process through volatiles release Eq. (19):

\[
\dot{Q}_{\text{reactions}, k} = \sum_{k=1}^{N} \Delta H_{rxn,k} \rho \dot{k}_i \\
\]

(19)

So \( \dot{Q}_{\text{total}} \) is:

\[
\dot{Q}_{\text{total}} = \sum_{i=1}^{7} \sum_{k=1}^{6} \Delta H_{rxn,k} \rho_i \dot{k}_i \\
\]

(20)
where \( H_{c,\text{ro}} \) represents the enthalpy of kinetic model reactions shown in Fig. 2 for \( i \) species and \( k \) reactions.

The boundary conditions are defined by:

\[
0 \leq y \leq h; \quad 0 \leq x \leq L.
\]

where \( h \) is the height of the sample (10 mm), \( x \) is the diameter (1.45 mm).

\[
x = 0; \quad -\lambda \frac{\partial T}{\partial x} = 0
\]

\[
x = L; \quad -\lambda \frac{\partial T}{\partial x} = \varepsilon \sigma (T^a - T^s)
\]

\[
y = 0; \quad \frac{\partial y}{\partial x} = \varepsilon \sigma (T^a - T^s)
\]

\[
x = 0; \quad y = h; \quad \frac{\partial y}{\partial x} = 0; \quad m_v, \nu = 0
\]

\[
y = h; \quad m_v, \nu = h_m \left( m_v, \nu - m_v, \nu^w \right)
\]

where \( y \) is the height of the sample inside of the cylindrical \( \nu \)-vial, \( x \) is the

Table 2

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Property</th>
<th>Value</th>
<th>Units</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>( \rho )</td>
<td>281.4 ± 0.23</td>
<td>kg/m³</td>
<td>Experimental</td>
</tr>
<tr>
<td></td>
<td>( C_p )</td>
<td>2.44 ± 0.28</td>
<td>kJ/kg·K</td>
<td>Experimental</td>
</tr>
<tr>
<td></td>
<td>( \lambda )</td>
<td>8.99 × 10⁻⁴</td>
<td>kW/m·K</td>
<td>Experimental</td>
</tr>
<tr>
<td></td>
<td>( \epsilon )</td>
<td>0.93 ± 0.08</td>
<td>N/m²·K</td>
<td>Debaste et al. (2008)</td>
</tr>
<tr>
<td></td>
<td>( B_b )</td>
<td>4.0 ± 10⁻¹³</td>
<td>m²</td>
<td>Granados et al. (2016)</td>
</tr>
<tr>
<td>Gas</td>
<td>( \rho_g )</td>
<td>0.5812</td>
<td>kg/m³</td>
<td>NIST (2011)</td>
</tr>
<tr>
<td></td>
<td>( C_p )</td>
<td>2.054</td>
<td>kJ/kg·K</td>
<td></td>
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<tr>
<td></td>
<td>( \lambda_g )</td>
<td>2.54 ± 10⁻⁵</td>
<td>kW/m·K</td>
<td></td>
</tr>
<tr>
<td>Over-roasted</td>
<td>( \rho_o )</td>
<td>210.1</td>
<td>kg/m³</td>
<td>Experimental</td>
</tr>
<tr>
<td></td>
<td>( C_p )</td>
<td>1.94</td>
<td>kJ/kg·K</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \lambda_o )</td>
<td>4.18 ± 10⁻⁴</td>
<td>kW/m·K</td>
<td></td>
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<tr>
<td></td>
<td>( \epsilon_o )</td>
<td>0.93</td>
<td>N/m²·K</td>
<td>Debaste et al. (2008)</td>
</tr>
<tr>
<td></td>
<td>( B_o )</td>
<td>1.0 ± 10⁻¹²</td>
<td>m²</td>
<td>Granados et al. (2016)</td>
</tr>
</tbody>
</table>

Table 3

<table>
<thead>
<tr>
<th>Phenomena</th>
<th>Type</th>
<th>Temperature (°C)</th>
<th>Enthalpy (kJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvation</td>
<td>Endothermic</td>
<td>161.85</td>
<td>79.01 ± 3.2</td>
</tr>
<tr>
<td>Chemical reaction 1</td>
<td>Exothermic</td>
<td>289.24</td>
<td>15.27 ± 1.5</td>
</tr>
<tr>
<td>Chemical reaction 2</td>
<td>Exothermic</td>
<td>333.87</td>
<td>1.70 ± 0.18</td>
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<table>
<thead>
<tr>
<th>( C_p (kJ/kg·°C) )</th>
<th>Before melting</th>
<th>Before solvation</th>
<th>Before Chemical reactions</th>
<th>After Chemical reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1.69 ± 0.04 )</td>
<td>( 2.48 ± 0.07 )</td>
<td>( 2.40 ± 0.03 )</td>
<td>( 1.94 ± 0.02 )</td>
<td></td>
</tr>
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</table>

Table 4

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( \beta_1 ) (2 °C sec⁻¹)</th>
<th>( \beta_2 ) (4 °C sec⁻¹)</th>
<th>( \beta_3 ) (8 °C sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_C )</td>
<td>1.03 × 10³</td>
<td>1.50 × 10³</td>
<td>2.00 × 10³</td>
</tr>
<tr>
<td>( E_C )</td>
<td>30.0</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td>( A_L )</td>
<td>3.92</td>
<td>4.04</td>
<td>10.09</td>
</tr>
<tr>
<td>( E_L )</td>
<td>17</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>( A_R )</td>
<td>1.41 × 10¹¹</td>
<td>1.70 × 10¹¹</td>
<td>7.59 × 10¹¹</td>
</tr>
<tr>
<td>( E_R )</td>
<td>149.5</td>
<td>149.0</td>
<td>148.0</td>
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<td>91.3</td>
<td>91.4</td>
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<tr>
<td>( E_s )</td>
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<tr>
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<tr>
<td>( E_k )</td>
<td>154.1</td>
<td>151.1</td>
<td>150.7</td>
</tr>
</tbody>
</table>

Table 3

Physical and thermal properties of raw cacao, gas, and over-roasted cocoa.

Table 4

Parameters of the kinetic model at different heating rates.

3. Results and discussion

3.1. Kinetics and temperature profile

The weight loss was more significant when using a slow heating rate of 2 °C sec⁻¹, with 24.7% mass loss, while for 4 and 8 °C sec⁻¹, the decreases were 19.3 and 15.2%, respectively. Also, the kinetic parameters obtained by fitting and used in the model are shown in Table 4. The activation energies showed no significant changes when increasing the heating rate, while the pre-exponential factors increased with faster heating, which led to a higher reaction rate; the compounds evaporated more quickly, however, not all of them did it simultaneously, some were released more slowly. These compounds probably did not have enough time to leave the interior of the particles and vaporize on the surface.

Thanks to the previously described model coupled to the kinetics, it was possible to predict that although the \( \mu \)-reactor system was very small, there is a slight temperature gradient in the sample (particle) and the center is colder than the walls (see Fig. 3). This gradient increased at the highest heating rate (8 °C sec⁻¹) because of the low conductivity in the powder material and the temperature changed faster. These gradients cause significant differences in variables such as weight loss, pressure, gas velocity, and conversion.

The temperature profile validation is shown in Fig. 3; the relative errors average of 4.3 at \( \beta_1 \), 8.5 at \( \beta_2 \), and 13.2% at \( \beta_3 \) are in the center. For the walls, the model was more accurate with slow heating. There was a proper prediction for the temperature in the center of the particle; the relative error percentage for the heating rates of 1.8 (\( \beta_1 \)) and 2.2%
(β2), while a considerable error of 13.9% for β3. This error increases with the higher heating rate because the thermal inertia and the thermal lag effect are more evident since the thermocouple used was the same in all experiments as its measurement accuracy is lower when the temperature changes faster. These temperature differentials can influence cocoa degradation (or conversion), resulting in non-uniformity. The conversion would be less in the colder zones, which is more evident when using the higher heating rate.

The results were better to predict the weight loss shown in Fig. 4. The volume fraction of the water was evaporated in all cases because the boiling water temperature is around 100 °C at 100 kPa, so water loss occurred before the heating ended. Drying is evident in both experimental and model-predicted weight loss curves, and its behavior is similar for slow and fast heating. That is, the water evaporates faster and the temperature is high enough to vaporize it in less time. In Fig. 5 a to c, the model shows how the water fraction (εw) decreased until it disappears three times faster for 8 °C sec⁻¹ (i.e., 20 s) compared to 2 °C sec⁻¹ (i.e., 60 s). The water goes from liquid to vapor and leaves the particle without involving chemical reactions. The heating rate caused more evident differences in the weight loss at higher temperatures such as 24.7% at β1, 19.3% at β2, and only 15.3% at β3. The lower weight loss is related to more significant thermal differences, which can cause caramelization of sugars on the particle surface when heating very quickly, thus preventing the exit of gases to the outside of the particle; therefore, the weight loss was lower. The heating rate determined the time to reach the temperature, so by heating slowly (β1) there was enough time (~150 s) for the thermal degradation to be more significant compared with β3 (~38 s).

3.1.1. Variation of volumetric and mass fractions during heating
The solid fraction of cocoa coexists with the fractions of water (εw) and gas (εg); the latter refers to the gases generated by vaporization and chemical reactions (Fig. 5 a-c). It can be said that the gases vaporization profiles, in general, were similar for all experiments. However, there is more significant volatilization in the last seconds when the heating rate is low because the precursor reagents have more time to generate volatile compounds (Fig. 5 a). In other words, a longer time allows more volatiles to be formed during solid-state reactions. Also, the gas fractions were slightly more significant on the walls (i.e., hottest zone) compared to the center (i.e., coldest zone); however, differences at temperatures below 300 °C are less than 6% for β1 and β2, and 8% for β3 (Fig. 5a–c). The temperature differences between the wall and the center also imply differences in water and gas volumetric fractions. However, the ones of temperature were more significant, ranging from 10 to 29%, than those of fractions ranging from 0.5 to 8%. After 310 °C, the difference in fractions increased significantly; therefore, for analysis at high temperatures heating rates, it is recommended to consider mass diffusion, which was not considered in this work. Fig. 5 d shows that faster heating leads gases to be generated quickly and accumulated, thus increasing the pressure and density of the gas fraction.

The model predicts the effect of the heating rate on the degradation of the solid mass fraction (dry biomass) and the resulting over-roasted
material (Fig. 6). Slower heating produced more over-roasted particles, for instance, 0.335 ($\beta_1$), 0.327 ($\beta_2$) and 0.274 ($\beta_3$). The difference between ($\beta_1$) and ($\beta_2$) was 18% while for ($\beta_1$) and ($\beta_3$) it was only 2%. This difference is a consequence of the more significant temperature differential between the walls and center obtained by $\beta_3$, where the model was less efficient than the lower heating rates.

3.1.2. Volatile fraction analysis

The gas fraction comprises various volatile and aromatic compounds released during heating, being acids the dominant species (Fig. 7 a). However, essential compounds in roasted cocoa characteristic of aroma such as pyrazines, aldehydes, and ketones, previously identified as aroma definers (Castro-Alayo et al., 2019) were also volatilized during heating above 150 °C. CO$_2$ is liberated from 175 °C when the sample is dried and the thermal degradation starts. In the gas fraction, the number of species increases with the temperature and after 175 °C, the lowest heating rate produces a higher number of species as shown in Fig. 7 b. Fig. 7 b also shows the highest amount of volatiles from 150 to 250 °C and decreases at a higher temperature because the compounds are transferred to the gas fraction. Similarly, a more considerable number of compounds vaporize with slow heating to the same temperatures after drying (≥175 °C), e.g., at 350 °C, 44 compounds were volatilized at $\beta_1$, 38 at $\beta_2$, and only 28 at $\beta_3$. These differences in the number of compounds indicate that with a faster heating, the chemical reactions occur quickly that not all intermediate volatiles are generated than slow heating, resulting in fewer species identified.

Cocoa drying occurs up to 150 °C together with the vaporization of acetic acid, alcohols (2,3 and 1,3 butanediol), 2-butane, and 3-hydroxy that were identified in all the heating rates evaluated. However, at lower heating rates ($\beta_1$ and $\beta_2$), tetramethylpyrazine (TMP) was also identified at 150 °C; it means that the residence time was long enough for it to be generated and vaporize. Similarly, the number of pyrazines in the gas fraction and their peak areas increases with the temperature and slower heating rates (Fig. 7 c). Acetic acid was identified in the gas from 100 to 350 °C; then, considering the boiling temperature of acetic acid is 118 °C (NIST, 2011), acetic acid evaporated from raw cocoa during the first heating stage (approximately up to 200 °C), while the acid evaporates at higher temperatures is a product of sugar fragmentation — explained in a mechanism proposed by Nursten (2005) — which is part of the Maillard Reaction.

After 150 °C, the pyrazines appear in the gas phase and their amount increased along with the temperature, being slightly higher using lower heating rates as shown in Fig. 7a and c. The solid fraction behavior was opposite to the gas fraction, meaning that higher heating rates resulted in more significant peak areas related to a higher content. The above shows that a longer time with a slow heating rate causes the transfer of the pyrazines generated in the solid to the gas phase by vaporization. Also, a longer residence time leads to secondary chemical reactions such as the fragmentation of heterocyclic compounds. For instance, the fragmentation of pyrazines in alkanes allowed us to identify a more significant number of alkanes in the solid fraction with slow heating (see Fig. 7 d). The pyrazines identified were: (1) Pyrazine, tetramethyl-; (2) Pyrazine, methyl-; (3) Pyrazine, trimethyl-; (4) Pyrazine, 3-ethyl-2,5-dimethyl-; (5) Pyrazine, 2-ethyl-6-methyl-; (6) 2-isoamyl-6-methylpyrazine; (7) 2,5-Dimethyl-3-α-butylpyrazine; (8) Pyrazine, 2,5-dimethyl-3-(3-methybutyl)-; (9) 2,3,5-Trimethyl-6-ethylpyrazine; and (10) Pyrazine, 2-ethyl-3-methyl-. According to the above, to favor a higher content of aromatic compounds such as pyrazines in the solid after roasting, rapid heating should be used since its release to the gas fraction or its degradation would be avoided.

Aldehydes appeared in the gas fraction after 200 °C, pyrroles at ≥ 250 °C, furans and phenols ≥ 300 °C. Likewise, the number of ketones increased from 3 to 7 from 300 to 350 °C (Fig. 7 a). However, it was possible to differentiate that most of the volatiles identified in the gas
fraction initially appeared with the slowest heating rate at the same temperatures evaluated. In other words, the process had enough time for the chemical reactions to generate the volatiles, which move within the gas of the μ-vial headspace and the liner of the PTV injector. In this way, pyrazines and other compounds related to the aroma of cocoa volatilize or degrade with slow heating. Therefore, it is necessary to rethink roaster heating systems to reduce residence times.

On the other hand, the slower heating ($\beta_1$) vaporized the caffeine and theobromine alkaloids from 200 °C on. These are natural products of cocoa and show that the decrease in the concentration of caffeine and theobromine after roasting cocoa and coffee — reported by other authors (Urbaniska et al., 2019) — is due to volatilization produced by high temperatures and long residence times.

4. Conclusions

The heating rate affects volatilization in cocoa roasting, thus causing more weight loss and volatile compounds generated and transferred to the gas fraction. In other words, the residence time defines the formation and permanence or loss of aromatics from the particles.

The heating rate does not affect the drying and vaporization of the raw cacao low molecular weight compounds because they only involve transport and state change. Then, temperature dependence is released when the vaporization temperature is heated rapidly or slowly.

The 2D model couple to kinetics was an efficient mathematical tool that allows a deeper understanding of thermochemical conversion because it identifies thermodynamic phenomena that is experimentally invisible, e.g., temperature differentials, conversion within the particle, fractions distribution, pressures, density, and the gas exit rate.

Declaration of competing interest

COI

The authors declare no conflict of interest.
Fig. 7. a) Volatiles released during heating, b) variation of the number of compounds according to the heating rate and temperature in the gas and solid fraction, c) variation of pyrazines and d) generation of alkanes.

Data availability statement
Research data are shared.

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