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PHYSICALCHEMICAL CHARACTERIZATION AND THERMOPHYSICAL PROPERTIES OF COCOA HONEY

CARACTERIZAÇÃO FÍSICO-QUÍMICA, PROPRIEDADES TERMOFÍSICAS DE MEL DE CACAU

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Abstract

The objective of this study was to determine the physicochemical characteristics and thermophysical properties of cocoa hoeny. The cocoa honey had the following physicalchemical characteristics: pH (2.76), titratable acidity (0.73 %), moisture (87,22 %), soluble solids (14,03 °Brix), reducing sugar (10,2 % in glucose), non-reducing sugar (4,06 % in saccharose) and ash (0,23 %). With respect to the thermophysical properties were determined the specific heat, density, thermal diffusivity and the dynamic viscosity as a function of temperature. The empirical models for each property were obtained. It was found that the temperature directly affects the cocoa liquor properties. The data are important for the development, adaptation and optimization of equipment for more efficient processing of cocoa honey, since the information on this subject is unknown.

Key-words: specific heat, thermal diffusivity, viscosity.

Resumo

O objetivo deste estudo foi determinar as características físico-químicas e propriedades termofísicas de mel de cacau. O mel de cacau possui as seguintes características físico-químicas:

pH (2,76), acidez titulável (0,73 %), umidade (87,22 %), sólidos solúveis (14,03 °Brix), açúcar redutor (10,2 % em glicose), açúcar não redutor (4,06 % em sacarose) e cinzas (0,23 %). Com respeito às propriedades termofísicas foram determinados o calor específico, densidade, difusividade térmica e a viscosidade dinâmica como uma função da temperatura. Foram obtidos os modelos empíricos para cada propriedade. Verificou-se que a temperatura afeta diretamente as propriedades do mel de cacau. Os dados obtidos são importantes para o desenvolvimento, adaptação e otimização de equipamentos para processamento mais eficiente de mel de cacau, já que a literatura sobre este assunto é rara.

Palavras-chave: calor específico, difusividade térmica, viscosidade.

1. Introduction

The cocoa tree (*Theobroma cacao*) is a plant belonging to the *Malvaceae* family, Theobroma genus commonly cultivated in the tropics, in countries such as Equador, Ivory Coast, Ghana and Brazil (Santos et al., 2014).

The cultivation of cocoa is associated with the production and economic exploitation of its almonds to used primarily for making chocolate. However, before fermentation, a mucilaginous liquid known as "cocoa honey" is released from the pulp that envelops the cocoa grains. The cocoa honey is basically composed by water (74.94 %), fermentable sugars (10-19 %), acidity no volatile (0.77-1.52 % in citric acid) and pectin (0.9-2.5 %) (SANTOS, 2012). Moreover, the cocoa honey has significant amount of dietary fiber, and it can be considered a natural source of bioactive phenolic compounds with considerable antioxidant activity (SILVA et al., 2014).

The cocoa honey is a typical product the South of Bahia poorly explored industrially, that can used in the preparation of energetic drinks, ice cream and popsicle, sweets, juices, nectars and jellies (MELO NETO et al., 2013). Ferreira e Dias (1982), cited by Santos et al. (2014), analyzed the production of "cocoa honey" as an economic activity and concluded that only 0.4% of the production of this by-product was being used. The authors attributed such reduced percentage of economic use to the lack of knowledge related to conservation, virtually non-existent technological improvement, as well as to the lack of intellectual property registration.

However, for better utilization of byproduct the knowledge about physicalchemical characteristics and thermophysical properties such as thermal diffusivity, specific heat, thermal conductivity, specific mass and viscosity are important information for the optimization of heating and cooling processes, as well as data needed for the correct equipment dimensioning (ARAÚJO et al., 2004).

According to Silva et al. (2014), studies on the physicochemical and other characteristics of "cocoa honey" are scarce in the literature, thereby hindering its exploitation and marketing. Therefore, the objective of the present study is to define the physicochemical and thermophysical properties of the cocoa honey produced in the State of Bahia.

2. Material and methods

The experiment was conducted at the laboratory of the Process Engineering Southeast Bahia State University (UESB), Itapetinga, Bahia, Brazil. The cocoa honey was obtained from healthy and ripe cocoa fruits, picked at random in the Food Technology Center (CTA) of Baiano Federal Institute, Uruçuca, Bahia, Brazil. Was packaged in sterilized pet bottles and kept at -18 ºC until the beginning of the tests.

2.1 Physical and chemical characterization

The jellies were analyzed regarding pH in pHmeter Quimis, model Q400MT, Brazil, lipid content in soxhlet extractor, soluble solids content expressed as ºBrix in digital refractometer Tecnal, model R2l300, Brazil, titratable acidity (expressed as g of citric acid in 100 g^{-1} sample, direct titration of the material with 0.01N NaOH, reducing and non-reducing sugars by titration and ashes in a muffle furnace, Quimis, Q318M, Brasil at 550 °C. All determinations were made in triplicate and three repetitions according to the methodologies established by Instituto Adolfo Lutz (IAL, 2008).

2.2 Thermophysical properties

2.2.1 Specific Heat

The determination of the specific heat was done through an adaptation of the method of Souza et al. (2010) using a mixing calorimeter that consists of a thermos bottle with a volumetric capacity of 1.0 L. covered by an isolation of expanded polystyrene which turns it into a closed system by not allowing energy exchange in form of heat with the environment. This technique consists in adding water (or another reference liquid) and the sample at different temperatures within the calorimeter, and wait till the thermal balance is achieved. Before starting the tests, the equipment was calibrated using distilled water as a reference with the intention to obtain the heat capacity of the calorimeter since the same receives/emits energy in the form of heat with the system. The samples with masses ranging between 40 and 50 grams were packed and sealed in polyethylene bags, whose initial temperatures were also previously recorded using a copper-constantan thermocouple. The system was periodically stirred until reaching thermal balance. Then the equillibrium temperature was registered and the specific heat calculated by Equation 1.

$$m_p \cdot c_p \left(T_p - T_{eq}\right) = \left(c_w \cdot m_w + C_{cal}\right)\left(T_{eq} - T_w\right) \quad (1)$$

Where,

m_p = product mass (kg);

c_p = specific product heat (kJ. kg^{-1}. K^{-1});

c_w = specific water heat (kJ. kg^{-1}.K^{-1});

m_w = water mass in the calorimeter (kg);

T_p = initial product temperature (°C);

T_{eq} = equilibrium temperature (°C); and

T_w = initial water temperature (°C).

2.2.2 Specific Mass

Specific masses were determined using a DMA 5000M Bench Digital Densimeter (ANTON PAAR) with a precision of +5 x 10^{-6} g.cm^{-3} and repeatability of +1 x 10^{-6} g.cm^{-3} in the operation range 0 to 3 g.cm^{-3}. The equipment's temperature range is 303.15 K to 353.15 K with a precision of +0.01 K and repeatability of +0.001K (SOUZA et al., 2010).

2.2.3 Thermal Diffusivity

A method adapted from Dickerson (1965) was used to determine thermal diffusivity. This method involved the use of a stainless steel metallic capsule (3.8 cm diameter; 25.5 cm height; 1.0 mm width) equipped with two copper-constantan thermocouples (Penta, São Paulo, Brazil ±0.1 °C of accuracy), one at the external surface of the capsule, and the other at the central plane of the capsule. The metallic capsule was then filled with sample, and immersed in a thermostatic bath at 2 °C (MA185 model, Marconi, São Paulo, Brazil, ±0.1 °C of accuracy) until thermal equilibrium between the bath and the cell was reached. The bath was then heated at a constant rate (1.1 °C /min) until the internal temperature of the capsule reached at least 85 °C. The temperatures marked by the two thermocouples were registered at one minute intervals until the end of the experiment. The thermal diffusivity of the encapsulated sample was calculated using Equation 2:

$$\alpha = \frac{A.R^2}{4.(T_{EXT} - T_{INT})} \qquad (2)$$

Where,

α = thermal diffusivity (m^2.s^{-1});

A = heating rate (ºC.s^{-1});

R = cylinder radius (m);

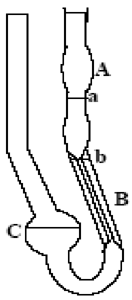
T_{EXT} (ºC) = external temperature; and

T_{INT} = internal temperature (ºC).

2.2.4 Dynamic Viscosity

The viscosity was established by the method with a capillar viscosimeter using an Ostwald viscosimeter previously calibrated with distilled water and kinematik bath for viscosimeter of the Marconi brand. In this technique the viscosity is obtained through the measuring of the pressure gradient of a laminar flow in a tube, where it is established by measuring the fluids flow in a defined capillar height. To establish the viscosity 15 mL of the cocoa honey was inserted into the viscosimeter and with the help of a pippetor the honey column was elevated until surpassing point “a”. Then the time of the fluids outflow from point “a” to point “b” was measured as shown in Figure 1.

Figure 1 – Ostwald Viscosimeter.



The results were achieved using the following Equation 3:

$$v = k \cdot t \qquad (3)$$

Where,

v = kinematic viscosity ($N.s.m^{-2}$);

k = Constant of the viscometer ($N.m^{-2}$); and

t = fluid outflow time (s).

2.2.5 Statistic Analysis

The experiment was done in a totally randomized design with three repetitions in triplicate, except for specific heat which was done in quintuplicate. To the experimantal data of the thermophysical properties were adjusted linear models observing the coefficient of determination and concordance with the studied phenomenon.The models were evaluated and the respective graphics built using the software SigmaPlot® 11.0.

3. Results and discussion

3.1 Physicalchemical characterization

The results of the physicalchemical characterization of cocoa honey are shown in Table 1. The cocoa honey is a product that due to its low pH (2.76) can be classified as being of high acidity (pH < 4.5). This value was lower than the one found by Santos et al. (2014) (3.30). The amount of acidity (0.073%) was similar to that found by the same author (0.07%). This high acidity value favors its industrialization process in form of sweets and jellies, a fact that also represents an advantage when using thermal processes for its conservation, because the pasteurization, which is a more gentle process would already be sufficient to guarantee the microbiological quality of the product (MELO NETO et al., 2013).

It has been found that the moisture content (87.22 %) of the cocoa honey is similar to that found by Santos et al. (2014) (83.21 %), but, with regard to the total soluble solids content, the ºBrix was most (14.03). The content of total soluble solids may fluctuate with the processing applied in the cocoa honey extraction, climate factors, variety of the fruit, soil types and diverse other agronomic factors.

Concentrations of reducing sugars were lower than those found by Penha e Matta (1998), who evaluated fresh cocoa pulp. The authors found levels of reducing sugars of 10.20 % (in glucose) and 4.6 % (in saccharose) for non-reducing sugars. According to Silva et al. (2014) this are attributed to the amount of non-soluble dietary fibers (0.06 %) being of cocoa honey. In the Brazilian legislation there are no reference standards for the determination of reducing and non reducing sugars in cocoa honey, therefore the found values can be useful for future works. With reaction to ashes content, it has been found the total value a 0,23 % similar to that found by Santos et al. (2014) (0,26 %).

Table 1 – The physicalchemical characteristics of cocoa honey .

Determinations	Cocoa honey
pH	2.76 ±0,02
Titratable acidity (% of citric acid)	0.73±0,0001
Moisture (%)	87.22±0,01
Total soluble solids (ºBrix)	14.03±0,06
Reducing sugars (% glucose)	10.2±0,0045
Non reducing sugars (% saccharose)	4.06±0,005
Ashes (%)	0.23±0,00025

Fonte: Autoria própria.

3.2 Thermophysical properties

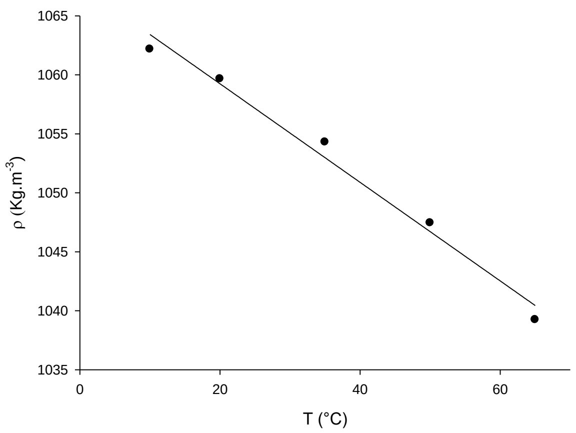
3.2.1 Specific heat

The average value found for the specific heat of frozen cocoa honey was of 4.061 kJ/kg.K ±0.035. This high value can be explained due to the high moisture content, because the studies show that there´s a strong relation between specific heat and water content of a product, because water presents a higher specific heat in relation to all other components of the food. Actually, due to the unique characteristics of the hydrogen bonds, water presents a quite high specific heat in relation to other substances, consequently, the specific heat of a food product is substantially affected by the water present and its physical state (LEWIS, 1993; SILVA et al., 2010).

3.2.2 Specific Mass

Starting from the values found for the density of cocoa honey a linear decreasing behavior was observed (Figure 2). This happens because by supplying energy for heating the cocoa honey, composing molecules migrate to higher energy levels.

Figure 2 – Specific mass of cocoa honey in function of temperature.



Fonte: Autoria própria.

The energy is transferred from molecule to molecule through collisions and, consequently, occurs the temperature increase. The higher energy content causes the molecular distancing and increase in the volume that the sample occupies, therefore the specific mass decreases (SOUZA et al., 2010).

The linear model adjusted itself to the registered experimental results (R^2=0.984), this way it´s possible to estimate the density values between 15 °C and 65 °C (Equation 4).

$$\rho = 1067{,}5983 - 0{,}4178T \quad (4)$$

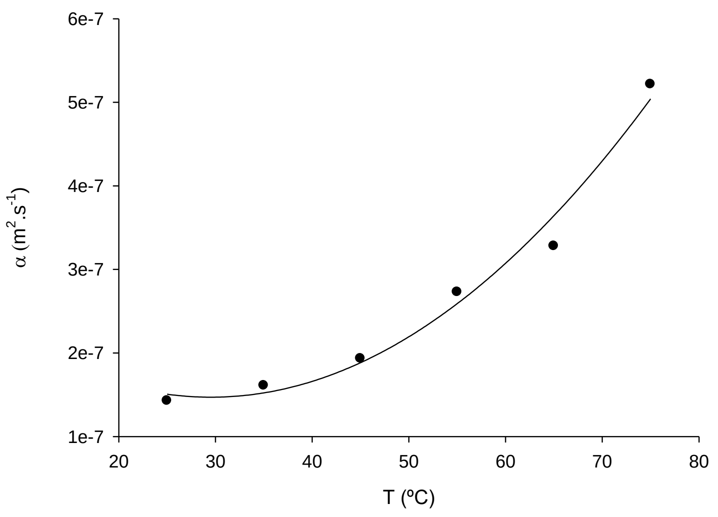
Where,
ρ = specific mass ($kg.m^{-3}$); and
T= temperature (ºC).

According to this equation the positive variation in one ºC of the cocoa honey´s temperature causes a decrease of 0.4178 $kg.m^{-3}$ in its specific mass.

3.2.3 Thermal diffusivity

According to the results found for the cocoa honey´s diffusivity (Figure 3) it can be seen that up to 35 ºC the percentual difference between the diffusivity values is less than 12.8 %. In higher temperatures the difference becomes bigger due to the changes that occur in the constitutents of the pulp caused by heating. That is, over 35 ºC the intermolecular interactions start to become ruptured and therefore, the energy in form of heat diffuses more easily through the cocoa honey.

Figure 3 – Thermal diffusivity of cocoa honey in function of temperature.



Fonte: Autoria própria.

The quadratic model was well adjusted to the experimental results (R^2 = 0.98) and the achieved equation can be used to estimate diffusivity values in the range between 15 to 75 ºC (Equation 5):

$$\propto = 2{,}9793x10^{-7} - 1{,}0211x10^{-8}\,T + 1{,}728x10^{-10}\,T^2 \quad (5)$$

Where,

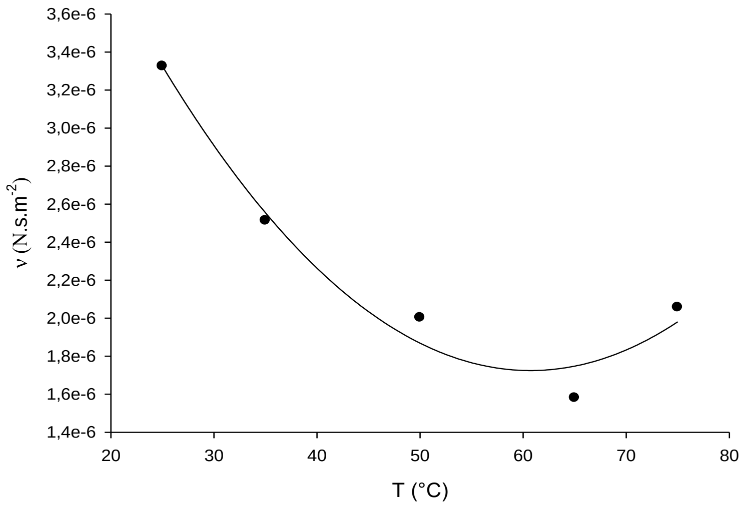
α = diffusivity ($m^2.s^{-1}$); and

T = temperature (ºC).

3.2.4 Dynamic viscosity

It was observed that the increase in temperature caused a decrease of 52.47 % in the viscosity of the cocoa honey up to a temperature of 65 °C. The energy supply to the cocoa honey´s molecules caused a weakening of intermolecular interactions. This way, the molecules achieve more mobility and so occurs a reduction in the resistance to outflow which implies in the viscosity decrease with the increase of temperature. However from 65 °C upwards there happened an approximate increase of 21.15 % in the studied property. This behaviour may have ocurred due to the presence of pectin in the honey which during the heating tends to form a gel (Figure 4).

Figure 4 – Dynamic viscosity of cocoa honey in function of temperature.



Fonte: Autoria própria.

The model was well adjusted to the experimental results (R^2 = 0.97) and the achieved equation can be used to estimate the viscosity values in the range from 25 to 65 ºC (Equation 6).

$$v = 6{,}3513x10^{-6} - 1{,}5242x10^{-7}T + 1{,}2553\ x\ 10^{-9}T^2 \qquad (6)$$

4. Conclusions

It was verified that cocoa honey is a food with high acidity, rich in sugars, mainly glucose and saccharose and high moisture content. Besides that, the thermophysical properties, specific mass, thermal diffusivity and viscosity are influenced by temperature. Starting from these informations it´s possible to obtain other properties through mathematical correlations, such as thermal conductivity. With this information, equipment for processing cocoa pulp and cocoa honey could be developed and adapted.

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