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Role of enthalpy and entropy in moisture sorption behavior of pineapple pulp powder produced by different drying methods

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ABSTRACT

Sorption mechanisms of pineapple powders produced by vibro-fluidized drying (VFD), spray drying (SD), freeze drying (FD) or vacuum drying (VD) were interpreted through enthalpy/entropy variations with respect to equilibrium moisture content (EMC) at 20, 30, 40 and 50 °C and water activity (a_w) between 0.059 and 0.907. Powders from SD and VFD were more hygroscopic and integral properties indicated higher stability at changing a_w compared to powders from VD and FD. Powders showed an enthalpy driven zone with equal isokinetic temperature (T_{B1} = 499.0 ± 4.8 K) due to their same composition, and an entropy controlled zone with different isokinetic temperature, T_{B2} (VD: 116.0 ± 40.6 K; FD: 118.3 ± 24.1 K; SD: 95.8 ± 23.4 K; VFD: 81.8 ± 6.3 K), caused by different microstructures resulting from different drying methods. Powders from SD and VFD presented larger entropic zones that shifted the minimum integral entropy to higher a_w, improving storage stability.

1. Introduction

Pineapple is a very popular fruit throughout the world, however in many developing countries only a limited quantity of pineapple products, such as canned fruit, canned juice or frozen juice concentrate, is produced. During the peak of harvest season, as a consequence of poor infrastructure, considerable quantities of the fruit can be wasted [1]. In addition, significant part of the harvest may consist of fruits with characteristics different from the desired pattern for industrialization, such as sunburn and deformed fruits. Production of fruit pulp powder can be a beneficial alternative to use the large amount of fruit wasted.

Drying has been used for hundreds of years for water removal from foods and in recent decades has become an important industrial tool for food preservation. Dehydrated fruit powders are useful food sources when fresh fruits are not available. Dried fruit juice is a stable, easy-to-handle form of juice that reconstitutes rapidly to a good quality product resembling the original juice. These products are served mainly as convenience foods and if appropriately produced and stored they can have a good shelf life [2–4].

Moisture sorption isotherms (MSI) describe the relationship between the water activity (a_w) and the equilibrium moisture content (EMC) of a food product. Knowledge of MSI is of essential importance to various food processes, such as drying, storage, and packaging, since they are used to calculate drying time, to predict ingredients behavior upon mixing, for packaging selection, to modeling moisture changes that occur during storage, and to estimate shelf life stability, which is very important mainly for food powders [5]. In addition, with MSI it is possible to determine the thermodynamic properties involved in the moisture sorption process [6,7].

The study of thermodynamic properties applied to food dehydration increased in recent decades, because thermodynamic functions help to explain the behavior and structure of water molecules on the surface and within foodstuffs [8]. Changes in some thermodynamic properties with respect to moisture content can provide a good description of the sorption mechanisms and can be used to estimate points of transition between mechanisms [9]. The minimum integral entropy can be considered as the a_w at which the foodstuff exhibits maximum stability [6,10,11]. Labuza [12] described applications of the enthalpy–entropy compensation law to reactions related to foods, and Beristain et al. [13] demonstrated that the enthalpy–entropy compensation is a useful tool for obtaining information regarding the mechanisms that control water vapor sorption in foods. Studies using integral thermodynamic properties have confirmed that the minimum integral entropy, proposed as the point of maximum stability of dry foods [14], occurs when the water molecules are adsorbed in the micropores [15].

The purpose of this work was to determine the sorption thermodynamic properties of pineapple pulp powder obtained from

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Nomenclature

μ	chemical potential (J/mol)
a_w	water activity
B	constant in Eq. (4)
ε	bulk porosity
C, K	constants in Eq. (2)
C_1	constant in Eq. (6)
ρ	density (kg/m^3)
H	isosteric heat or adsorption enthalpy (J/mol)
N_1	number of moles of water adsorbed
P	pressure (Pa)
R	universal gas constant (8.314 J/mol K)
S	entropy (J/mol K)
T	temperature (K)
W	molecular weight (g/mol)
X	moisture content (dry basis)
α_1	constant in Eq. (11)
ΔG	change in free energy (J/mol)
ΔH	change in enthalpy (J/mol)
ΔS	change in entropy (J/mol K)
Φ	diffusion pressure (J/mol)

Subscript

0	corresponding to the micropore volume
a	adsorbent in the condensed phase
ap	pure adsorbent
b	bulk
B	isokinetic
diff	differential
exp,i	experimental values
hm	mean harmonic
int	integral
l	molar differential
L	molar of water pure in equilibrium with vapor
m	first layer
pred,i	predicted values
r	real
t	total
v	water vapor

Superscript

0	pure water

different drying methods, and to interpret the mechanisms of the sorption process by analyzing the variation of enthalpy and entropy with respect to moisture content of powders.

2. Materials and methods

2.1. Raw material

Pineapple samples (*Ananas comosus*) without the characteristics desired for industrialization of canned fruit, such as sunburn and deformed, of the Smooth Cayenne variety [soluble solids content of 12–16°Brix (method 983.17 [16]); moisture content of 83–87% (wet basis) (method 920.151 [16]) and total sugars of 10.1 kg/100 kg (methods 925.35 and 925.36 [16])] were obtained and stored at 7 °C prior to their use. A batch of pineapple pulp was prepared in a pilot plant finisher and sieved through a 1.6 mm-mesh.

An aqueous solution with 50% solids (mass basis) was prepared by dispersing commercial maltodextrin (MOR-REX® 1920 Corn Products International, Jundiaí – SP, Brazil) in distilled water at 40 °C using a mechanical stirrer. This solution was added to pineapple pulp in order to result in a mass ratio of 50% maltodextrin on dry basis (i.e., 50 kg of maltodextrin/100 kg total solids). According to technical specifications provided by the manufacturer, maltodextrin MOR-REX® 1920 presents $17.0 \leq DE \leq 19.9$. Pineapple pulp with added maltodextrin was subjected to different drying methods described as follows and a batch of pineapple pulp powder was produced from each dryer.

2.2. Drying methods

2.2.1. Vibro-fluidized bed

Drying in vibro-fluidized bed with inert particles was performed in equipment composed by a vertical cylindrical glass chamber of 0.165 m in diameter and 0.704 m high. The chamber was suspended by a spindle and connected to a DC motor that drove an eccentric wheel that imparted vertical sinusoidal vibrations to the drying chamber. The frequency and amplitude of vibration could be set from 15 to 40 Hz and from 1 to 3 mm, respectively. The temperature of the drying air was 85 °C, the relative humidity (RH) was 2.6% (at 85 °C) and the air velocity was 3.8 m/s. The inert particles were supported by a grid having 9.4% free cross-sectional area, which was made from 2.5 mm holes punched in a 2 mm stainless steel sheet, forming a 60° rotated triangular staggered array configuration. The mixture to be dried was fed continuously into the drying chamber at constant rate with a peristaltic pump and dispersed by a central single stream nozzle 5 mm in diameter. The powder, with a final moisture content of 0.043 kg/kg dry solids, was separated from the inert particles by attrition outside of the drying chamber along with the exhausted air and collected in a cyclone.

2.2.2. Spray dryer

Spray drying was carried out in a spray dryer (Labmaq do Brazil LTDA, Ribeirão Preto – SP, Brazil) operating concurrently and fitted with an orifice sprayer nozzle of 2 mm in diameter. The inlet and outlet air temperatures were about 140 °C and 102 °C, respectively, and the inlet RH was 0.6% (at 140 °C). The liquid feed to the dryer was between 2.8×10^{-7} and 4.2×10^{-7} m^3/s. The flow of drying air was about 3.33×10^{-3} m^3/s. The experiments were performed at constant process conditions. The dry powder was removed from the drying chamber along with the exhausted air and collected in a cyclone. The final moisture content of the powder obtained by this method was of 0.033 kg/kg dry solids.

2.2.3. Freeze dryer

For freeze drying, the pineapple pulp was placed in stainless steel trays and placed in a freezer (LIOBRAS, São Carlos – SP, Brazil) at −40 °C. After freezing the trays were transferred to the freeze dryer (LIOBRAS, São Carlos – SP, Brazil) and kept during 48 h in the vacuum chamber with total pressure equal to 13.3 Pa and condenser temperature of −45 °C. The dried product was removed and ground in a hammer mill. The powder obtained by freeze drying had final moisture content of 0.026 kg/kg dry solids.

2.2.4. Vacuum chamber dryer

Vacuum drying was accomplished by placing the samples in stainless steel trays kept into a vacuum chamber (MARCONI, Piracicaba – SP, Brazil) at 60 °C and 8 kPa for 48 h. The dried product, which had final moisture content of 0.029 kg/kg dry solids, was ground in a hammer mill.

2.3. Moisture sorption isotherms (MSI)

The EMC of pineapple pulp powder obtained by the different drying methods, at several water activities were determined by the