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Optimisation of the reaction conditions for the production of cross-linked starch with high resistant starch content

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ABSTRACT

The optimum reaction conditions (temperature and pH) for the preparation of cross-linked (CL) corn and wheat starches with maximum resistant starch (RS) content were investigated by using response surface methodology (RSM). According to the preliminary results, five levels were selected for reaction temperature (38–70 °C) and pH (10–12) in the main study. RS contents of the CL corn and wheat starch samples increased with increasing temperature and pH, and pH had a greater influence on RS content than had temperature. The maximum RS content (with a maximum *p* value of 0.4%) was obtained in wheat starch cross-linked at 38 °C and pH 12. In the case of CL corn starch, the optimum condition was 70 °C and pH 12. CL corn and wheat starch samples were also produced separately under the optimum conditions and their RS contents were 80.4% and 83.9%, respectively. These results were also in agreement with the values predicted by RSM.

1. Introduction

Resistant starch (RS) has been defined as the starch fraction which escapes digestion in the small intestine of healthy individuals (Englyst, Kingman, & Cummings, 1992). Due to its similar physiological properties, it is considered as a constituent of dietary fibre. As it is fermented to short chain fatty acids in the colon, it may improve colonic health (Huth, Dongowski, Gebhardt, & Flamme, 2000; Wollowski, Rechkemmer, & Pool-Zobel, 2001). It lowers plasma cholesterol and lipids and improves glucose tolerance (Niba & Hoffman, 2003; Voragen, 1998). For a healthy diet, it is recommended to decrease fat intake and increase dietary fibre consumption (Wolf, Bauer, & Fahey, 1999). RS can be found naturally in foods in the range of 0–4%; however, a higher amount of RS in the diet is recommended, due to its preventative and therapeutical health effects (Lehmann, Rössler, Schmiedl, & Jacobasch, 2003). Therefore, there has been a great interest in increasing RS content of foods by various modification techniques. RS is classified into four types: physically inaccessible starch (RS1), native granular starch (RS2), retrograded starch (RS3), and chemically modified starch (RS4) (Eerlingen, Crombez, & Delcour, 1993; Shamai, Bianco-Peled, & Shimoni, 2003; Patil, 2004).

Cross-linking (CL) is one of the chemical modification techniques that have been used to improve functional properties, and freeze-thaw and cold storage stabilities of starch pastes (Chung, Woo, & Lim, 2004; BeMiller, 2011). It has also been reported that cross-linking of starches, using reagents such as STMP (sodium trimetaphosphate), or an STMP–STPP (sodium tripolyphosphate) mixture, caused resistance to digestion and therefore these resultant starches fit within the RS4 category (Woo, 1999; Woo, Maningat, & Seib, 2009). Cross-linking is generally performed by treatment of granular starch with multifunctional reagents capable of forming ether or ester linkages between hydroxyl groups on starch molecules (Rutenberg & Solarek, 1984; Wurzburg, 1986a,b; Singh, Kaur, & McCarthy, 2007). Cross-linking is intended to add intra- and inter-molecular bonds at random locations in the starch granule that stabilize and strengthen the granule (Acquarone & Rao, 2003; Singh et al., 2007). Xie and Liu (2004) indicated that CL starches cannot be completely digested since the substituents hinder enzymatic attack.

The chemical and functional properties of the CL starches depend on the starch source, reaction conditions (reaction time, temperature, pH, presence of catalyst) and type/concentration of reactant (Lim & Seib, 1993; Hirsch & Kokini, 2002; Wang & Wang, 2002; Singh et al., 2007). Woo and Seib (2002) reported that the RS contents of CL wheat, potato, corn and rice starches reached 75.7%, 72.8%, 57.8% and 5.4%, respectively, after a 3 h cross-linking reaction at 45 °C and pH 11.5, using STMP:STPP (12%, sb: starch

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basis) mixture (99:1). Yeo and Seib (2009) had cross-linked wheat starch under the same cross-linking conditions as Woo and Seib (2002) and achieved an RS content of 80%. Woo and Seib (2002) also investigated the effect of reaction time on the RS content of CL starches and reported that the RS contents of the CL wheat starches increased as the reaction time increased. Chung et al. (2004) investigated the effect of STMP:STPP (99:1) amount on the RS content of CL wheat starches. The RS contents of the CL starches cross-linked at 45 °C, pH 11.5, for 3 h, using 4%, 8% and 12% (sb) STMP:STPP (99:1), were increased to 24.5%, 60.0% and 81.6%, respectively (Chung et al., 2004).

Response surface methodology (RSM) is a statistical method, used to design experiments, build models, evaluate the effects of factors and search optimum conditions of factors for desirable responses (Myers & Montgomery, 1995). RSM generates a mathematical model that accurately describes the overall process with limited number of experiments (Senanayake & Shahidi, 2002). Although, various investigators (Woo & Seib, 2002; Chung et al., 2004; Yeo & Seib, 2009) have produced CL wheat starches at some reaction temperature, pH and time combinations, as well as utilising various STMP:STPP concentrations, investigating the effects of temperature and pH to obtain maximum RS content, use of RSM is expected to bring about additional significant information. In this study RSM was used to investigate the optimum reaction conditions (temperature and pH) for the preparation of cross-linked corn and wheat starches with high RS content with a permissible phosphorus level of 0.4%.

2. Materials and methods

2.1. Materials

Corn and wheat starches were obtained from Ingredion Inc. (formerly National Starch Chemical Co., Bridgewater, NJ, USA) and MGP Ingredients (Atchison, KS, USA), respectively. The chemicals used in the study were of analytical grade unless stated otherwise.

2.2. Methods

2.2.1. Production of cross-linked starch

Cross-linked starch samples were produced according to the method of Woo and Seib (2002) with some modifications of the reaction conditions. Corn and wheat starches (50 g, db) were dispersed in 70 ml of water containing 12% STMP:STPP (99:1) and 10% sodium sulphate, both based on starch weight. The dispersion was allowed to react at various temperature (T) and pH combinations (Table 1), using a magnetic stirrer equipped with a temperature controller (Heidolph Mei Tech Heater, Germany). After a 3 h reaction time, the pH of the dispersion was adjusted to 6.5 by adding 1.0 M NaOH in order to stop the reaction. The starch was collected by centrifugation, washed with distilled water (140 ml, 7 times), dried at 50 °C and ground to pass through a 212 μm sieve. Moisture contents of the samples were determined according to AACCI Approved Method 44-15A (AACCI, 2000).

Table 1
Independent variables and their levels used in the preliminary and main experiments.

Independent variables		Coded factor levels[a]				
		−1	−0.5	0	+0.5	+1
Preliminary experiments	pH (X_1)	8	9	10	11	12
	Temperature (X_2, °C)	25	35	45	55	65
Main experiments	pH (X_1)	10	10.5	11	11.5	12
	Temperature (X_2, °C)	38	46	54	62	70

[a] Independent variable levels were assigned coded factor designations for purposes of statistical analysis.

2.2.2. Experimental design for the cross-linked starch production

In this study, response surface methodology (RSM) was used to optimise the cross-linking conditions of corn and wheat starches to obtain maximum RS content. Design Expert (Stat-Ease, Minneapolis, MN, USA) was used to generate the experimental design. Temperature (T) and pH were chosen as two independent variables in the cross-linking process. Resistant starch (RS) and phosphorus (P) contents of the cross-linked samples were selected as the dependent variables in order to estimate the RS production efficiency.

Preliminary experiments were conducted to select the approximate range for each independent variable before the optimisation process. In the preliminary experiments, five levels were selected for both reaction temperature and pH. Temperature and pH were varied from 25 °C to 65 °C and from 8 to 12, respectively (Table 1). Based on the preliminary experiments, narrower temperature and pH ranges were selected for the main experiments. For the main experimental design, five levels, for each factor, were selected and reaction temperature was varied from 38 °C to 70 °C and reaction pH was varied from 10 to 12 (Table 1).

2.2.3. Determination of RS content as total dietary fibre

In the method commonly used for the determination of RS content (AACCI 32–40; AACCI, 2000), the samples are digested using α-amylase and amyloglucosidase. The undigested part (RS) is dissolved with KOH and converted into glucose by using amyloglucosidase. Then RS content is estimated, based on the amount of glucose determined by GOPOD reagent. However, CL starches were not dissolved to any considerable extent, as has also been indicated in the literature (Wu & Seib, 1990; Hwang et al., 2009). Therefore, it was not possible to use AACCI Method 32–40 for the determination of RS content in CL starches. Hence, RS contents of the CL starches were determined according to "AOAC 991.43: Total dietary fibre determination method" (AOAC, 1998). Sequential enzymatic digestion was applied to the samples using heat-stable α-amylase, protease and amyloglucosidase to remove digestible starch and protein. Enzyme digestate was treated with alcohol before filtering, and total dietary fibre residue was washed with alcohol and acetone, dried, weighed and expressed as % (g RS/100 g dry sample). RS contents of the native corn and wheat starch samples were also determined, using the same procedure.

2.2.4. Determination of phosphorus content

Phosphorus (P) contents of the native and CL starch samples were determined according to the AOAC 986.24 Method (AOAC, 1998) with some modifications. A starch sample (1 g) was weighed into a porcelain crucible and ignited in a muffle furnace at 700 °C for 16 h. After cooling, 10 ml of HCl (25% v/v) and 1 ml of HNO_3 were added to each crucible. The mixture was brought to boil on a hot plate, cooled and transferred quantitatively into a 100 ml flask and diluted to volume with distilled water. One ml of this solution was mixed with 1 ml of vanadate-molybdate solution (Fluka, Switzerland) and 3 ml of distilled water. The absorbance of the solution was measured at 400 nm (Ultraspec III, Pharmacia LKB Biochrom Ltd., England) after the solution was allowed to stand for 10 min at room temperature. A calibration curve was prepared with standard phosphate solutions (KH_2PO_4) containing 0.1–0.6 mg of phosphorus per ml. Phosphorus contents were calculated as follows:

$$P = \frac{A}{16.76} \quad (1)$$