J. Dairy Sci. 101:1–5
https://doi.org/10.3168/jds.2017-13813

Short communication: Development of a rapid laboratory method to polymerize lactose to nondigestible carbohydrates

A. F. Kuechel and T. C. Schoenfuss[1]
Department of Food Science and Nutrition, University of Minnesota, 1334 Eckles Ave., St. Paul 55108

ABSTRACT

Nondigestible carbohydrates with a degree of polymerization between 3 and 10 (oligosaccharides) are commonly used as dietary fiber ingredients in the food industry, once they have been confirmed to have positive effects on human health by regulatory authorities. These carbohydrates are produced through chemical or enzymatic synthesis. Polylactose, a polymerization product of lactose and glucose, has been produced by reactive extrusion using a twin-screw extruder, with citric acid as the catalyst. Trials using powdered cheese whey permeate as the lactose source for this reaction were unsuccessful. The development of a laboratory method was necessary to investigate the effect of ingredients present in permeate powder that could be inhibiting polymerization. A Mars 6 Microwave Digestion System (CEM Corp., Matthews, NC) was used to heat and polymerize the sugars. The temperatures had to be lowered from extrusion conditions to produce a caramel-like product and not decompose the sugars. Small amounts of water had to be added to the reaction vessels to allow consistent heating of sugars between vessels. Elevated levels of water (22.86 and 28.57%, vol/wt) and calcium phosphate (0.928 and 1.856%, wt/wt) reduced the oligosaccharide yield in the laboratory method. Increasing the citric acid (catalyst) concentration increased the oligosaccharide yield for the pure sugar blend and when permeate powder was used. The utility of the laboratory method to predict oligosaccharide yields was confirmed during extrusion trials of permeate when this increased acid catalyst concentration resulted in similar oligosaccharide concentrations.
Key words: lactose, polylactose, oligosaccharides

Short Communication

Oligosaccharides, nondigestible carbohydrates with a degree of polymerization between 3 and 10, account for a large percentage of the US food fiber market (Frost and Sullivan, 2012). Oligosaccharides become more valuable to the food industry when they are determined, after appropriate regulatory review of evidence of human health benefits, to be dietary fiber. In some cases, they also positively influence the texture and mouthfeel of a product, unlike insoluble fibers (Tungland and Meyer, 2002). Fiber-containing foods are becoming increasingly popular as consumers learn of the health benefits associated with fiber, such as colon cancer prevention, improved digestive health, and obesity prevention through improved satiation (USDA, 2015; Mintel Group Ltd., 2016).

Polydextrose, a commercially available oligosaccharide product, is produced through melt polymerization (also called condensation polymerization) of glucose and sorbitol using either citric acid or phosphoric acid as catalyst in a batch process under vacuum. The reactants are heated to melt glucose and provide favorable reaction conditions, while being held under vacuum, resulting in a loss of water and the formation of glycosidic linkages between glucose molecules or sorbitol (Rennhard, 1973; Tungland and Meyer, 2002). Polylactose, the polymerization of glucose and galactose using lactose as the primary ingredient, has been produced at the pilot plant scale (batch of ~14 kg) by reactive extrusion of lactose and glucose, using citric acid as the catalyst (Tremaine et al., 2014). Traditional acid-catalyzed melt polymerization of sugars to synthesize oligosaccharides under vacuum has been reported on a laboratory scale by various researchers (Manley-Harris and Richards, 1991, 1993; Daines et al., 2015). Acid-catalyzed polymerization with a microwave reaction system, another laboratory method, was reported to produce polydextrose that was comparable to commercial product (Wang et al., 2014). Daines et al. (2015) reported that they were not successful in polymerizing lactose to oligosaccharides with citric acid and sorbitol by a benchtop method (although they succeeded in producing polydextrose). They believed this occurred because the melting point of lactose in the presence of various levels of citric acid was close to the sugar decomposition temperature, so polymerization could

Received September 10, 2017.
Accepted December 18, 2017.
[1]Corresponding author: tschoenf@umn.edu

not occur as it can with glucose. Tremaine et al. (2014) also noted that lactose did not melt readily during a short extrusion process, and that the addition of glucose greatly improved the process by reducing the melting temperature, allowing for polymerization during extrusion. To successfully produce oligosaccharides from lactose, Daines et al. (2015) first used phosphoric acid to hydrolyze lactose to glucose and galactose in a microwave, followed by the traditional melt polymerization process under vacuum. Extensive identification of sugars and polymers was reported; however, the quantity of nondigestible oligosaccharides in the material was not measured.

Laboratory-scale benchtop methods would be useful for understanding the effect of formula constituents before expensive extrusion trials. However, vacuum melt polymerization benchtop methods do not simulate the conditions experienced in an extruder, and have not been successful in polymerizing lactose. The tubes in a microwave reactor would undergo the pressure build-up that is experienced during extrusion. A rapid, direct microwave method to polymerize lactose to oligosaccharides, without a pre-hydrolysis step, would allow for hypothesis-driven research before reactive extrusion trials. The effect of formulation (e.g., ingredient constituents and acid catalyst concentration) on the polymerization reaction is not well understood. Previous reactive extrusion trials in our pilot plant with lactose-rich whey permeate powders and acid whey did not yield oligosaccharides (data not shown). The main differences between the edible lactose and glucose used in our successful trials and whey permeate are the presence of milk minerals and nitrogen, higher moisture concentration, and the presence of amorphous lactose (Sienkiewicz and Riedel, 1990). Establishing an understanding of the effect of formulation using a laboratory method, such as a microwave reactor, could allow for the production of novel oligosaccharides from dairy coproducts through reactive extrusion.

The objective of this study was to develop a microwave reactor method for the polymerization of lactose and glucose to a product similar to what can be achieved by reactive extrusion. A second objective was to determine whether the developed microwave method could be used to understand the effect of different components in permeate that could be inhibiting the polymerization of lactose, and determine whether formulas could be devised to reduce this inhibition. Specifically, calcium and water were investigated to test the method utility as they are both higher in permeate than in edible lactose. Water is a known inhibitor of polymerization in the production of polydextrose, and this is one reason why the reaction is done under vacuum (to remove water generated during the condensation reaction; Rennhard, 1973). Minerals such as calcium and phosphorous in permeate could also interfere with the effectiveness of the acid catalyst by affecting the pH or by some other mechanism. The effect of additional acid catalyst could be investigated by this method to see whether it counteracts the effect of minerals.

The materials used included α-lactose monohydrate, glucose, citric acid, calcium phosphate (Sigma Aldrich, St. Louis, MO), and IdaPro permeate powder (Idaho Milk Products, Jerome, ID) for the microwave reaction system trials. IdaPro permeate powder and citric acid (Jungbunzlauer, Basel, Switzerland) were used for extrusion of the permeate-acid blend. Seven grams of an α-lactose monohydrate (74%), glucose (20%), and citric acid (6%) blend and 1 mL of reverse osmosis water were added to a 110-mL MARSXpress Plus Teflon microwave reactor vessel (CEM Corp., Matthews, NC). The vessel was closed and the product equilibrated for 24 h. During experimentation with permeate, 7 g of the permeate-acid blend and 1 mL of reverse osmosis water were added to the MARSXpress Plus Teflon microwave reactor vessel. After 24 h, the vessels were placed in a Mars 6 microwave reactor (CEM Corp.) and the heating profile was varied until we achieved a caramel-like product that contained oligosaccharides (confirmed through quantification using the integrated dietary fiber method, described below). The final heating profile selected to simulate extrusion was a 14-min ramp time to 140°C at 1,800 W. Once the heating ramp time was complete, the product was immediately removed from the vessels, placed in disposable aluminum weighing dishes, and stored in a desiccator at room temperature until cool. We scaled up the polymerization of whey permeate powder (90%) and citric acid (10%) blend using the reactive extrusion method described in Tremaine et al. (2014). The product was collected from the outlet of the extruder on metal baking sheets and allowed to cool to room temperature. It was stored at room temperature until analysis.

The integrated total dietary fiber assay (K-INTDF 02/15, Megazyme International, Bray, Ireland) was used to quantify oligosaccharides formed during the polymerization reaction. The nondigestible oligosaccharides quantified by this method are termed "low-molecular-weight soluble dietary fiber." The method was modified as follows. D-Ribose (Sigma Aldrich) was used as the internal standard for HPLC analysis. All HPLC analysis used a CHO-411 column (Transgenomics, Omaha, NE), and a Sedex 85 LT low-temperature evaporative light scattering detector (ELSD-LT, Shimadzu Corp., Kyoto, Japan) was used instead of a refractive index detector. The HPLC conditions used were column temperature of 80°C, flow rate of 0.3 mL/min, and a double distilled water mobile phase. The