# The Synthesis and Properties of a Cation-Exchange Resin Prepared by the Pyrolysis of Starch in the Presence of Phytic Acid*

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SYNOPSIS

A black charcoal-like material having cation exchange and adsorption properties was prepared by the controlled pyrolysis of starch in the presence of a commercial phytic acid solution. Resins with binding capacities of 0.7–5.7 meq/g of calcium were prepared by varying the phytic acid to starch ratio, the temperature, or the duration of heating of the reaction mixture. SEM photomicrographs of some of these new materials showed that they are composed of particles similar in size and shape to the starting starch granules. These resins also removed atrazine from aqueous solutions. © 1995 John Wiley & Sons, Inc.‡

## INTRODUCTION

The use of ion exchangers will increase annually by an estimated 5.8% into the foreseeable future. Resins for municipal water treatment, food and pharmaceutical product purification, and process cleanup and metal recycling will require 132 million pounds of anion and cation ion exchangers by 1998. The capacity of the ion-exchange resin is the most important attribute for many of these applications. Nevertheless, the type of resin chosen for a particular application will be determined by a balance between stability, capacity, cost of manufacture, and special process requirements. Specificity is another important attribute of an ion-exchange resin. Special types of ion exchangers are required for some applications. For example, resins that have a special affinity for the actinides, and the various radioactive elements will be the purview of the atomic energy scientist while resins that separate enantiomers will be of interest to the medicinal chemist. It is often found that one of the optically active forms of a drug may have a significant beneficial pharmacological effect, whereas its enantiomer may be inactive or possess antagonistic activity. A series of resins based upon the cyclodextrins[1] and the 3,5-dimethylphenylcarbamates of cellulose[2] and amylose[2] have been used to separate stereoisomers.

The incorporation of phytic acid onto the starch matrix offers a number of interesting possibilities. Phytic acid has six phosphate groups. The attachment of one phytic acid molecule to the starch backbone via a phosphate ester bond establishes a highly charged compact locus on the starch backbone. Although the addition of one phosphate molecule to starch affords two exchangeable hydrogens, the addition of one phytate to starch affords 11 exchangeable hydrogens. Because of the high density of phosphates, the modified polymer should have unique properties in terms of its selectivity for cations. It may be possible to separate enantiomers with this new polymer. Crosslinked cylodextrins show a propensity for separating chiral compounds. Amylose has a similar structure in that the helix has six to eight anhydroglucose units per turn just like $\beta$-cyclodextrin. An additional advantage to this type of copolymer is the relative low cost of the starting materials. Starch is inexpensive, and phytic acid is

* Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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a waste product from corn starch production. In 1 year it is estimated that 100 million kg of phytic acid can be found in the steeping liquors produced by the corn wet milling industry. Worldwide, another 2 billion kg could be available from rice.[3]

The immobilization of phytic acid on a biopolymer was reported some years ago.[4] Phytic acid was grafted onto Sepharose-4B to prepare an affinity chromatography column. The biopolymer was activated and crosslinked with base and epichlorohydrin. Then 1,6-diamino hexane was added to give a derivatized sepharose having a 6 + 3 spacer arm. The phosphate groups on phytic acid were activated with dicyclohexylcarbodiimide and immobilized as a phosphoramide onto the terminal amino group. This expensive series of reactions is suitable only for very high-value products such as specialty resins for biochemistry or medicinal chemistry to analyze complex mixtures or to isolate and purify proteins, peptides, carbohydrates, or pharmaceuticals.

A simpler approach for bonding phytic acid phosphate onto the starch backbone is through an ester bond. Thermal dehydration can be used to prepare phosphate esters.[5] A suitable temperature range for this reaction is 120–200°C. Starch undergoes a number of molecular changes in this temperature range, but the monomeric unit is not degraded. Commercially, "dry" starches (in the presence or absence of basic or acid catalysts) are heated at 79–220°C to produce a group of products called pyrodextrins or dextrins.[6–8] During heating, extensive restructuring of the starch molecule occurs. Bond shifting occurs from predominantly 1–4 (depending on the type of starch) to mixtures of 1–4, 1–6, 1–2, and 1–3. The final products are highly branched and have lower molecular weights. When starch is first heated, the small amount of tightly bound water causes hydrolysis. As the water is removed from the reaction milieu, transglycosylation and reversion occur forming new bonds with different configurations ($\alpha \rightarrow \beta$). Small amounts of acids catalyze these reactions. Even though these molecular changes may be extensive, they are not necessarily reflected in the overt appearance of the starch granule.[8] These new materials are called white dextrins (79–120°C, 3–8 h with acid), canary or yellow dextrins (150–220°C, 6–18 h with acid), and British gums (130–220°C, 10–20 h with alkali), and are extensively used as adhesives.[6]

Phytic acid is a strong acid. It would be expected not only to catalyze the above reactions, but also to promote dehydration and result in the formation of highly colored products. Ester formation and crosslinking would occur at the same time. Consequently, the expected product from heating starch in the presence of phytic acid would be a colored polymer having a large cation exchange capacity. The starch granules may or may not appear intact, but the starch backbone will be greatly branched and extensively crosslinked. This report describes the synthesis of such a cation exchange polymer prepared from starch and phytic acid with the use of heat and vacuum. The effects of reagent ratios, temperature, reaction time, and pressure on the calcium ion-binding capacity of these new materials will be discussed.

## EXPERIMENTAL

### Materials and Equipment

A standard size Kugelrohr distillation apparatus (Aldrich, Milwaukee, WI) with temperature control by a Digitherm Model TC-10 (Nichols Scientific Instruments, Columbus, MO) was used for all the pyrolysis experiments. Amylomaize Vll starch (American Maize-Products Co, Hammond, IN) and phytic acid (40% w/w solution in water; Aldrich, Milwaukee, WI) were used as furnished. For HPLC, a BioRad HPX-87H (Hercules, CA) 7.8 × 300 mm, Shandon Ltd. Hypersil MOS-2 C-8 5 μ (Runcorn, Cheshire, UK) 4.6 × 250 mm, and a Hamilton PRP-1 5 μ (Reno, NV) 4.1 × 150 mm, columns were used. Detection of peaks was with an Altex Model 156 RI detector (Beckmann Inst., Allendale, NJ) or with a Spectraphysics Model 8440 UV (Fremont, CA) detector.

### Preparation of Ion Exchange Resins

#### *Method A*

Starch (100 g) was suspended in a solution comprised of 100 mL methanol and 25 mL of the 40% phytic acid aqueous solution. The phytic acid solution contained 560 mg solids/mL. Water and methanol were removed under reduced pressure, and the residue was dried in a heated vacuum oven (85°C) for 16 h. The powder was mixed in a Waring blender to ensure homogeneity. Ten grams of powder in a 500 mL round-bottom flask was placed in the agitated, preheated Kugelrohr (135°C) under vacuum (water aspirator) for 20 min to 3 h. The dark brown to black residue that formed was washed with 200 mL water, filtered, and then washed with 100 mL methanol. The yields of air-dried solids were 4.2–7.6 g.

### *Method B*

Starch (10 g) was suspended in 50 mL of water or methanol in a 500 mL round-bottom flask. Variable amounts of the aqueous phytic acid solution were added to the suspension. Solvent was removed on a rotary evaporator under reduced pressure. The flasks were placed in the agitated preheated Kugelrohr (180°C) under vacuum for 20 min. The residue was treated as described above. The yields of air-dried solids were 3.6–15.0 g.

## HPLC

### *Phytic Acid Solution*

A methanol–water (51.5%, v/v) solution, buffered with tetrabutylammoniumhydroxide–formic acid–sulfuric acid (pH 4.1), was pumped through the heated (45°C) PRP-1 column at 1 mL/min.[9] Detection was with RI.

### *Distillates from Resin Preparation*

A 0.01 *N* sulfuric acid solution was pumped through the heated (45°C) BioRad column at 0.7 mL/min. Peak detection was by RI.

### *Atrazine*

A 57% buffered (5.0 m*M* phosphate buffer; pH 6.8) methanol–water solution was pumped through the C-8 column at 1 mL/min. The atrazine peak appeared at 9.8 min, and was detected by UV (254 nm).

## Measurement of Calcium-Binding Capacity

A sample of the resin (100–200 mg) was suspended 2 h in a stirred, buffered solution (100 mL, pH 7.0–7.2) containing 2.0 m*M* calcium chloride. Unbound calcium ion was determined colorimetrically with tetramethylmurexide.[10]

## Measurement of Atrazine Binding

Samples of resin (22–24 mg) were suspended in aqueous atrazine (1 mL; 70 μg/mL) and shaken for 20 min. The samples were centrifuged at 14000 RPM for 6 min, and aliquots of the supernatant solutions were injected onto the C-8 column. The analyzed solutions contained only 2.8 μg/mL of residual atrazine; a removal of 96%. In similar experiments performed with suspensions containing 50 mg of starch, essentially all of the atrazine remained in solution.

## SEM Photomicrographs

The material was mounted on the surface of aluminum specimen stubs, sputter-coated with 300 Å of 60% Au–40% Pd, and then examined in a JEOL 6400 V Scanning Electron Microscope using accelerating voltages of 1 to 10 KEV. Photographs of representative areas were taken at magnifications of 20×, 100×, and 1000×.

# RESULTS AND DISCUSSION

## Phytic Acid Solution

The phytic acid used to demonstrate the feasibility of preparing ion-exchange materials with starch was a commercial phytic acid solution available from a number of vendors. A sample of this material was analyzed by HPLC and was found to contain a mixture of inositol phosphates (tris-, tetrakis-, pentakis-, and hexakisinositol phosphates; IP3, IP4, IP5, and phytic acid (IP6), respectively). The normalized peak areas were: 11.2% (IP3), 20.9% (IP4), 37.2% (IP5), and 30.7% (IP6, phytic acid). Commercial crystalline sodium phytate is a pure material and shows a single peak on HPLC chromatograms (Fig. 1). Although different batches from the same vendor differed in their phytic acid contents (30–43%), the HPLC profiles of all of the phytic acid solutions were similar. One would anticipate that a resin made from pure phytic acid would have an exchange capacity even greater than the 5.7 meq/g obtained in one of the current experiments. However, the cost of phytic acid purification may exceed the increased value of the ion-exchange material.

## Variables Affecting the Yield and Ion-Exchange Capacity of the Resin

The temperature of the reaction, the time of exposure at that temperature, the ratio of phytic acid to starch, and the pressure at which the reaction was run all affected the quality of the product. Materials having calcium ion-binding capacities from 0.7–5.7 mEq/g have been prepared by changes in these parameters. The lowest capacity value was obtained from a suboptimal extrusion run. However, this run demonstrated feasible production of these materials on a continuous basis in an extruder.

Method A was used to evaluate the effect of time of exposure at 135°C on the binding capacities of the resins produced (Table I). From the data, it is readily apparent that there is an optimum heat-

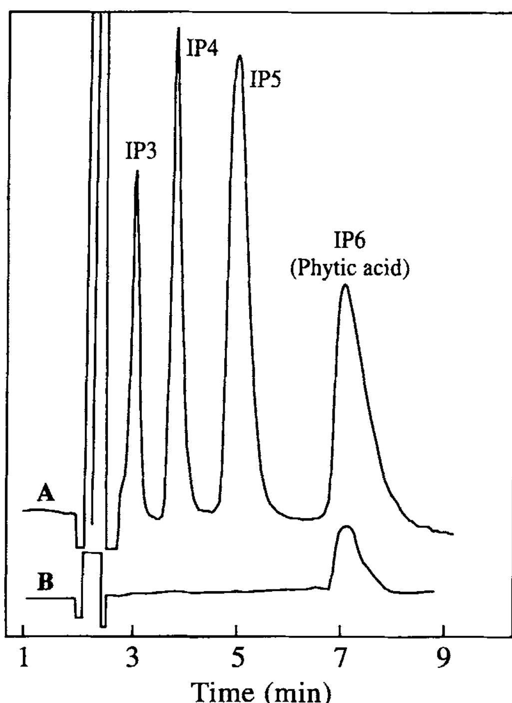


**Figure 1** HPLC chromatogram of a commercial phytic acid solution (a) and pure crystalline sodium phytate. A PRP-1 5 $\mu$ 4.1 × 150 mm column was used with a 51.5% methanol water-buffered solvent system (tetrabutylammonium hydroxide–formic acid–sulfuric acid at pH of 4.1). The eluting solvent was pumped through the heated column (45°C) at 1 mL/min.

ing period for production of a resin having maximal ion-binding capacity. This optimal period will vary with the temperature. For 135°C, it is about 2 h. The SEM photomicrographs show an interesting transition from 1 to 2 h (Fig. 2). After 1 h, discrete granules are still visible. They are somewhat distorted in that many have caved-in centers. After 2 h, many of these granules have coalesced.

Distilled material was collected from each of these runs and analyzed by HPLC (HPX 87H). A total of 14 discrete peaks was found (Fig. 3). The profiles for all the runs were similar, but displayed slight differences in peak area percentages. Surprisingly, a peak corresponding to levoglucosan was not found (Fig. 3).[6] Peaks coincidental with hydroxymethyfurfural[11] and formic acid represented 12% and 37%, respectively, of the normalized peak areas (Fig. 3). Other peaks in the chromatogram correspond to glyoxylic and pyruvic acids. However, positive identification will require additional chromatographic effort or the isolation and independent identification of these materials.

**Table I Effect of Heating at 135°C on the Yield and Ion-Binding Capacity of the Resin**

| Time (Min) | Weight (g) | Ion-Binding Capacity (MEq/g) |
|---|---|---|
| 20 | 4.2 | 0.87 |
| 60 | 6.4 | 1.08 |
| 120 | 6.6 | 2.81 |
| 180 | 7.6 | 1.76 |

The effect of temperature had a similar effect on the ion-binding capacity of the resin produced. A temperature of 180°C for 20 min *in vacuo* gave a good balance between yield (g of resin obtained), ion-binding capacity of resin, and time of reaction. A mixture containing 10 g of starch and 10 mL of phytic acid solution gave 10.2 g of resin having an ion-binding capacity of 3.96 meq/g. When the temperature was raised 20°C, the yield of resin fell by 18% and the ion-binding capacity of the resin fell by 25%.

The effect of vacuum can best be illustrated by comparing two SEM photomicrographs (Fig. 4).

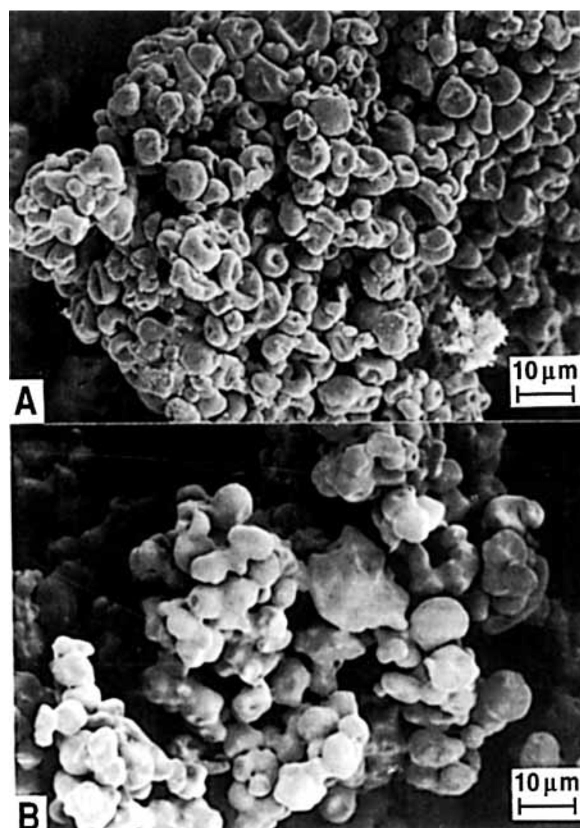


**Figure 2** SEM photomicrographs of a starch–phytic acid mixture heated at 135°C. (A) 1 h, (B) 2 h.

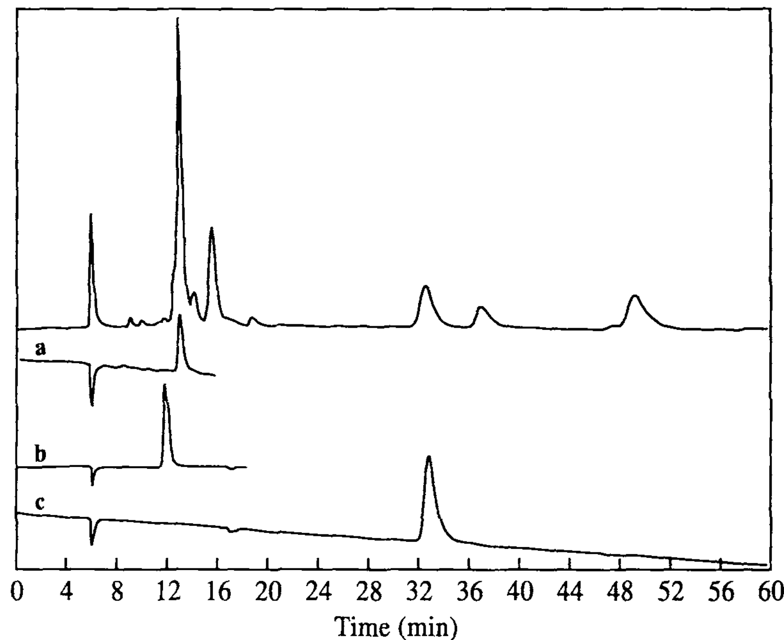


**Figure 3** HPLC chromatogram of distillate from starch–phytic acid mixture heated at 135°C. The heated column (45°C) was a BioRad HPX 87H 7.8 × 300 mm and the eluting solvent (0.7 mL/min) was 0.01 *N* sulfuric acid. Comparison standards: (a) formic acid, (b) levoglucosan, (c) hydroxymethylfurfural.

This series of resins was prepared at 140°C, and the samples still contained a small amount of moisture. Because the sample was heated under reduced pressure, bound water was lost gradually as the temperature increased, and the starch granules remained intact. The sample heated at atmospheric pressure apparently lost its water explosively when the temperature reached the boiling point, and the integrity of the granules was destroyed. It also appears that extensive coalescence of the matrix occurred, which was also apparent from the appearance of the product. The resin prepared in vacuum consisted of fine particles, while the resin prepared at atmospheric pressure was a large cluster that had the appearance of popped corn. Its weight, yields, and ion-binding capacity were reduced by about two-thirds.

An increase in the ratio of phytic acid to starch results in the production of a resin with increased ion-binding capacity. The response, however, is not linear. For example, the resin produced from a 1 : 1 mixture (10 g of starch and 10 mL of phytic acid solution) at 180°C had an ion-binding capacity of 3.96 meq/g, while the resin produced from a 1 : 2 mixture (10 g of starch and 20 mL of phytic acid solution) had an ion-binding capacity of 5.79 meq/g. The granular structure of starch is lost in those resins having high binding capacities.

## Resin Stability

The stability of the resin having an ion exchange capacity of 1.29 meq/g and a discrete granular structure was quite good. After being heated with 2 *N* HCl at 130°C for 5 h in a sealed tube, 70% of the material was recovered and the loss of ion-binding capacity was only 25%. Under similar conditions (2 *N* HCl, 130°C, 2 h), the starch starting material was degraded. The peaks in the HPLC profile of the test solution corresponded to glucose, a disaccharide, oligosaccharides, and a degradation product that emerged at 15.8 min. The material was stable to 0.1 *N* sodium hydroxide and 0.1 *N* HCl. A sample stirred 16 h at room temperature was recovered unchanged. When the granules were treated with a high-temperature amylase (Sigma 3306), only 10% of the mass and 15% ion-binding capacity were lost. This result was not surprising in light of the fact that, at the temperature of the reaction, extensive anomerization, and bond migration have occurred. However, mixtures of glycosidases might degrade this material such as occurs with Polydextrose.[12]

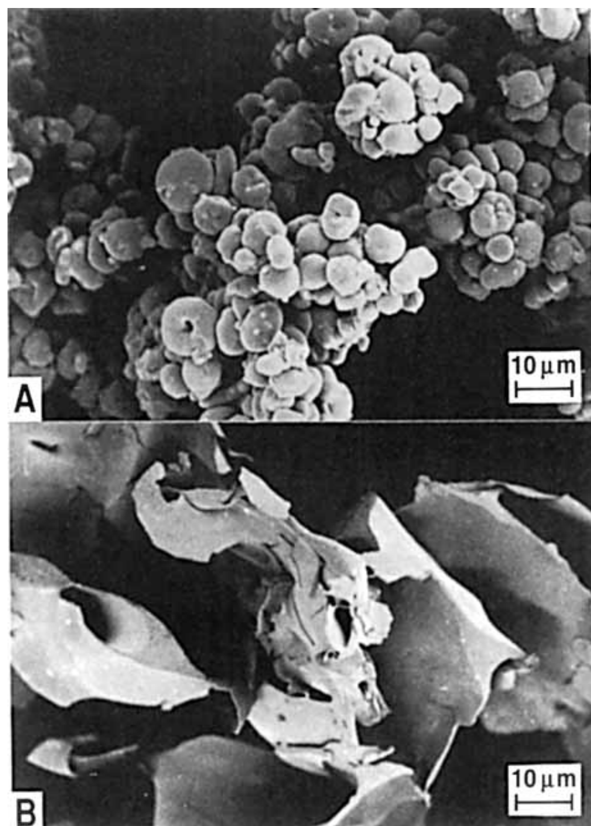


**Figure 4** SEM photomicrographs of starch–phytic acid mixture heated at 140°C. (A) Heated in vacuo, (B) heated at atmospheric pressure.

## CONCLUSION

A new polymer having cation-exchange properties is prepared by the torrefaction of starch and phytic acid. Resins with different ion-exchange capacities (0.7–5.7 meq/g) are prepared by changes in reaction conditions. The starting materials are abundant and relatively inexpensive. This new material is stable to 2 *N* acid and 0.1 *N* base, but should be biodegradable by a host of naturally occurring microorganisms.

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