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Original Research Paper

Antioxidant capacity of spray-dried plant extracts: Experiments and simulations

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ABSTRACT

The effects of different inlet air temperatures (70–150 °C) have been studied on the antioxidant retention and yields of a spray-dried bioactive solution (*Hibiscus sabdariffa* L.) from a Buchi B-290 spray dryer and compared with plug-flow spray drying simulations. Antioxidant retention has been tested using the Oxygen Reducing Antioxidant Capacity assay (ORAC). Experimentally, a peak yield of between 65% and 70% of the solids fed to the dryer has been found at an outlet gas temperature of 60–65 °C and an inlet air temperature of 110 °C, regardless of the batch of material or the liquid feed rate. The varying outlet gas temperatures did not significantly affect the antioxidant retention of the sample, and the simulations demonstrate that this result is due to the competing effects of increasing air temperature and decreasing water activity (at higher inlet air temperatures) on the degradation kinetics. These results suggest that it is more important to obtain greater product yields rather than minimising the degradation amount in this spray-drying situation.

1. Introduction

Spray dryers are frequently used in a variety of industries for producing powder products [1]. Apart from reducing the moisture content of the final products, it has long been realised that other powder properties are affected by the way in which the spray dryer is operated, such as bulk density [2]. At a fundamental level, the physical powder structure changes during spray drying, due to changes in the degree of crystallinity [3], and reactions can also take place, such as the degradation of vitamin C [4,5]. Modelling approaches in spray drying based on plug flow and parallel flow of gas and solids are fit for the purpose of predicting trends in these aspects (product crystallinity and reaction extent) with changes in the operating conditions [6]. Plug-flow simulation approaches may be useful [6] in conjunction with the more sophisticated but also more demanding modelling approach [7] of Computational Fluid Dynamics (CFD).

In terms of the applications for spray-dried powders, health, food and nutrition are key outcomes. Heart disease and cancer are amongst the leading causes of death in Australia and many other industrialised countries [8], and oxidative stress is thought to play a role in their development [8,9]. Oxidative stress is an imbalance between reactive oxygen species (ROS) and antioxidant defence and may lead to oxidative damage to body tissues [8,9]. This can result from either an increase in ROS or a breakdown in the level of antioxidant defence, and therefore the balance of antioxidants and ROS in the body is crucial. An increase in ROS within the body can arise from common sources such as smoking, exposure to heat and UV light. The antioxidants used to protect against ROS can come from internal sources, i.e. the antioxidants produced within the human body, or external sources, such as antioxidants obtained from fruits and vegetables. The use of traditional synthetic antioxidants, such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), has been reduced in recent times since these chemicals are suspected to be carcinogenic and to cause liver damage [10–13]. Therefore there is a significant market demand to replace these synthetic antioxidants with natural antioxidants derived from plant material.

In this study, a commercially available extract, namely rosella extract (*Hibiscus sabdariffa* L.), which is high in antioxidants, has been chosen as the sample material. The main antioxidants in *H. sabdariffa* L. are anthocyanins, which are the largest group of natural pigments in plants and are responsible for many attractive colours in plants, such as flowers, fruits (particularly berries) and vegetables [14]. Drying the antioxidant-rich extract would facilitate increased shelf-life and reduced microbial degradation due to the reduction of water content. Also, the reduction of weight through the removal of water would allow the product to be transported at a greatly reduced cost, which may increase the likelihood of the product being made available globally. Creating a powdered product may also increase the ease of adding this antioxidant-rich powder to consumer food products.

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There is significant interest in the drying of natural biological products, particularly foods and these types of biological extracts, together with maximising the antioxidant levels in these materials as a measure of their quality. For example, in the tray drying of red peppers, Vega-Galvez et al. [15] found that the overall antioxidant activity (as characterised by the total phenolic content [16,17]) of the dried material was lower than the fresh material. However, within the dried products, the antioxidant levels increased slightly, but significantly, when the air-drying temperature was increased from 50 °C to 90 °C. At the same time, the vitamin C levels decreased with increasing temperature. There were at least two explanations for the increase in overall antioxidant activity. The first explanation was that low air-drying temperatures correspond to long air-drying times, which mean long periods where the material being dried is warm and wet, having a high water activity. It was possible, but somewhat counter-intuitive, that this situation may promote the degradation of antioxidant compounds relative to high-temperature drying, which reduces the moisture content and water activity of materials quickly. The degradation rates of antioxidants, such as vitamin C, have been found to be high at both high temperature and high water activities [5]. Whether low or high-temperature drying results in the largest amount of antioxidant degradation depends on whether the temperature effect or the water-activity effect on the degradation rate is greatest. A second explanation was that drying may have promoted the generation and accumulation of Maillard reaction products, such as some melanoidins, which may have antioxidant properties.

Another work that reported a counter-intuitive temperature effect in drying (higher temperature giving higher antioxidant activity) was Que et al. [18]. They found higher antioxidant activity from hot air drying than by freeze drying with pumpkin flour, suggesting that the higher temperature conditions might have resulted in more antioxidant Maillard reaction products. They cited Nicoli et al. [19], who suggested that the formation of Maillard reaction products was responsible for the increase in the antioxidant activity for slightly-roasted coffee (after 10 min of roasting).

Yet another example of the motivation for this type of work comes from the work of Piga et al. [20] on prunes, which result from the drying of plums, so this work shows the effect of processing (drying) on a fruit (food) product. They point out that prunes have high radical scavenging ability, the strongest of all fruit and vegetable products in the human diet [21], and that prunes have shown antimutagenic activity by in vitro tests [22]. In addition, prunes contain substantial amounts of chlorogenic and neochlorogenic acids (collectively known as hydroxycinnamic acids), which lower the glycemic index in humans [23,24] and inhibit LDL oxidation in vitro [25]. They studied the drying of two plum varieties, sugar and President, with air drying at two temperatures, 60 °C and 85 °C. The antioxidant activity increased significantly at the higher temperature (85 °C) in the sugar variety. For the President variety, drying at 60 °C gave a lower antioxidant capacity than the fresh fruit, but the antioxidant capacity was two and a half times greater for fruit dried at 85 °C than for fresh fruit. This surprising result was attributed to the generation of a Maillard reaction intermediate product, hydroxymethylfural, which showed higher concentrations in the higher-temperature dried product and whose concentrations were strongly correlated with the antioxidant capacity.

Even more closely related to this work is that of Fang and Bhandari [26]. They spray dried bayberry juice with maltodextrin (DE 10), finding 96% retention of the total phenolic content and 94% retention of total anthocyanins in the spray-dried products. However, they produced no model that simulated this behaviour, so their explanation was qualitative in nature. Chiou and Langrish [27] found that the encapsulation of the *H. sabdariffa* L. with natural fruit fibres results in the production of a free-flowing powder. This work has continued the previous work to explore the retention of antioxidant activity. The previous work of Fang and Bhandari [26] has been extended to show how the effect of a key controllable variable, the inlet gas temperature, on the antioxidant activity of the spray-dried powder can be simulated and partly explained by a similar reaction kinetic expression to Goula and Adamopoulus [5] with a parallel/plug flow simulation approach. The experimental work will be described first, before the modelling and simulation approaches are presented.

2. Experimental

2.1. Materials and methods

2.1.1. Fibre and extract mixture

The ingredients used to make the slurry mixture used in the spray-drying process consisted of fine-milled sugar cane fibre (<30 μm Fibacel, KFSU Pty., Ltd.) and rosella extract (*H. sabdariffa L.*, Vic Cherikoff Food Services Pty., Ltd.). The slurry mixture was prepared using equal parts of fibre and extract based on the mass of the total dissolved solids. The combined extract was diluted with water until the mixture had a solids concentration of 10%. The slurry mixture was agitated, throughout the spray-drying process, with a magnetic stirrer to ensure that a homogenous solution was fed into the dryer.

2.1.2. Drying conditions

The slurry mixture was fed into a Buchi B-290 mini spray dryer with a height of 0.48 m. The settings were as follows: aspirator (main drying air flow) rate 0.0127 kg/s (100%); inlet air temperatures ranging from 70 to 150 °C; liquid feed pump rate of 1.9 mL/min (5%); atomisation air flow rate ~455 L/h (rotameter 35 to the bottom of the gauge ball); and the nozzle cleaner set to 51 strikes/min (setting 9). These operating conditions resulted in outlet air temperatures ranging from 41 to 82 °C.

2.1.3. Extraction of samples

Two extraction techniques were employed throughout this study. The first was a very simple water extraction method, where a spray-dried sample (1 g) was extracted in a 70 mL screw cap jar with 20 mL of water. To ensure the powder was wetted, the jar was gently shaken and then the solution was kept at room temperature for 1 h. After the hour, the supernatant was removed, appropriately diluted and analysed for antioxidant capacity via the Oxygen Reducing Antioxidant Capacity (ORAC) assay [28,29]. The differences in solution concentrations were taken into account by obtaining the total dissolved solids (TDSs) of the supernatant and comparing the samples in terms of TDS.

The second technique was a slightly modified version of one previously used by Prior and colleagues [28]. The spray-dried powder was mixed with a solution of acetone, water and acetic acid (70:29.5:0.5). The mixture was vortexed for 30 s and then sonicated for 5 min, with the tube being inverted once during the sonication step to ensure that the powder was still adequately suspended. After the sonication, the tube was left at room temperature for 10 min with occasional shaking. The tube was then centrifuged at 3500 rpm for 15 min before the supernatant was removed and transferred to a 25 mL volumetric flask, where the solution was made up to 25 mL through the addition of water.

2.1.4. Oxygen Reducing Antioxidant Capacity assay

The ORAC method used here was based on the one developed by Prior and colleagues [28] since it was chosen by the US Department of Agriculture [29] as the reference method when assessing other analytical techniques. The method used in this study in-