Changes on chemical composition of cocoa beans due to combined convection and infrared radiation on a rotary dryer

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Abstract. Cocoa production around the world is characterized by a lack of technical facilities for post-harvest activities, and therefore a good quality of beans is hard to achieve. This situation can be changed by using technological solutions, particularly when they are adapted to specific needs of cocoa producers. Mechanical dryers used in intensive cocoa production exceed the smallholders’ requirements and because of the large amounts of energy they consume, there is a substantial economic and environmental impact. At this regard, improvement of alternative mechanical drying techniques requires a careful assessment of their impact on cocoa quality. Then this work looks forward to evaluating the chemical changes on cocoa beans due to the combined use of convection and radiation in a rotary dryer. It highlights not only the experimental set ups but also the analysis methods involved in the chemical characterization. High Performance Liquid Chromatography (HPLC) and Spectrophotometry are the chemical analysis tools used in this study. On one hand, total polyphenols content is determined by means of a spectrophotometric method based on the use of the Folin & Ciocalteu’s reagent and a mix of hexane-isopropanol at pH=9 as extraction solution. Similarly, in order to identify the impact of the combined drying strategy on the concentration not only of Polyphenols (Catechin and Epicathechin) but also of Methylxanthines (Caffeine and Theobromine) a chemical identification and quantification of these compounds are done using HPLC with UV detector and a C-18 column, using water, methanol and acetic acid as mobile phase.

1. Introduction
According to its industrial process, the supply chain of cocoa is divided in three phases: Upstream, Middlestream and Downstream [1]. The upstream is related primarily to the farmers work, and it begins after harvest, when cocoa beans are extracted from the pod, to undergo a postharvest process. Then, they are commercialized for industrial transformation purposes that depend on market needs. The postharvest process is composed by several stages. First occurs the fermentation step, where beans are stored in a ventilated place for five days to allow bacteria and yeast to grow on the grain. Well fermented cocoa is featured by a swollen, dark brown, easily breakable bean releasing a pleasant aroma and offering a bitter taste [2]. Afterwards, the drying process in performed to reduce water activity in the bean, and finally, there is a selection step to eliminate impurities such as soil particles and moldy or broken beans, among others. Drying step plays a major role to assure quality of the final product and sun drying is the most common method used by small producers. When the weather is in good conditions, solar drying may be efficient and cheap, but there is a lack of ability to control the process, and a possible degradation due to biochemical and microbiological reactions and to insect infestation. It is important to point out that if production has to be augmented, there would be a serious limitation due to an increase of labor cost and area requirements. Additionally, lack of control results...
in different moisture content among beans which is a major problem due to the fact that traders mix beans because they store the raw material for some time until its amount is economically transportable to bigger traders’ warehouses.

Cocoa quality depends on every one of the production processes, from the farming where is cultivated until the transportation to industrial facility where is transformed. It is well known the influence of different varieties, the country of origin and farming activities in the characteristics of the cocoa beans, and on the flavor profile of the cocoa derived products [3]. Likewise, many studies have showed that amino acid, sugar, polyphenols of fat contents are dependent of the origin of cacao beans [4–7]. Nevertheless, according to literature, postharvest processing has a strong influence in the final quality of the row material. Drying of cocoa beans is a process of heating which reduces its moisture content to less than 7.5%. Considering the results of the studies related with the variables of the drying process and their effects on cocoa beans and chocolate, there are three principal issues that had been addressed: Duration, Temperature and Method of drying. It is a common practice that the duration of the drying process ends up when the desired moisture content in reached. Unfortunately, the moisture content and the consequential overall quality of the dried cocoa beans might vary considerable between samples [8]. Drying is also a continuation of the oxidative stage of the fermentation process and therefore plays an important role in reducing astringency, bitterness and acidity. During this process, the characteristic brown color of the chocolate is developed due to the enzymatic oxidation of polyphenols [9,10]. The drying rate is of crucial importance for the cocoa beans’ finally quality. When drying rate is too fast, the beans would tend to retain an excessive amount of acids, including acetic acid, which is deleterious of the flavor. By contrast, a slower drying rate would result in low acidity, poorer color and high presence of moulds [9,11–16]. Recent studies identified 58 volatile compounds in cocoa beans at different times and drying temperatures in order to improve the conditions in the processing of cocoa beans. It was determined that six days of fermentation were enough to produce volatile compounds with flavor notes and that drying at 70°C and 80°C after six fermentation days presented a volatile profile similar to the one obtained by sun drying [15].

In reference to the method of drying, many studies that compare natural and artificial drying methods conclude that natural sun drying gives the best result [16,17]. Likewise, the moisture profile during drying and different temperatures and different conditions is available in the literature [11], [13,18,19]. Thus, knowing the conditions of drying it would be possible to predict in real time the ideal duration of drying to reach a standardized moisture content by the use of prediction models like those proposed by several authors [18,20,21]. Artificial drying methods are believed to be able to improve cocoa drying processes but more research have to be done in this area [22]. Most of studies in the literature deals with convective hot air drying. The use of combined convective and IR drying for cocoa beans has not been studied yet but considering some advantages of IR drying techniques, there is an important potential to improve the cocoa drying process. IR radiation could reduce the drying time and it can be applied directly on the surface of the product without heating surroundings.

From a strict chemical point of view, recent works detail different methodologies and equipment to analytically determine specific chemical compounds: Fatty acids, sugars, polyphenols, methylxanthines and aromatic compounds. Volatile compounds are extracted and quantified using combined technique like solid phase micro-extraction (SPME-HS), gas chromatography and mass spectrometry (GC-MS) [15,23]. High performance liquid chromatography (HPLC) and Ultra Performance Liquid Chromatography (UPLC) had been used in various studies to analyze most of the polyphenols present in cocoa and chocolate extracts [5,24–26]. No volatile acids, methylxanthines and carbohydrates had been determined using also HPLC, following well documented procedures [23,26–28]. High resolution gas chromatography -mass spectrometry (HRGC-MS) has been used for identification and quantification of volatile compounds [29]. Recently, methylxanthines, organic acids, amino acids, carbohydrates and polyphenols have been identified using Nuclear Magnetic Resonance (NMR) spectroscopy (1H NMR) [30,31].
Then this work is a preliminary experimental study looking forward to evaluating the chemical changes on cocoa beans due to the combined use of convection and radiation in a mechanical dryer when cocoa beans surface temperature is controlled. It highlights not only the experimental set up but also the analysis methods involved in the chemical characterization. On one hand, total polyphenols content (TPC) are determined using a spectrophotometric method based on the Folin & Ciocalteu’s reagent [32]. Likewise, to assess the impact of the combined drying strategy on the concentration not only of Polyphenols ((+)-catechin and (-)-epicatechin) but also of Methilxanthines (Caffeine and Theobromine) a chemical identification and quantification of these compounds are done using High Performance Liquid Chromatography (HPLC), chemical standards and liquid micro-extraction technique. HPLC has been employed in several cocoa studies to successfully identify specific compounds based on their retention time [24].

2. Materials and methods

2.1. Mechanical dryer

Drying experiments were carried out at Bucaramanga, Colombia, the capital of Santander Department, which is the major cocoa producer of this country. The experimental facilities are located at the Universidad Pontificia Bolivariana Bucaramanga, specifically at the Automation and Control for Agro-industrial Processes Laboratory. Two automated units were used in this study; the first one is a conditioning device allowing to control humidity and temperature of high amounts of air, developed to evaluate the performance of experimental dryers [33]. The second one is a rotary dryer equipped with an electric heater and a set of infrared lamps. It features temperature, humidity, speed and weight sensors, and automatic control of product’s surface temperature and drum’s rotation speed. Figure 1 shows the aforementioned equipment with some of their components.

![Figure 1. Air conditioning unit with rotary dryer](image)

2.2. Drying procedure

Fresh cocoa pots of the Forastero variety were supplied by farmers of a production zone nearby (Lebrijia, Santander). After harvesting, cocoa pots were transported to the drying facilities. Using a
sharp knife cocoa shells were opened in two halves and then the cocoa beans were manually extracted. Afterwards, fermentation of 10 kg of the later was then done in a cylindrical wooden drum for 5 days while temperature of the product load was monitored. Cocoa beans were periodically turned over by rotating the drum. After fermentation, cocoa beans were loaded into the rotary dryer where three different drying configurations were set for the study. For all experiments temperature of the hot air was set at 50 °C, while surface temperature of cocoa beans was controlled by turning on and off the infrared lamps. Set points were established at 50 °C, 55 °C and 60 °C respectively. Drying was stopped when there were not significant changes in drum weight. Average time for the former treatments were 7.1 hours, 8.5 hours and 9.25 hours respectively.

2.3. Chemicals and reagents
All solvents were analytical or HPLC grade supplied by Panreac and Merck. Standard compounds, i.e. caffeine, theobromine, (+)-catechin, (-)-epicatechin were supplied by Fitolab, while the Gallic acid by Merck. The Folin & Ciocalteu’s reagent was obtained from Merck. Deionized water was obtained with a Synergy UV ultrapure (Type 1) system.

2.4. Samples preparation
Dried beans were grinded using an electric milling machine just before a 200µm mesh size was attained. Some small pieces of solid carbon dioxide were mixed with the beans to avoid heat generation. Subsequently, 100 mg of this powder was degreased by adding 2 mL of hexane, centrifuged at 1565 g for 10 minutes, decanted and then, another 2 mL of hexane was added. This procedure was repeated three times. Afterwards, the fat reduced cocoa powder was extracted at room temperature with 1.5 mL aqueous 2-propanol (60%, pH 9.0) for 60 min in an ultrasonic bath. The mixture was centrifuged for 10 minutes at 391 g at 4°C and the supernatant was decanted and filtered through a nylon membrane (0.45 µm). The supernatant was poured into a flask to obtain 2mL of extract. This extract was stored at -20°C if not used immediately.

2.5. Determination of polyphenol content
Total polyphenols content (TCP) of extracts was determined spectrophotometrically using a method proposed by Londoño et al. [34]. First, it was prepared a mixture of 30 µm of the later extract, 30 µm of 20% Na₂CO₃, 225 µm of distilled water and15 µm of Folin & Ciocalteu’s reagent. Then, one hour later the absorbance of the blue was measured at 760 nm against a blank sample and a calibration curve with gallic acid as standard was produced. The TCP is then expressed as milligram equivalent of gallic acid (mg GAE) per gram of dried sample material. All measurements were run in triplicate.

2.6. HPLC Analysis of Catechins and Methylxanthines
Analysis of catechins and methylxanthines were performed with a Flexar HPLC System (Perkin Elmer Technology) featuring an UV detector, a vacuum degasser, an auto-sampler and a quaternary pump. Before HPLC analysis, samples were centrifuged for 15 minutes at 10581 g and 4°C. After this, it was filtered with a 0.45 µm nylon membrane.

To separate the compounds, the flow rate used varied between 0.75 and 1.0 mL/min and the analysis was carried out at 30 °C. A Zorbax Eclipse Plus C18 (25 cm × 4.6 mm, with a 5 µm particle size) column was used for the chromatographic separation. Water with 0.1% acetic acid as eluent A and methanol as eluent B were used as mobile phase. Due to variety of components, to obtain an ideal resolution of all peaks, it was followed an isocratic elution, using: 5% A and 95%B, for 10 minutes, with wavelength between 200 and 400 nm. Polyphenols ((+-)-catechin and (-)-epicatechin) and Methylxanthines (theobromine and caffeine) were identified by comparing the retention times and spectral data to those of standards. All analyses were run in triplicate. Quantitative interpretation of chromatograms involved a comparison with an equal volume standard; this method is useful to determine the concentration of a single component and require analyze duplicates to guarantee system reliability [35].
2.7. Statistical Analysis

TPC and concentrations of the Methylxanthines and Polyphenols compounds were statistically evaluated with MS Excel, and a completed randomized design was applied with three replications. Data are presented then as means ± standard deviation.

3. Results and discussion

3.1. Total polyphenols content (TPC).

Figure 2 shows TPC of cocoa samples expressed in mg GAE/g dry cocoa for each treatment. Here, surface temperature of grains was imposed by controlling the FIR power input, while air temperature was fixed at 50°C by the heating and humidification unit.

![Figure 2. TPC as a function of cocoa beans surface temperature. Data are presented as mean±SD (n=3)](Image)

These averaged values indicate that polyphenols content basically does not change when beans surface temperature is increased. However, these results are lower than those obtained for row samples of Amazon and Forastero cultivar from Equator, Colombia and Ivory Coast. (84 mg GAE g⁻¹, 81 mg GAE g⁻¹ and 81.50 respectively)[36]. There is only one study that obtained similar concentrations in samples of the Trinitarian cultivar -approximately 29 mgGAEg⁻¹-. In this case, cocoa beans were dried 20 hours with air at 50°C. Additionally, it was also found a concentration of about 13 mgGAEg⁻¹ when air temperature was 60°C [37].

In this same framework, a study on commercially available sun-dried samples of Colombian cocoa beans (from 11 different geographic areas), obtained TPC values ranging between 44.940 ± 1.174 mgGAEg⁻¹ and 70.090 ± 1.988 mgGAEg⁻¹[24]. Likewise, sun dried cocoa beans samples from Venezuela yielded a TPC of 66.6±0.4 mgGAEg⁻¹[38]. Besides, samples from Malaysia were also assessed under two different experimental approaches. On the one hand, cocoa beans were dried in a convection oven for 24 hours with air at 60°C, registering a TPC of 42.1±0.4 mg GAE g⁻¹[39]. On the other hand, cocoa beans were processed in a convection oven with relative humidity control, showing a TPC of 34.7±0.9 mgGAEg⁻¹ after 40 hours of drying at 80°C.[40].

3.2. Caffeine, theobromine, epicatechin and catechin content

Quantification of the methylxanthines and polyphenols compounds of interest were performed by HPLC. Accordingly, standard curves for caffeine, theobromine, (-)-epicatechin and (+)-catechin were obtained with standards in concentrations between 10ppm and 60ppm, following the method described in section 2.6. The equation standards derived to quantify the molecules in the samples are displayed in table 1.

| Table 1. Equation standards |
| Standards    | Equation       | R²   |
|--------------|----------------|------|
| (+)-catechin | Y = 1392.4X - 7850.5 | 0.9918 |
| (-)-epicatechin | Y = 1374.5X + 6968.9 | 0.9942 |
| Theobromine  | Y = 26446X + 87767  | 0.9949 |
| Caffeine     | Y = 4250.2X + 55001 | 0.9971 |

Y= Area under the curve; X= compound(ppm).

In this study, methanol and diluted acetic acid as solvent allowed the identification of the former compounds by their retention times, HPLC-UV spectra (280 nm), and chromatographic comparisons with primary standards. Figure 3 shows a chromatogram for one of the samples of this study. Results in general showed no qualitative differences in chromatographic profiles between cocoa extracts of all treatments. However, there are quantitative differences in their concentrations as is shown in Table 2.

![Figure 3. HPLC chromatographic profiles for cocoa bean extracts at 60 °C. Chromatographic peaks for theobromine (1), (+)-catechin (2), caffeine (3) and (-)-epicatechin (4); with retention times of 3.88 min, 9.12 min, 13.5 min and 25 min respectively.](image)

Chromatograms also revealed the evolution of new peak concentrations as surface temperature of cocoa beans was increased. That is, while concentrations of (+)-catechin and (-)-epicatechin peaks decreases (see figure 4), there is a rise of peaks to the right of the former analytes that could suggest the formation of new molecules. Nonetheless, caffeine picks are stable at all surface temperatures.

Regarding chemical species concentrations, results agree well with other previous studies. Theobromine amounts are much higher than the other compounds as it has been already founded in most of the previous cocoa studies. However, it is particularly higher, especially for cocoa beans at 50°C surface temperature[24]. Furthermore, with the increase of beans surface temperature, concentration of all compounds is lower. Still, total polyphenols content (mg GAE/g) keeps almost constant with bean surface temperature, which could be explained by the presence of other phenolic compounds like procyanidins [36,41] or new compounds resulting from thermally induced epimerization of (-)-epicatechin and (+)-catechin [42,43].
Figure 4. HPLC chromatograms evolution with cocoa beans surface temperature (Ts) increase. Doted areas show the evolution of two compounds next to (+)-catechin and (-)-epicatechin.

Table 2. Concentrations of Methylxanthines and polyphenols according to beans surface temperature.

| Chemical compound        | Surface temperature(°C) | 50         | 55         | 60         |
|--------------------------|-------------------------|------------|------------|------------|
| (+)-catechin content (mg/g) |                         | 6.78±0.82  | 4.65±0.77  | 2.62±0.67  |
| (-)-epicatechin content (mg/g) |                       | 3.84±0.008 | 3.84±0.013 | 2.02±0.023 |
| Theobromine content (mg/g)       |                         | 21.66±0.56 | 15.06±1.26 | 12.99±1.70 |
| Caffeine (mg/g)        |                         | 1.38±0.12  | 0.80±0.06  | 0.61±0.023 |

Data are presented as mean ± SD (n=3).
3.2.1. Theobromine and caffeine ratio
This ratio has been used to identify cocoa cultivars. According to former studies, ratios over 9
normally correspond to Forastero samples and ratios under 3 are correlated to Criollo ones.
Trinitario variety normally yields ratios between 3 and 9 [24]. The calculated values in this study
(Figure 5) are similar to those reported for diverse cacao samples from Peru [44].

![Figure 5. Ratio Theobromine/caffeine for the evaluated samples at 50°C, 55°C and 60°C.](image)

4. Conclusions
Bearing in mind that combined convective and infrared drying for cocoa beans has not been well
studied yet, this research work has revealed its potential to support cocoa postharvest processes. On
one hand, the analysis of cocoa samples dried under this combined strategy in the rotary unit, indicates
that chemical compounds like Methylxanthines and Polyphenols can be found in similar amounts
than those in fresh cocoa and sun-dried cocoa beans. This fact added the use of a mechanical dryer
can improve overall quality of cocoa beans, allowing control of the process and reducing drying times.
Results also indicate that TPC does not essentially change when the cocoa beans surface temperature
in the dryer was increased from 50°C to 60°C.

This experimental work also suggest that it is required a more comprehensive study to weigh the
effect of other variables like cocoa cultivars, drying air temperature, cocoa beans surface temperature
and drying time not only on the chemical composition of the samples but also on other quality criteria
related to organoleptic evaluation and colour assessment. It is also worth using HPLC or similar
analytical techniques to assess the presence of other active polyphenol compounds in the dried
samples and evaluate the impact of infrared radiation on their respective concentrations.

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