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Thermodynamic sorption properties, water plasticizing effect and particle characteristics of blueberry powders produced from juices, fruits and pomaces

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ABSTRACT

Fresh blueberries were processed into three powder forms through freeze drying, namely juice powders containing 8% whey protein isolate (WPI), fruit powders and pomace powders. The water binding behaviors of these blueberry powders were studied through thermodynamic sorption analysis, quantification of water plasticizing effect and characterization of particle properties. The GAB model was successful in fitting the water sorption isotherms of blueberry powders at 20, 35 and 50 °C. Thermodynamic studies revealed that the sorption processes of all the samples were enthalpy-driven and only the sorption process of blueberry juice powders containing WPI was spontaneous ($\Delta G < 0$). Meanwhile, the highest absolute integral entropy values for blueberry juice powders containing 8% WPI, fruit powders and pomace powders were obtained at the moisture contents of 0.011, 0.013 and 0.024 kg H_2O/kg dried matter, respectively. Furthermore, the plasticizing effect of water on blueberry pomace powders was the weakest, since its k value of Gordon-Taylor model was lower than that of other samples. These results implied that blueberry pomace powders had the weakest affinity with water molecules. Thus, blueberry juice powders containing 8% WPI and fruit powders were suggested to be stored at a lower relative humidity than pomace powders. Besides, it was temporarily found that the difference in water binding capacity among blueberry powders was associated with the distribution of functional groups derived from sugars and acids, as well as the particle size. All the results can be a reference for drying, packaging, storage and distribution of blueberry powders in practical applications.

1. Introduction

Blueberry is a popular soft fruit, which is rich in bioactive phenolic compounds, including anthocyanins, proanthocyanidins and other flavonoids [1]. Due to the short shelf-life and seasonal availability of fresh blueberries, blueberries are usually processed into various products besides fresh consumption. To date, blueberry derived products, including juices, wines, dried fruits, powders, have already been commercialized in the market.

Drying of blueberries in the powder form is a unique way to extend the shelf life [2]. Compared with other blueberry products, blueberry powders have the advantages of easier storage and distribution. Furthermore, blueberry powders can be used as an ingredient to formulated foods. Both fresh blueberry fruits and blueberry juices have been utilized as the raw materials for the production of blueberry powders [3]. Besides, blueberry pomace that is the byproduct after juice processing still contains a considerably high amount of anthocyanins [4]. Thus, blueberry pomace can also be dried and ground to the powder form, so as to make some economic benefits. On the other hand, extra attention should be paid when it comes to dry blueberry juices. Fruit juices are featured by low glass transition temperature due to the high contents of sugars and acids [5]. As a result, a severe stickiness problem appears during juice drying, resulting in a low yield, poor quality properties and high energy consumption [6]. To overcome this problem, a series of drying aids, including maltodextrin with different dextrose equivalent, isolated proteins and food grade anticaking agents can be added into fruit juices during drying [5,7,8].

Blueberry powders are amorphous dry granular material, which are highly hygroscopic in nature [9]. Therefore, special packaging and careful handing are needed during storage, transportation and marketing. The physical, chemical and microbiological stabilities of fruit powders are strongly influenced by their moisture sorption characteristics [10]. Water sorption isotherms describe the relationship between equilibrium moisture content of food matrixes and the environmental relative humidity at a specific temperature. The information provided by

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water sorption isotherm is of particular significance to predict shelf-life stability of food matrixes, as well as provide guidance about food drying, packaging and storage processes [11,12]. At the same time, the structural features of food matrixes can also be obtained from sorption isotherm data, including specific surface area, crystallinity and pore radius [13]. Besides, the thermodynamic analysis of water sorption isotherm has been continuously performed to investigate the water binding mechanism of various dehydrated food products in the last decade, since this methodology can provide a more reasonable criterion for selecting storage and packaging conditions for food products [14]. Thermodynamic parameters usually involve differential enthalpy and entropy, spreading pressure, and integral enthalpy and entropy.

The knowledge about differential enthalpy refers to the state of adsorbed water in food matrixes, while differential entropy is an indicator about the number of available sorption sites at a specific energy level [15,16]. Spreading pressure denotes to the surface excess energy, which can indicate the enhancement in surface tension of sorption sites due to water sorption [17]. Furthermore, integral enthalpy describes the binding strength between water molecules and food matrixes similar to differential enthalpy, whereas the spreading pressure level stays constant [18]. Integral entropy represents the randomness of motion or degree of disorder of adsorbed water molecules [19]. Integral entropy allows for the quantification of mobility of water molecules. In summary, water sorption isotherm of fruit powders, together with the resulting structural and thermodynamic properties, play an important role on understanding the water-powder interaction mechanisms and optimizing the drying, storage and packaging processes. In our best knowledge, the sorption isotherm and differential enthalpy of dried blueberry fruits have been previously studied by Vásquez et al. and Vega-Gálvez et al. [3,20]. However, there are no studies investigating the thermodynamic sorption properties of blueberry powders systematically. Considering that thermodynamic sorption properties of fruit powders have a strong dependence on their compositions [10], it is of particular interest to study the water sorption behavior and thermodynamic properties of the powders produced from blueberry juices, fruits and pomaces.

Water has a plasticizing effect on amorphous materials after adsorption [21]. At certain temperatures, the increase of plasticizer amount may lead to the physical change of amorphous materials from glassy state to rubbery state [18]. The stickiness, caking, collapse, agglomeration, crystallization and microbiological deterioration problems can be avoided if the amorphous materials stay in the glassy state [22]. From this point, the plasticizing effect of water on blueberry powders can be quantified through the determination of glass transition temperature (T_g). Therefore, T_g is also a critical parameter to study the water binding mechanism of fruit powders and their stabilities during processing and storage. The variations of T_g for lyophilized blueberries as a function of water content have been reported by Vásquez et al. [3]. However, the plasticizing effect of water on different types of blueberry powders has not yet been studied.

Intrinsically, the water adsorption and binding properties of food matrix should be closely associated with their physical and chemical properties, such as the distribution of function groups relating to water binding, morphological structure, particle size, etc. [13,23,24]. Thus, it is necessary to study the particle properties of blueberry powders when it comes to investigate their water adsorption behaviors and the water plasticizing effect.

In this paper, different blueberry powders were produced, including blueberry juice powders containing 8% WPI, blueberry fruit powders and blueberry pomace powders. The aims of this study were: (a) to study the water adsorption isotherms of aforementioned blueberry powders at different temperatures; (b) to determine the structural and thermodynamic properties of blueberry powders; (3) to quantify the water plasticizing effect on blueberry powders through the measurement of T_g; (4) to characterize the particle properties of blueberry powders relating to water adsorption. The obtained results are helpful to understand the water adsorption mechanisms of various blueberry powders, as well as provide guidance about drying, packaging, storage and distribution of blueberry powders.

2. Materials and methods

2.1. Blueberries

Blueberries (*Vaccinium ashei*) named garden blue were purchased from a plantation in Lishui, Nanjing, China in the end of July 2016. High-quality blueberry fruits were presorted manually, while the soft, excessively small and visually damaged ones were discarded. Samples were washed, drained and stored at −18 °C in dark until use.

2.2. Preparation of blueberry fruit, juice and pomace powders

Blueberry fruits after thawing were first pressed by a domestic juicer (MJ-WBL2521H, Midea, Foshan, China) to obtain blueberry juices and pomaces, separately. Our preliminary studies revealed that it was difficult to process blueberry juices directly to powders through freeze drying and grinding due to the considerably high sugar and acid content. To overcome this problem, whey protein isolate (WPI) was used as a drying agent to assist freeze drying of blueberry juices in this study. Thus, WPI was added to blueberry juices at a concentration of 8% (w:w). The amount of WPI added was selected according to our preliminary studies (data not shown) and literatures [25]. Next, the mixture was homogenized at 8000 rpm for 10 min. Besides, the whole blueberry fruits were mashed manually and mixed well.

Blueberry juices containing 8% WPI, mashed blueberry fruits and blueberry pomace were dried in a freeze drier (Freezezone 4.5, Labconoco, USA) under a pressure lower than 0.003 mBar at −45 °C for 48 h. Lyophilized samples were then ground immediately using a laboratory-scale grinder (All basic S25, IKA, Guangzhou, China), so as to obtain fine powders of blueberry juices, fruits and pomaces, respectively. The figures of resulting blueberry powders are shown in Supplementary Fig. 1.

2.3. Determination and modeling of sorption isotherms

The sorption isotherms of blueberry powders produced from juices, fruits and pomaces were determined by gravimetric method described by Vega-Gálvez et al [20]. To be exact, saturated salt solutions of LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, KI, NaCl, KCl were prepared and placed in different glass desiccators. All these solutions were equilibrated at the target experimental temperatures for 24 h before experiments.

One gram of blueberry powders were spread on a Perish dish and then moved to each desiccator. The lids of desiccators were sealed strictly to ensure an airtight environment in the desiccator. To avoid the microbial growth in blueberry powders, a small amount of thymol was placed in each desiccator [26]. The weight of each portion of blueberry powders was measured periodically using a four-figure (±0.0001 g) analytical balance (BSA124S, Sartorius, Germany). Equilibrium conditions were achieved if the mass variation between three successive measurements was smaller than 0.001 g. To determine the water content of blueberry powders after equilibration, samples were dried in a vacuum drier (DZF-6020, Yiheng, Shanghai, China) at 80 °C for 24 h [26]. Adsorption isotherms of blueberry juice, fruit and pomace powders were measured at 20, 35 and 50 °C, respectively. For each temperature, the whole procedure was performed in triplicate.

The well-established Guggenheim-Anderson-De Boer (GAB) model was used to simulate the change in equilibrium moisture content of blueberry powders as a function of water activity, which is written as:

$$M_e = \frac{M_0 C K a_w}{(1 - K a_w)(1 - K a_w + C K a_w)} \tag{1}$$