



Fractionation of starch hydrolysate into dextrin fractions with low dispersity by gradient alcohol precipitation



Xiuting Hu^{a,b}, Chengmei Liu^{a,b}, Zhengyu Jin^c, Yaoqi Tian^{c,*}

^aThe State Key Laboratory of Food Science and Technology, Nanchang University, Nanchang 330047, China

^bSchool of Food Science and Technology, Nanchang University, Nanchang 330047, China

^cThe State Key Laboratory of Food Science and Technology, Jiangnan University, Wuxi 214122, China

ARTICLE INFO

Article history:

Received 19 May 2015

Received in revised form 13 July 2015

Accepted 19 July 2015

Available online 22 July 2015

Keywords:

Fractionation

Gradient alcohol precipitation

Dextrin

Dispersity

ABSTRACT

Gradient alcohol precipitation was established as a fractionation method, and used for fractionating the 1-butanol-HCl-hydrolyzed cassava starch into dextrin fractions with a narrower molecular weight distribution. The addition of alcohol may have led to very high alcohol concentration in some parts of the dextrin solution, which may have impeded the fractionation process. Therefore, the rate of alcohol addition should be rigorously controlled during fractionation. The effects of the alcohol type and the initial dextrin concentration on fractionation were studied using the molecular-weight dispersity (D_M) as index. The parent dextrin was fractionated by gradient alcohol precipitation into seven fractions with decreasing D_M , with the volume ratios of the dextrin solution to alcohol at 4:1, 2:1, 1:1, 1:2, 1:3, 1:4, and 1:5, respectively. The better fractionation effect of different alcohols was in the order of methanol > ethanol > isopropanol; whereas the dextrin yield by these alcohols was in the reverse order. Furthermore, the peak molecular weight of each fraction tended to decrease with an increase in the alcohol concentration at which it was precipitated. The optimal initial concentration was in the range of 1.8%–2.7%, and lower or higher concentrations resulted in inferior fractionation. These results suggest that gradient alcohol precipitation is an efficient method for fractionating dextrin into fractions with different molar masses of low D_M , which would allow dextrin fractions to be tailor-made for specific application.

Crown Copyright © 2015 Published by Elsevier B.V. All rights reserved.

1. Introduction

Starch and its derivatives often have a wide molecular weight distribution, which restricts their application. For instance, the molar mass of the hydroxyethyl starch, which is generally used in clinical applications, ranges 40,000–450,000 Da [1]. Hydroxyethyl starch with higher molar mass may cause anaphylactoid reactions; conversely, the hydroxyethyl starch with very low molar mass may be excreted too quickly through the kidneys. Therefore, fractionating starch hydrolysate into dextrin fractions with a narrower molecular weight distribution is essential for diversifying the application of starch and its derivatives.

The fractionation of polymers is mainly achieved by chromatography, especially size exclusion chromatography [2–5], ultrafiltration [6–8], and antisolvent precipitation [9–15]. Since the advent of chromatography and ultrafiltration, these fractionation objectives have become less time-consuming. However, these two techniques are costly and chromatography is still incapable of producing

large-scale fractions. In contrast, antisolvent precipitation seems to present a superior fractionation route when preparing large amounts of narrow-distribution polymers. Among diversified antisolvent precipitation, alcohol precipitation has been frequently applied for the purification and fractionation of non-starch polysaccharides, such as dextran [9,16–19], inulin [20,21], hemicellulose [22–25], and lignin [26,27], as well as other non-starch polysaccharides [28–34]. These reports have found that varying the concentration of alcohol can precipitate these polysaccharides into fractions of different molecular sizes. Additionally, alcohol precipitation has been used to fractionate starch and starch hydrolysates. In 1942, Schoch [35] separated amylose from amylopectin by precipitating amylose with 1-butanol. Subsequently, a few reports fractionated starch into amylose and amylopectin according to Schoch's method or Schoch's method with slight modifications [36–38]. In 1989, Bretoft [39] fractionated α -dextrin by methanol precipitation and analyzed fractions using gel chromatography. Defloor et al. [40] found in 1998 that the initial maltodextrin concentration significantly affected the fractionation of maltodextrin by ethanol. Subsequently, in 2003, Gelders et al. [41] used alcohol precipitation to fractionate starch hydrolysates

* Corresponding author.

E-mail address: yqtian@jiangnan.edu.cn (Y. Tian).

into dextrin fractions with narrow molecular mass distribution, and found that fractionation results were strongly dependent on the fractionation temperature and the molecular weight of the parent starch hydrolysate.

However, the fractionation procedures used in above studies were extremely diverse and lack of regularity. Consequently, it is different for readers to establish a method for fractionating the same polysaccharides with different molecular weight distributions or new polysaccharides according to these studies. As a result, the aim of this study was to establish a method of fractionating starch hydrolysate by gradient alcohol precipitation based on the laws of precipitating starch hydrolysate using different alcohols. In this case, the method of fractionation using gradient alcohol precipitation could be extended to other polymers. Additionally, no quantitative techniques were used to identify the effect of fractionating starch or dextrin by alcohol precipitation. The molecular-weight dispersity (D_M) can be used to indicate the width of molecular weight distributions [42]. The D_M is calculated as the ratio of the weight-average molecular weight (M_w) to the number-average molecular weight (M_n). The values of D_M are greater than or equal to 1. A lower D_M indicates a narrower molecular weight distribution of the polymers, and a D_M of 1 signifies that the polymer is monodisperse, such as bovine serum albumin. Therefore, this study chose D_M as the indicator for assessing the effect of fractionation.

In summary, the aim of this study was to establish and explore a method of fractionating starch hydrolysate by gradient alcohol precipitation. Specifically, the effects of the rate of alcohol addition, the alcohol type, and the initial dextrin concentration on fractionation were studied with D_M as index. The molecular weight information, including D_M , was determined using high-performance size-exclusion chromatography coupled with a multi-angle laser light-scattering detector and a refractive index detector (HPSEC-MALLS-RI).

2. Materials and methods

2.1. Materials

Cassava starch was purchased from Hainan Benlu Starch Factory (Hainan, China). Methanol, ethanol, isopropanol, 1-butanol, and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All other chemicals and reagents were of analytical grade unless otherwise stated.

2.2. Dextrinization of cassava starch by 1-butanol-HCl-hydrolysis

1-Butanol-HCl hydrolysis of cassava starch was performed according to the procedure described previously [43]. Starch (25 g, dry basis) was dispersed in 100 mL anhydrous 1-butanol. The reaction was started by adding 1 mL of concentrated (36% by weight) HCl and proceed at 40 °C for 3 d with constant stirring. The reaction was stopped by adding 14 mL of 1 M NaHCO_3 to the solution, which was then cooled in an ice bath for 15 min and centrifuged at 3500g for another 5 min. The precipitate was washed several times with 50% ethanol and dried in an air oven at 35 °C. Finally, 1-butanol-HCl-hydrolyzed cassava starch was crushed.

2.3. Precipitation of 1-butanol-HCl-hydrolyzed cassava starch using different alcohols

Precipitation of starch hydrolysate by the quick addition of alcohol was executed as follows. 1-Butanol-HCl-hydrolyzed cassava starch was dissolved in water at a concentration of 2% by stirring

for 30 min at 90 °C, cooled to 25 °C, and centrifuged at 10,000g for 10 min to remove the insoluble fraction. Alcohol (methanol, ethanol, or isopropanol) was directly added to the dextrin solution, until the volume ratio of the dextrin solution to alcohol was 2:1, 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9, and 1:10, respectively. The mixture was stirred for 30 min and kept at 4 °C for 24 h. The precipitate was obtained by centrifugation (10,000g, 20 min) at 4 °C. Thereafter, the precipitate was dried and weighted to calculate the dextrin yield.

Precipitation of starch hydrolysate by the slow addition of alcohol was carried out as follows. 1-Butanol-HCl-hydrolyzed cassava starch was dissolved in water at a concentration of 2% by stirring for 30 min at 90 °C, cooled to 25 °C, and centrifuged at 10,000g for 10 min to remove the insoluble fraction. Alcohol (methanol, ethanol, or isopropanol) was added to the dextrin solution at a rate of 0.5 mL/min using the apparatus shown in Fig. 1, until the volume ratio of the dextrin solution to alcohol was 2:1, 1:1, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9, and 1:10, respectively. The mixture was stirred for 30 min and kept at 4 °C for 24 h. The precipitate was obtained by centrifugation (10,000g, 20 min) at 4 °C. Thereafter, the precipitate was dried and weighed to calculate the dextrin yield.

2.4. Fractionation of 1-butanol-HCl-hydrolyzed cassava starch by gradient alcohol precipitation

The fractionation of 1-butanol-HCl-hydrolyzed cassava starch by gradient alcohol precipitation was performed according to the procedure described in Fig. 2. Specifically, 1-butanol-HCl-hydrolyzed cassava starch was dissolved in water at a concentration of 2% by stirring for 30 min at 90 °C, cooled to 25 °C, and centrifuged at 10,000g for 10 min to remove the insoluble fraction. Subsequently, alcohol (methanol, ethanol, or isopropanol) was added into the dextrin solution (with continuous stirring) at a rate of 0.5 mL/min using the apparatus shown in Fig. 1, until the volume ratio of the dextrin solution to alcohol reached 4:1. The mixture was stirred for an additional 30 min and kept at 4 °C for 24 h. The precipitated material was recovered by centrifugation at 4 °C (10,000g, 20 min), and the precipitate, hereafter referred to as F4:1, was dried and crushed. Alcohol was further added to the supernatant, until the volume ratio of the dextrin solution to alcohol reached 2:1 to obtain the dextrin fraction, F2:1. The above procedure was repeated to obtain dextrin fractions F1:1, F1:2, F1:3, F1:4, and F1:5, respectively. Finally, the supernatant was evaporated to remove water and alcohol, and then dried to obtain the fraction $F > 1:5$.

2.5. Influence of the initial dextrin concentration on fractionation of 1-butanol-HCl-hydrolyzed cassava starch by gradient alcohol precipitation

1-Butanol-HCl-hydrolyzed cassava starch (4 g, dry basis) was dissolved in water (100 mL) by stirring for 30 min at 90 °C, cooled

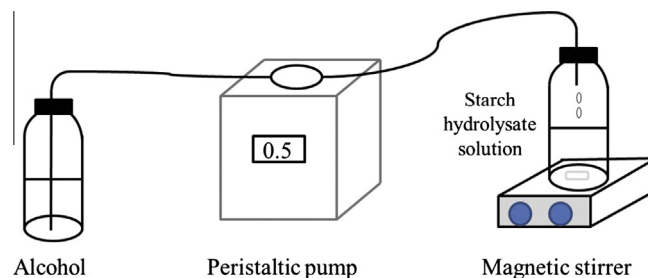


Fig. 1. The apparatus for alcohol addition into the starch hydrolysate solution.

Download English Version:

<https://daneshyari.com/en/article/640427>

Download Persian Version:

<https://daneshyari.com/article/640427>

[Daneshyari.com](https://daneshyari.com)