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Liquefaction concentration impacts the fine structure of maltodextrin

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ABSTRACT

Designing a high-concentration (45%, w/w) corn starch liquefaction process is a challenge, as more than just the rate of enzymatic hydrolysis must be considered. Maltodextrins with the same dextrose equivalent value were produced in an industrial liquefaction process using normal corn starch suspensions at low (10%, w/w), normal (30%), and high (45%) concentration. The starch concentration noticeably influenced the fine structure of the starch hydrolysate. Increasing the starch concentration from 10% to 45% limited the cleavage of long chains and enhanced the generation of linear maltooligosaccharides and the survival of large molecules. These effects contributed to a bimodal molecular size distribution and high iodine binding by the product maltodextrin. We propose that high starch concentration may induce a higher level of multiple enzyme attack, in which α-amylase attack of external chains is enhanced. As a result of its structural heterogeneity, maltodextrin derived from 45% starch exhibited higher viscosity and was a poorer substrate for amyloglucosidase. This led to lower saccharification efficiency even though this maltodextrin was diluted to conventional concentration (30%, w/w). Thus, further work is needed to produce maltodextrins suitable for saccharification through the liquefaction of corn starch at high concentration.

1. Introduction

The enzymatic hydrolysis of corn starch is among the most important enzymatic reactions in industry (Myat and Ryu, 2014). Maltodextrin is a liquefied starch product intermediate between native starch and starch syrup, with dextrose equivalent (DE) values ranging from 2 to 20. Besides, maltodextrin has also found wide application in the food industry as a bodying agent, coating agent, and flavor carrier (Dokic et al., 1998).

Currently, industrial processes producing maltodextrin or starch syrup from starch use excess water. Starch is hydrolyzed using an initial solids content of about 30% (w/w, dry basis) but during the process, approximately 5% of the initial water is used for chemical gain. The excess water must be evaporated from the final product, increasing processing costs and complicating the process layout (Van der Veen et al., 2006). Thus, it is desirable to enhance the initial concentration of the starch slurry in order to reduce the amount of moisture that must be evaporated. Additional benefits of using a higher initial slurry concentration include improvements in both productivity and enzyme stability (Baks et al., 2008). Unfortunately, it is very hard to hydrolyze high-concentration starch slurries because the viscosity of the gelatinized starch paste increases exponentially with concentration. The lack of water restrains complete gelatinization and hinders mixing during the reaction.

Abbreviations: DE, dextrose equivalent; DNS, 3,5-dinitrosalicylic acid; TAKA, *Aspergillus oryzae* α-amylase; L-DE5, DE5 maltodextrin obtained from the liquefaction of 10% starch; L-DE10, DE10 maltodextrin from the liquefaction of 10% starch; L-DE15, DE15 maltodextrin from the liquefaction of 10% starch; N-DE5, DE5 maltodextrin from the liquefaction of 30% starch; N-DE10, DE10 maltodextrin from the liquefaction of 30% starch; N-DE15, DE15 maltodextrin from the liquefaction of 30% starch; H-DE5, DE5 maltodextrin from the liquefaction of 45% starch; H-DE10, DE10 maltodextrin from the liquefaction of 45% starch; H-DE15, DE15 maltodextrin from the liquefaction of 45% starch; HPSEC, high-performance size-exclusion chromatography; HPAEC, high-performance anion exchange chromatography; PAD, pulsed amperometric detection; PI, polydispersity index; M_w, weight-average molar mass; DP, degree of polymerization; RBV, relative blue value; G1, glucose; G2, maltose; G3, maltotriose; G4, maltotetraose; G5, maltopentaose; G6, maltohexaose; G7, maltoheptaose; G8, maltooctaose; G9, maltononaose; G10, maltodecaose; DIL, degree of isoamylolysis limit; DBL, degree of β-amylolysis limit; CL, average chain length; ICL, average internal chain length; ECL, average external chain length; T_2, spin-spin relaxation time; *Km*, Michaelis constant

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Recently, several authors have made efforts to use extruders (Baks et al., 2008), high-speed shearing devices (Van der Veen et al., 2006) and ultrasonic pretreatment (Li et al., 2017) to handle more concentrated starch slurries. Enzymatic hydrolysis under highly concentrated conditions can be successful with 40–45% (w/w, dry basis) starch (Li et al., 2016a, 2017; Słomińska et al., 2013). The DE value of the starch hydrolysate has generally been used to estimate the effectiveness of high-concentration liquefaction processes, and few studies have focused on the fine structure of the starch hydrolysate. Maltodextrins with the same DE value may exhibit significant diversity in carbohydrate composition and physicochemical properties (Dokic-Baucal et al., 2004). Moreover, differences in structure would clearly affect the usefulness of maltodextrin preparations in different applications (Avaltroni et al., 2004; Takeiti et al., 2010; Wang and Wang, 2000).

It is possible to produce maltodextrins that have similar DE values using different hydrolysis procedures. Many previous studies have shown that differences in pH and temperature can change the action pattern of amylases; consequently, starch hydrolysates with the same DE value may have different structures (Bijttebier et al., 2007; Marchal et al., 1999; Robyt and French, 1967, 1970). In the present study, maltodextrins with the same DE value obtained from starch slurries of different concentration were investigated. To explain the differences in fine structure of the hydrolysates produced at different concentrations, an unusual α-amylase attack action pattern is proposed at high substrate concentration. The results may provide additional insight into the liquefaction of corn starch at high concentrations.

2. Materials and methods

2.1. Materials

Normal corn starch (moisture content, 12.3%; protein content, 0.45% [w/w, dry basis]; purity, > 99%) was obtained from Hebei Yufeng Industry Group Co., Ltd (Hebei, China) and used as substrate for the liquefaction process. α-Amylase (Clearflow AA, 28,000 U/mL) was obtained from Genencor International (Palo Alto, CA, USA). Amyloglucosidase (500 U/mL), isoamylase (500,000 U/mL), sodium hydroxide solution for ion chromatography, and sodium acetate for molecular biology were purchased from Sigma Chemical Co. (St. Louis, MO USA). Pullulanase (600 U/mL) was a gift from Novozymes (China) Biotechnology Co., Ltd (Tianjin, China). HPLC-grade dimethyl sulfoxide was obtained from Thermo Fisher Scientific Co., Ltd (Waltham, MA USA) All other chemicals were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China).

2.2. Starch liquefaction process and preparation of maltodextrins at different concentrations

Starch liquefaction was performed in a four-neck flask. Two-hundred-gram portions of slurry containing 10%, 30% or 45% (w/w, dry basis) starch were prepared in distilled water and adjusted to pH 6.0 with 0.1 M HCl. Each four-neck flask containing corn starch slurry was immersed in a constant-temperature water bath at 60 °C. The mixture was stirred at 300 rpm for 15 min while being kept at 60 °C. Thermostable α-amylase (12 U/g dry starch) was added to the slurry and then the temperature was increased to 90 °C at a rate of 1 °C/min. Liquefaction was continued for 2 h at a constant temperature of 90 °C. At different time intervals, approximately 0.8 g (accurately weighed) of starch hydrolysate was withdrawn for analysis and the hydrolysis was immediately stopped by the addition of 4 mL of 1 mM HCl.

In order to prepare maltodextrins of the same DE value, liquefactions were sustained for different times (as shown in Table 1) at different initial starch concentrations. After their respective incubation periods, the starch hydrolysates were acidified by the addition of 5 mL of 0.1 M HCl to stop the reaction. Then, the products were freeze-dried and ground to powders fine enough to pass through a 100-mesh sieve to obtain different maltodextrin powders of different DE value (DE 5, DE 10 and DE 15) for each initial starch concentration.

2.3. Dextrose equivalence of starch hydrolysates

The DE values of starch hydrolysates were determined by measuring the content of reducing sugar using the 3,5-dinitrosalicylic acid (DNS) method (Miller, 1959).

2.4. Relative blue values of starch hydrolysates

The relative blue value (RBV) was determined using the method of Bijttebier et al. (2007) with slight modifications. To determine the blue value of the polysaccharide-iodine complex of a hydrolysate, 750 μL of a maltodextrin solution (5 mg/mL) was diluted with 4.0 mL of distilled water and then mixed with 250 μL of iodine reagent (0.2% KI and 0.02% I_2). After thorough mixing, the solution was kept in the dark for 15 min. Finally, the absorbance of each solution was measured at 525 nm. The RBV was expressed as a percentage of the absorbance of the sample compare with that of normal corn starch, which had an RBV of 100%.

2.5. Molecular size distribution analysis

Molecular size distribution was performed using a Dawn Heleos II high-performance size-exclusion chromatography (HPSEC) system (Wyatt Technology, Santa Barbara, CA). The HPSEC system was equipped with two Phenogel columns, namely Styragel HMW6E (5000–10,000,000) and Styragel HMW7 (500,000–100,000,000) (Waters, Inc., Torrance, CA, USA), a multi-angle laser light scattering detector and a differential refractive index detector. Sample treatment and chromatographic condition followed a previously described method (Liu et al., 2017).

2.6. Maltooligosaccharide profile analysis

The maltodextrin samples obtained using the procedures described in Section 2.2 were dissolved and appropriately diluted with ultrapure water, and then filtered a 0.22 μm syringe filter. The filtrate (10 μL) was analyzed using a high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) system (ICS-5000, Thermo Fisher Scientific Co., Ltd, Waltham, MA USA) equipped with a CarboPac PA200 chromatographic column (3 × 200 mm, Thermo Fisher Scientific Co., Ltd, Waltham, MA USA) (Roussel et al., 2013). Oligosaccharides (including glucose) were eluted with an eluent gradient at 30°C and a flow rate of 0.5 mL/min. The eluents contained 250 mM sodium hydroxide (eluent A), 1 M sodium acetate (eluent B) and ultrapure water (eluent C). Eluent A increased from 8% to 24% at 22 min, and then decreased to 8% at 40 min. This proportion was kept constant till 50 min. Eluent B was maintained at 2% until 6.5 min; 4% from 6.5 to 18 min, 8% from 18 to 22 min; 10% from 22 to 31 min; and 36% from 31 to 40.2 min. After this time, the eluent was returned to the initial conditions. The remainder was eluent C. Maltooligosaccharides were quantified with an external standard method using a mixture containing maltooligosaccharides from glucose (G1) to maltoheptaose (G7) in a concentration from 2 to 10 μg/mL (Morales et al., 2008). However, maltooctaose (G8), maltononaose (G9) and maltodecaose (G10) were not quantified in this study for lack of commercial standards.

2.7. Debranched linear chain length distribution analysis

The linear chain length distribution of debranched starch was determined using a previously reported HPAEC-PAD method (Li et al., 2016b), with slight modifications. A series of lyophilized maltodextrin