# ANALYSIS OF THERMODYNAMIC PROPERTIES OF COFFEE BERRIES DURING DRYING

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**ABSTRACT** Drying process is an important post harvest procedure, which grants the possibility to prevent or minimize the quantity and quality losses of agricultural products. This process decreases the water activity of the product, which is the main factor that affects the respiration rate of the product, fermentation processes and plague attack. Drying procedure is affected by several parameters, in which thermodynamic parameters have been recently investigated. The correct knowledge of the thermodynamic properties of the drying process of agricultural products is an important attribute in order to design drying equipments, calculate the energy required to do so, to study the properties of adsorbed water, evaluate the microstructure of foodstuff and to study the physical phenomenon that occurs on the food surface. Thus, the aim of the present work was to evaluate and obtain thermodynamic parameters of the drying process of coffee grain (*Coffea arabica* L.), cv. Catuaí Amarelo. The dynamic method was employed to obtain the equilibrium moisture content. Entropy, enthalpy and Gibbs free energy were investigated in the present research. Three conditions of temperature and relative humidity were used (35 ºC and 32.1 %; 45 ºC and 15.7 % and; 55 ºC and 10.2 %). Coffee berries were manually harvested with initial moisture content of 1.25 dry basis (d.b.), being submitted to the drying process until an average moisture content of 0.13 (d.b.). Enthalpy and entropy increased with the decrease of the drying air temperature. Gibbs free energy had an increment behavior with the increase of temperature.

**Keywords:** Enthalpy, entropy, Gibbs free energy, *Coffea arabica* L., drying.

**INTRODUCTION** Coffee is one of the most important agricultural products in the world, with a total production of 4.76 million tons, and according to ICO (2008), Brazil is the leader in exporting of this product, representing approximately 28.45 % of world exports. The species *Coffea arabica* L. represents 76.92 % of coffee production in Brazil, being that Minas Gerais state has the highest contribution, 66.20 % (CONAB, 2008).

Moisture content of agricultural products is of extreme importance to acknowledge water properties and its relations with the products components, relating directly with drying processes and storage (Ghodake et al., 2007). At elevated moisture contents, the risk of fungi and insects growth becomes higher, seriously compromising the seeds germination and vigor, deteriorating the fruits and grains quality and increasing the post-harvest losses. On the other hand, the moisture content reduction promotes economic losses due to the products weight loss (Yasdani et al., 2006). Also, this reduction decreases the products biological activity and the physical and chemical alterations that occur during storage.

The knowledge of thermodynamic properties at drying processes of agricultural products is an important source of information in order to develop drying equipments, calculate the energy required in the drying process, study the adsorbed water properties, evaluate the foodstuff microstructure and to study the physical phenomenon that occur on the food surface.

Enthalpy alterations provide a measure of the energy variation that occurs on the mixture between the water molecules and the material during the sorption processes. Entropy can be associated with the attraction or repulse of the system forces, and is associated with the arrangement of the relationship among water-product molecules. Therefore, entropy characterizes the order or disorder degree that exists in the water-product system (McMinn et al., 2005).

Gibbs free energy in an indicative value of the affinity among the product and water, providing an evaluation criteria of water sorption. Negative Gibbs free energy values means that the process is spontaneous, whilst positive values indicates that the process is non-spontaneous (Telis et al., 2000). Alterations of Gibbs free energy during the exchange of moisture between the product and the environment is the energy required to transfer water molecules in vapor state to a solid surface or vice-versa. This is the quantity that can be considered to be a measure of the work made by the system to accomplish the adsorption or desorption process. The equilibrium is reached when the Gibbs free energy gradient is zero (Nayak & Pandey, 2000).

Considering the importance of the theoretical study of the drying process of agricultural products, this work was developed with the goal to obtain the thermodynamic properties during the dehydration of coffee berries (*Coffea arabica* L.).

## MATERIALS AND METHODS

The present work was conducted in the Laboratory of Physical Properties and Quality Evaluation of Agricultural Products at the National Grain Storage Training Center – CENTREINAR, Federal University of Viçosa, Viçosa, MG, Brazil.

Coffee berries (cv. Catuaí Amarelo) from Viçosa-MG were manually harvested with initial moisture content of 1.25 dry basis (d.b.). Moisture content was determined by the oven method (105 ± 1 ºC) until constant weight.

Drying was accomplished in three conditions: 35 ºC and 32.1%; 45 ºC and 15.7% and; 55 ºC and 10.2% of temperature and relative humidities, respectively. These environmental conditions for the performance of the tests consisted of a temperature-controlled chamber, manufactured by Aminco (model Aminco-Aire 150/300 CFM). Removable perforated trays were placed inside the apparatus to allow air to pass through the samples, each containing 50 g of product. Airflow was monitored with an anemometer with rotating blades and it was about 4 $m^3$ $min^{-1}$ $m^{-2}$. Temperature and air RH were monitored using a psychrometer installed next to the trays containing the samples. The trays containing the product were periodically removed and weighted during the drying process. Equilibrium was attained when weight variation was less than 0.01 g during three consecutive measurements.

The Arrhenius equation (Equation 1) was used to calculate the activation energy of the drying kinetics of coffee berries. This equation demonstrates the relationship among the activation energy and the velocity that the reaction occurs.

$$k = A_0 \exp\left( -\frac{E_a}{RT} \right) \qquad (1)$$

In which

$k$: drying constant, $h^{-1}$;

$A_0$: pre-exponential factor, $h^{-1}$;

$E_a$: activation energy, J $mol^{-1}$;

$R$: universal constant of gases, 8.314 J $mol^{-1}$ $K^{-1}$;

$T$: temperature, K.

The thermodynamic properties of the drying process of coffee berries were obtained by the method described by Jideani and Mpotokwana (2009).

$$\Delta H = E_a - RT \qquad (2)$$

$$\Delta S = R\left( \ln A_0 - \ln \frac{k_B}{h_P} - \ln T \right) \qquad (3)$$

$$\Delta G = \Delta H - T\Delta S \qquad (4)$$

In which

$\Delta H$: enthalpy, J $mol^{-1}$;

$\Delta S$: entropy, J $mol^{-1}$;

$\Delta G$: Gibbs free energy, J $mol^{-1}$;

$k_B$: Boltzmann constant, 1.38 x $10^{-23}$ J $K^{-1}$;

$h_P$: Planck constant, 6.626 x $10^{-34}$ J $s^{-1}$.

## RESULTS AND DISCUSSION

Activation energy of the drying process obtained was 38,389.90 J $mol^{-1}$. Corrêa et al. (2006) presented an activation energy for coffee fruits (cv. Mundo Novo) of 22,619 J $mol^{-1}$, to the temperatures of (40, 50 and 60) ºC. The disparity can be explained by the difference in coffee components of cultivars. In drying processes, the highest activation energy, the higher will be the water diffusivity of the product. In other words, less energy is required so the chemical reaction occurs. In this case, the transformation of liquid free water in water vapor (drying).

Enthalpy increased with temperature decrease. Lower values of enthalpy indicate less energy needed to remove the water linked to the product. The present work presented, as expected, lower values of enthalpy at higher drying temperatures, indicating that a less quantity of energy is required so the drying process is able to proceed. Enthalpy values related to the drying process of coffee berries were 35,827.85; 35,744.71 and 35,661.57 J $mol^{-1}$ for temperatures of (35, 45 and 55) ºC, respectively.

Nkolo Meze'e et al. (2008) reported that Gibbs free energy is attributed to the work necessary to make the sorption sites available. Gibbs free energy increased with the temperature increase, being that its values were positive, indicating that the drying under this work conditions was non-spontaneous. The positive Gibbs free energy is characteristic of an endergonic reaction, which requires an input of energy from the surrounding environment (non-spontaneous). These positive values are expected, since desorption is a non-spontaneous process. It is non-spontaneous because the samples were pre-conditioned at a high level of RH, and then submitted to a low level of RH, and afterwards achieved equilibrium (Nkolo Meze'e et al., 2008). This trend was also found by Goneli et al. (2010) working with okra seeds. The values encountered were 79,646.81; 81,070.10 and 82,496.01 J $mol^{-1}$ for the temperatures of (35, 45 and 55) ºC, respectively.

Entropy is a thermodynamic parameter associated to the disorder degree, in which its values increase during a natural process in an isolated system. The values obtained in the present work were -142.20; -142.46 and -142.72 J $mol^{-1}$ $K^{-1}$ for temperatures of (35, 45 and 55) ºC, respectively. Analyzing the entropy behavior, it was concluded that this thermodynamic property presented a similar behavior of enthalpy, in which the obtained values increased (absolute values) with the temperature decrease. This fact is expected, since that the temperature decrease leads to lower excitation levels of water molecules, resulting in an increase of the degree order of the water-product system. The negative values are attributed to the existence of chemical and/or structural modifications of the adsorbent (Moreira et al., 2008).

**CONCLUSION** The relationship between the drying constant with drying temperatures was well described by the Arrhenius equation. The activation energy for the liquid diffusion during drying was 38,389.90 J $mol^{-1}$.

Enthalpy decreased with temperature increase, however altering only 0.46 % from its initial values at 35 ºC. Gibbs free energy decreased with temperature decrease, being its magnitude being positive in the temperature range utilized, indicating that drying in the used conditions is non-spontaneous. Its values increased 3.45 % with temperature increase. Entropy was negative in the temperature range studied, indicating that occurred an alteration of the fruits components during drying.

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