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Degradation of polyphenols during the cocoa drying process

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ABSTRACT

The effect of cocoa drying process on polyphenols was studied. The least degradation of polyphenols during the process of drying was accomplished at a temperature of 40 °C, with a concentration of polyphenols was of 3329.76 mg Ac. Gallic/100 g dried fruit, which corresponds to a reduction of 45%; while the higher degradation of polyphenols was presented at a temperature of 60 °C. It was concluded that the degradation depends of temperature, moisture and dry times. These are factors which affect the irreversible oxidative processes of polyphenols and can also be affected by cellular destruction. This experimental analysis was completed with the development of a phenomenological model, which simulates the behavior of water desorption and the degradation of polyphenols.

1. Introduction

The cocoa, from the therapeutic viewpoint, is important due to the high contents of polyphenols as antioxidants. These are characterized by the presence of one or more benzoic rings, and are related to food with flavor, color and nutritional value. The organoleptic features of cocoa are mainly developed during the fermentation, drying and roasting processes (Sakharov and Ardila, 1999). During fermentation, biochemical reactions are produced, causing a reduction of the bitterness and astringency, originating the precursor compounds of the aroma and flavor of chocolate. During this stage, the microbial decomposition is generated; originating acetic and lactic acid which are spread to the cotyledon; thus, acidity increases and hydrolysis reactions are generated, avoiding the growth of the cocoa embryo (Sakharov and Ardila, 1999).

During drying process, the oxidation reactions that started in fermenting continue. Also, reactions that make polyphenols to degrade take place; as well as acetic acid evaporates, pigments are formed due to the Quinone condensation and aldehyde synthesis is present (Jinap et al., 1994). For this reason, to favor the reactions that are responsible for flavor and aroma, the drying process must be slowly carried out at a controlled temperature. When there are temperatures below 60 °C, good quality in the cocoa is obtained (Faborode et al., 1995). Kyi et al. (2005) demonstrated that the phenol degradation increases with temperature (Kyi et al., 2005). This is why it is important to develop models which are able to predict the evolution of temperature during the drying process, aiming at designing systems under optimal conditions.

Currently, the development of phenomenological models that describe the behavior of some chemical species such as acetic acid and the polyphenols are not sufficient. Hii et al., 2009a, 2009b demonstrate that the studies regarding the cocoa drying process modelling are few, they mostly view water as the only species (Akmel et al., 2009; Hii et al., 2009a, 2009b; Nganhou, 2004; Nganhou et al., 2003), for this purpose it refers some works (Daud et al., 1996, 2007; Nganhou, 2004; Nganhou et al., 2003) and claims that most of the literature on cocoa drying is experimental and is focused on the flavor, quality and acidity of the grain (Hii et al., 2009a).

Curcio et al. (2008) developed a model for the transfer of mass, momentum and heat during the drying of cocoa. The contribution is related to the analysis of turbulence and the arrangement of the grains (Curcio et al., 2008). Erdogdu (2008) conducted a literature review on thermal diffusivity in the grain and applied mathematical methods that allowed to analytically determine the heat transfer coefficient. The assessment of the thermal diffusivity and the coefficient of heat transfer is not easy, so it is suggested that the experimental temperature changes are known thoroughly (Erdogdu, 2008).

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Akmel et al. (2009) studied the solar drying of cocoa and analyzed several experimental models; it was found that the logarithmic model described the results satisfactorily. The diffusion coefficient varied from 3.70×10^{-11} to 5.80×10^{-11} m^2 s^{-1} and the activation energy was 22.48 kJ mol^{-1} (Akmel et al., 2009). MacManus Chinenye et al., 2010 studied the kinetics of the drying of cocoa manipulating three temperatures, Lewis model and Fick's second law were used to predict the diffusivity, obtaining values of 6.6137×10^{-10} to 2.1855×10^{-9} m^2 s^{-1} and the activation energy of 39.94 kJ mol^{-1} (MacManus Chinenye et al., 2010).

Hii et al., 2009a, 2009b proposed a semi-theoretical model of convective drying of cocoa. It was found that effective diffusivity was between 7.46×10^{-11} and 1.87×10^{-10} m^2 s^{-1}, the Arrhenius constant was 8.43×10^{-4} m^2 s^{-1} and the activation energy 44.92 kJ mol^{-1}. When dried at 60 °C, the acidity of the grain is lower, and it has a good flavor.

Nganhou et al. (2003) studied the transfer of water and acetic acid in the dried cocoa. With the results they demonstrated that as drying accelerates, the mass transfer coefficient of the acid increases, due to its volatility (Nganhou et al., 2003). García-Alamilla et al. (2007) proposed a model for the drying of cocoa, analyzing the moisture and acidity variation. The model takes into account the profiles of mass and energy transfer of the two species in a fixed bed, the mean percentage error obtained was less than 18% (García-Alamilla et al., 2007).

Daud et al. (2007) modeled the drying of cocoa considering polyphenols and water, the mathematical model of Daud and Fick's law (Daud et al., 2007) were taken as the basis. Only the solid phase was considered, neither air nor convective effects were taken into account. The contribution was related to the kinetics of polyphenols. They estimated the effective diffusivity of water between 8.19×10^{-9}–8.54×10^{-9} m^2 s^{-1} and 8.33×10^{-12}–1×10^{-11} m^2 s^{-1} for polyphenols. Hii et al. (2009b) studied the kinetics of the drying of cocoa, based on a diffusive model in which only water is taken into account. The assessment of the polyphenols was experimentally carried out. They compared the quality of sun-dried and air-dried grains. Color, texture and polyphenols content were also evaluated (Hii et al., 2009b). They found that the texture, color and phenol content in the sun-dried and oven-dried grains had significant differences.

This paper presents a theoretical model and experimental results of the influence of drying on cocoa. The model is capable of predicting the evolution of the temperature and concentration of the two species (water and polyphenols) during processing. The model considers the convective, diffusive and kinetic effects. Finally, it was analyzed how temperature, moisture and drying times affect the concentration of polyphenols.

2. Materials and methods

2.1. Raw materials

In this work a Trinitarian variety of Cocoa beans were used (Coleccion Castro Naranjal - CCN51), they were grown in Antioquia (Colombia) and subsequently fermented. Grains dimensions were 1 cm thickness and 0.7 cm wide. The initial moisture content of the grains was between 0.428 and 1.289 (Kg water Kg^{-1} dry material).

2.2. Method of total polyphenols

The total polyphenols content was determined according to the adapted Folin-Ciocalteu method (Singleton and Rossi, 1965). This method has the advantage of measuring the reductive substance, not just the level of polyphenols. The extracts (50 mL) were mixed with 125 mL of Folin-Ciocalteu reagent and 400 mL of sodium carbonate solution (7.1%) to complete 1 L. The mixture was stirred and stored at room temperature for 30 min in the darkness. The absorbance was measured at 760 nm against a blank. A standard calibration curve of Gallic acid was used.

2.3. Mathematical model

The model takes into account the mass and energy transfer in the system. Considering the diagram as a thin layer. Scheme of the system is shown in Fig 1, where Y is the absolute gas moisture, T is the gas temperature, V is the gas velocity and z is the specific length of fixed bed.

In the system, two phases are considered (solid and gas). In the model, cocoa beans are considered as spheres; the mass balance for the gas phase in a control volume (Eq. (1)), takes into account the effects of convection, diffusion of water and degradation of polyphenols. In the solid phase mass balance only was taken into account the changes in concentration of water and polyphenols (Eq. (2) and Eq. (3)). The energy balance for the gas phase takes into account the effects of convection and phase change (Eq. (4)). The energy balance for the solid phase takes into account the effects of convection, conduction and phase change (Eq. (5)).

$$\varepsilon\rho_{gas}\frac{\partial Y}{\partial t} = -\rho_{gas}\vec{v}_{gas}\frac{\partial Y}{\partial z} + \frac{\partial}{\partial z}\left(\rho_{gas}D_{effec}\frac{\partial Y}{\partial z}\right) + \dot{m}'''_{water}\rho_{sol} \quad (1)$$

$$(1-\varepsilon)\rho_{sol}\frac{\partial X_{water}}{\partial t} = -\dot{m}'''_{water} \quad (2)$$

$$(1-\varepsilon)\rho_{sol}\frac{\partial X_{pol}}{\partial t} = -\dot{m}'''_{pol} \quad (3)$$

$$\varepsilon(\rho C_P)_{gas}\frac{\partial T_{gas}}{\partial t} = -\left(\rho\vec{v}C_P\right)_{gas}\frac{\partial T_{gas}}{\partial z} - Ua(T_{gas}-T_{sol}) - \dot{m}'''_{water}\left[C_{Pv}(T_{gas}-T_{sol})+\lambda\right] \quad (4)$$

$$(1-\varepsilon)(\rho C_p)_{sol}\frac{\partial T_{sol}}{\partial t} = \frac{\partial}{\partial z}\left(K_{effec}\frac{\partial T_{sol}}{\partial z}\right) + Ua(T_{gas}-T_{sol}) - \dot{m}''_{water}\lambda \quad (5)$$

The average porosity (ε) corresponds to the bed porosity, i.e. the void fraction between grains and intra-grains. It is determined from the vkolume fraction (ρ_{sol}) occupied by the solid product; in addition, the grain porosity is included in the bed porosity. The surface product's density (σ) is linked to the average porosity (ε) by the relation (Mabrouk et al., 2006):

$$\frac{\sigma}{e} = (1-\varepsilon)\rho_{sol} \quad (6)$$

$$a = \frac{6(1-\varepsilon)}{\phi_{sol}} \quad (7)$$

Where e is the fixed bed height and ϕ_{sol} represents the granular

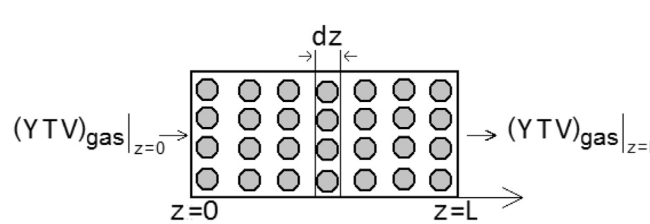

Fig. 1. Cocoa bean bed.