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Effect of Enzyme Modification of Corn Grits on their Properties as an Adsorbent in a Skarstrom Pressure Swing Cycle Dryer

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Abstract. Corn grits have been tested as a desiccant in a pressure swing adsorption (PSA) system to produce dry air. Two sizes of unmodified corn grits were tested in the PSA system: 2.16 and 0.978 mm in diameter, which dried moist air to dew points of -42°C and -69°C, respectively. A modification technology has been developed for the corn grits that gives an increase in the operational adsorptive capacity in a pressure swing adsorption system, so that they remove as much moisture from air as molecular sieves at the same conditions. After modification, 2.16 mm corn grits dry moist air to a -56°C dew point and the 0.978 mm corn grits dry air to a -80°C dew point. The modification process creates surface modifications on the corn grits apparently making more adsorption sites easily available. The modification procedure increases the specific surface area of the grits and possibly decreases the crystallinity, which would make more hydroxyl groups available for adsorption of water. Possible applications of using corn grits in the pressure swing adsorption system include industrial gas dryers, sorptive cooling air conditioners, and recycling equipment for industrial solvents.

Keywords: materials, synthesis techniques, biochemical, pressure swing adsorption, characterization of properties

Background

Starch, starch-based materials, cellulose, and hemicellulose have an affinity for water (Bushuk and Winkler, 1957; Rodriguez-Arias et al., 1963; Chung and Pfost, 1967) and selectively adsorb water from alcohols and other organic vapors (Ladisch and Dyck, 1979; Hong et al., 1982; Westgate and Ladisch, 1993a). The adsorption properties have been studied for corn starch, corn grits and particles synthesized from a mixture of corn starch and either corn cobs or hemicellulose (Neuman et al., 1986; Westgate et al., 1992; Anderson et al., 1996).

Currently, corn grits are used in industry to dry 2.8 billion liters annually of fuel-grade ethanol produced by fermentation, which is over half of the fuel-grade ethanol produced in the U.S. (Goetz, 1995; Ladisch et al., 1984). Distillation is used to enrich the ethanol from about 10% by mass in the broth to over 90% overhead (Gulati et al., 1996). At atmospheric pressure, simple distillation can produce a maximum ethanol concentration of 95.6% (azeotropic composition). The overhead stream from the distillation column, when passed over a fixed bed of previously dried corn grits, is essentially water free. The concentration of ethanol in the overhead stream can be less than 90% and the adsorption system will still yield a dry product (Ladisch et al., 1984).

The industrially used adsorption system consists of at least two corn grit beds, one of which is in service

to remove water from ethanol-water vapors, and one which is being regenerated. The ethanol-water vapor feed is passed upflow through the bed, and the corn grits adsorb the water, giving a dried ethanol product stream. This ethanol is condensed and collected. The heat given off when the water vapor adsorbs onto the corn grits is stored in the bed directly above the mass transfer zone (Neuman et al., 1986). Hence, a temperature rise at the outlet of the bed signals breakthrough. At this point, the feed is immediately transferred to another bed and regeneration begins. Regeneration is accomplished by passing a noncondensable, preheated, dry gas such as N_2 or CO_2 downflow through the bed. CO_2 is preferred because it is a product of the ethanol fermentation and is currently used as the regeneration gas in industry (Lee and Ladisch, 1987). The incoming, preheated gas is further heated as it passes through the warmer zone at the top of the bed, and as it flows down it causes the water to desorb from the corn grits and be carried out of the system by the regeneration gas.

This system is an energy efficient alternative to breaking the azeotrope using benzene or other organic extracting agents in an azeotropic distillation column. The main energy costs for the corn grit adsorption system are the costs of drying, compressing, and heating the regeneration gas. The feed from the distillation tower is already in vapor form.

This research explores the use of corn grits as an adsorbent in a pressure swing adsorption (PSA) system, where adsorption occurs at pressures above 0.2 MPa (2 atm), and the regeneration of the adsorbent occurs during decompression of the column. Cycling between adsorption and desorption typically occurs at short intervals of 30 seconds to several minutes. Since heat is not added to the system for regeneration, this type of apparatus is sometimes referred to as a heatless dryer.

Introduction

Corn grits are derived from grinding the endosperm portion of the corn seed, which is the storage tissue of the seed. The endosperm composes approximately 82% of the dry weight of the seed and consists of four major components (Fig. 1). The cells of the endosperm contain starch granules (Fig. 2) that are held together by a protein matrix.

There are two types of endosperm: the horny endosperm, which is hard and translucent, and the floury endosperm, which is soft and relatively opaque. The ratio of horny to floury endosperm is approximately 2 : 1 in dent corn, which is the type used in this research. The

Table 1. Composition of Horny and Floury Regions of Dent Corn (dry basis). Data from Kerr (1950).

Constituent	Horny endosperm (%)	Floury endosperm (%)
Starch	80.4	85.6
Protein	13.3	7.7
Sugar	0.4	0.5
Oil	0.7	0.3
Ash	0.3	0.4
Other	4.9	5.5

Table 2. Typical composition of the corn grits (as is basis). Data from Anderson et al. (1996).

Component	% by weight (dry weight basis)
Starch	88.1
Protein	8.5
Fat	0.8
Ash	0.3
Other	2.3

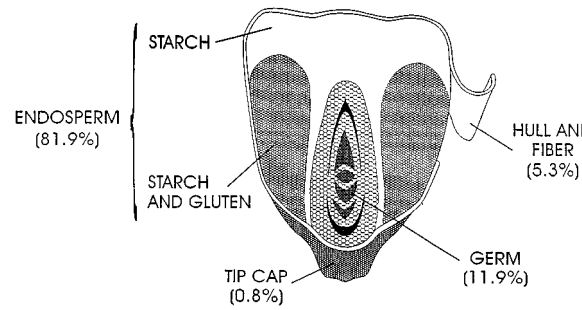


Figure 1. The substructure of a kernel of corn showing the endosperm, hull, tip cap, and germ.

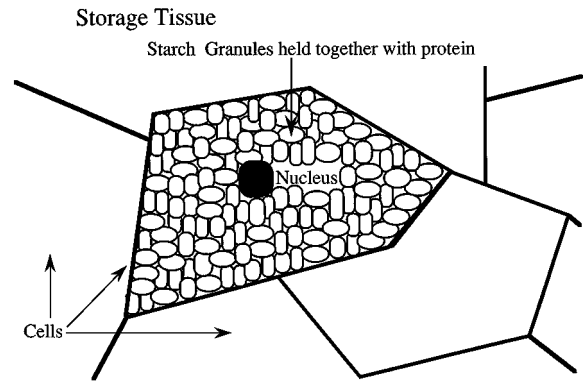
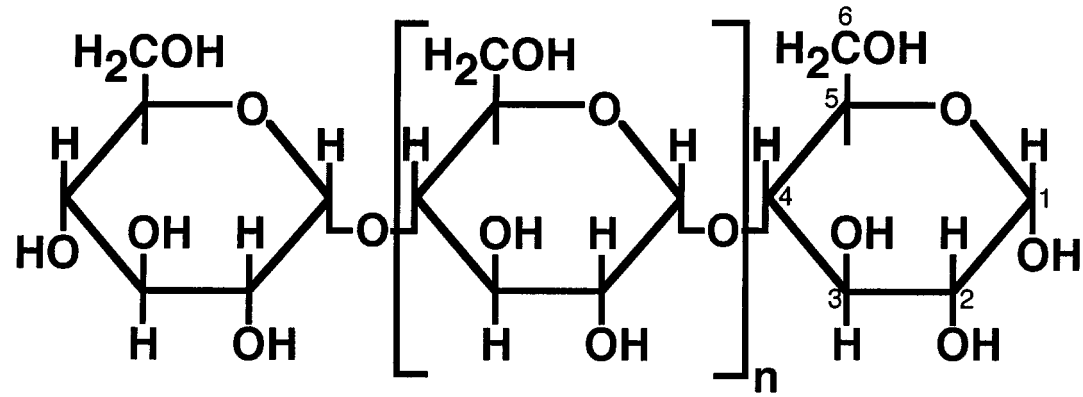
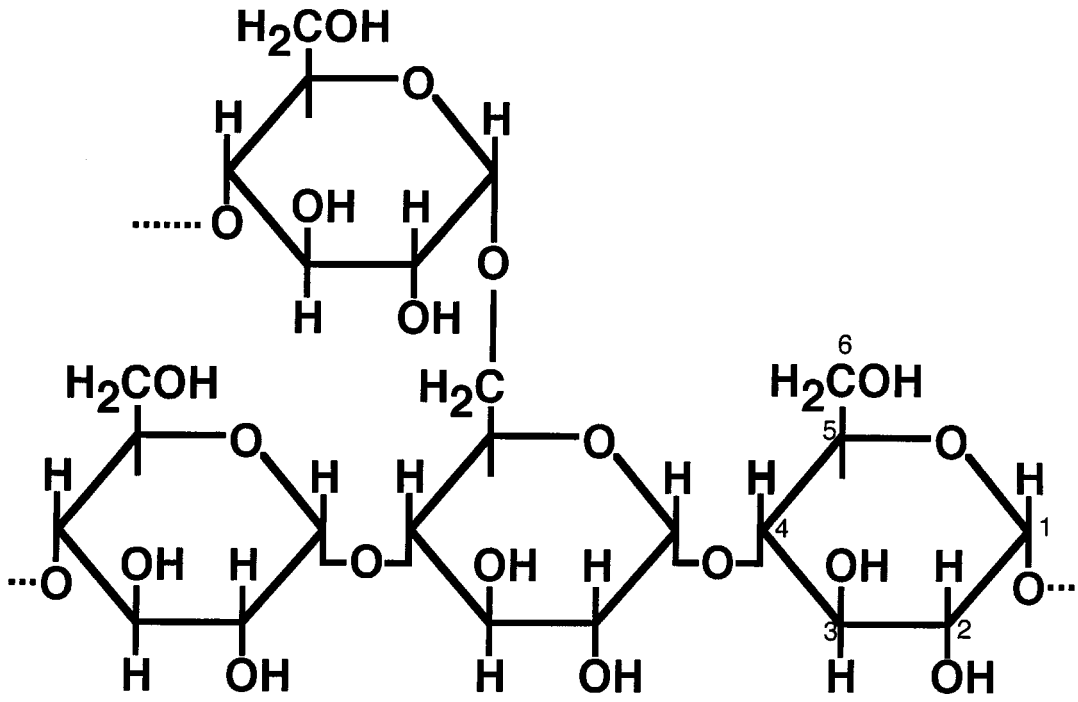


Figure 2. The cellular structure of the endosperm of corn showing the granular organization of starch.



Amylose



Amylopectin

Figure 3. The atomic structural formula of amylose and amylopectin.

compositions of the two types of endosperm are shown in Table 1 and are similar to the overall composition of corn grits (Table 2). The higher amount of protein in the horny endosperm leads to a more compact structure of the starch granules than in the floury endosperm. There are two types of starch in the corn grits, amylose and amylopectin (structures given in Fig. 3). The ratio is approximately 25% amylose to 75% amylopectin. Amylose consists of D-glucose units bound together by α-1,4 O-glycosidic bonds. The structure of amylose

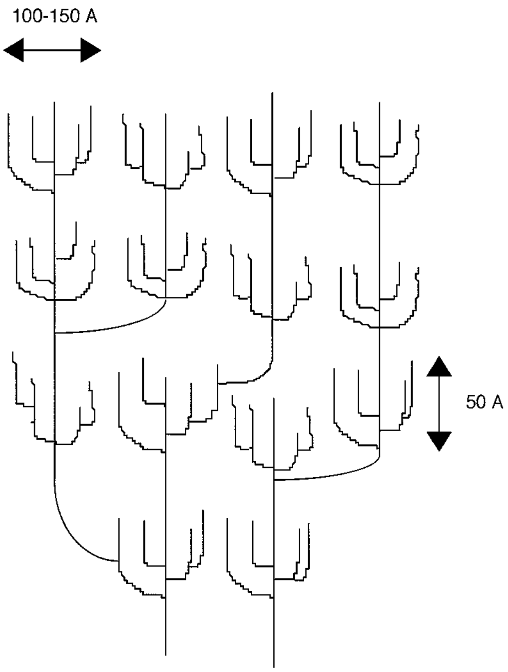


Figure 4. Schematic view of crystalline areas in amylopectin branches. The numbers indicate the approximate length and width of individual branch clusters. (50 Å = 5 nm).

is a helix. Amylopectin is similar to amylose, but it also has α-1,6 O-glycosidic branches every 25–30 units (Fig. 4). The crystallinity of the starch is due to both the amylose and the amylopectin. Amylopectin, even though it branches, will form crystalline double helices between branches (Zobel, 1988).

The mechanism of adsorption of water is understood to involve hydrogen bonding with the hydroxyl (—OH) groups on the starch chains (Rebar et al., 1984) (Fig. 5). Both types of starch chains, amylose and amylopectin, interact with water molecules in this manner. However, the amylopectin structures also physically trap water molecules in the matrix of chain branches (Rebar et al., 1984). When the water molecules are trapped this way, some of the nearby —OH groups become unavailable for hydrogen bonding. The starch chains interact with water as described above even in the presence of a mixture of organic and water vapors. An inverse gas chromatography column packed with starch was found to remove water preferentially from other organic water vapor mixtures, including air-water, alcohol-water, aldehyde-water, organic acid-water, ether-water, pyridine-water, and ketone-water (Westgate and Ladisch, 1993a). The organic compounds were found to elute near the void volume, while

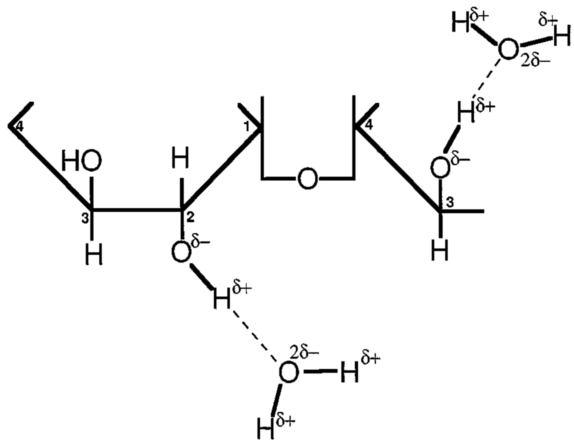


Figure 5. Hydrogen bonding of water with the hydroxyl groups on the starch chains.

the water peak eluted at approximately 4.8 min. Tailing was seen with the organics, but in most cases the tailing had stopped before the water peak eluted. The focus of the current research is the drying of moist air.

Scanning electron microscope (SEM) images taken of the horny and floury endosperm are shown in Figs. 6 and 7, respectively. The larger amount of protein in the horny endosperm leads to a smooth surface with relatively few free starch granules seen on the surface. The floury endosperm contains less protein, so free starch granules are not tightly bound and can be seen covering the surface. The protein in these SEM images is not seen, because it is not stained.

During the testing of several sizes of corn grits in a pressure swing dryer, it was observed that the specific surface area of the corn grits and dew point of the product air were inversely related (Westgate and Ladisch, 1993b; Anderson et al., 1996). This led to the research hypothesis that an induced increase in specific surface area of the corn grits would lower the dew point of the product air in a PSA system. The theoretical maximum specific surface area available is that of starch granules, which, at 5–10 μm diameter, have a specific surface area of 210 m^2/g. However, the corn grits, at 0.978–2.16 mm diameter, have a specific surface area of less than 1 m^2/g. Research was thus initiated to increase the specific surface area of the corn grits by chemical or enzyme treatment while retaining other desirable characteristics of density, flowability, and resistance to attrition.

The modification technology was designed to make the corn grits perform as well as currently used desiccants. To determine if the modified corn grits could

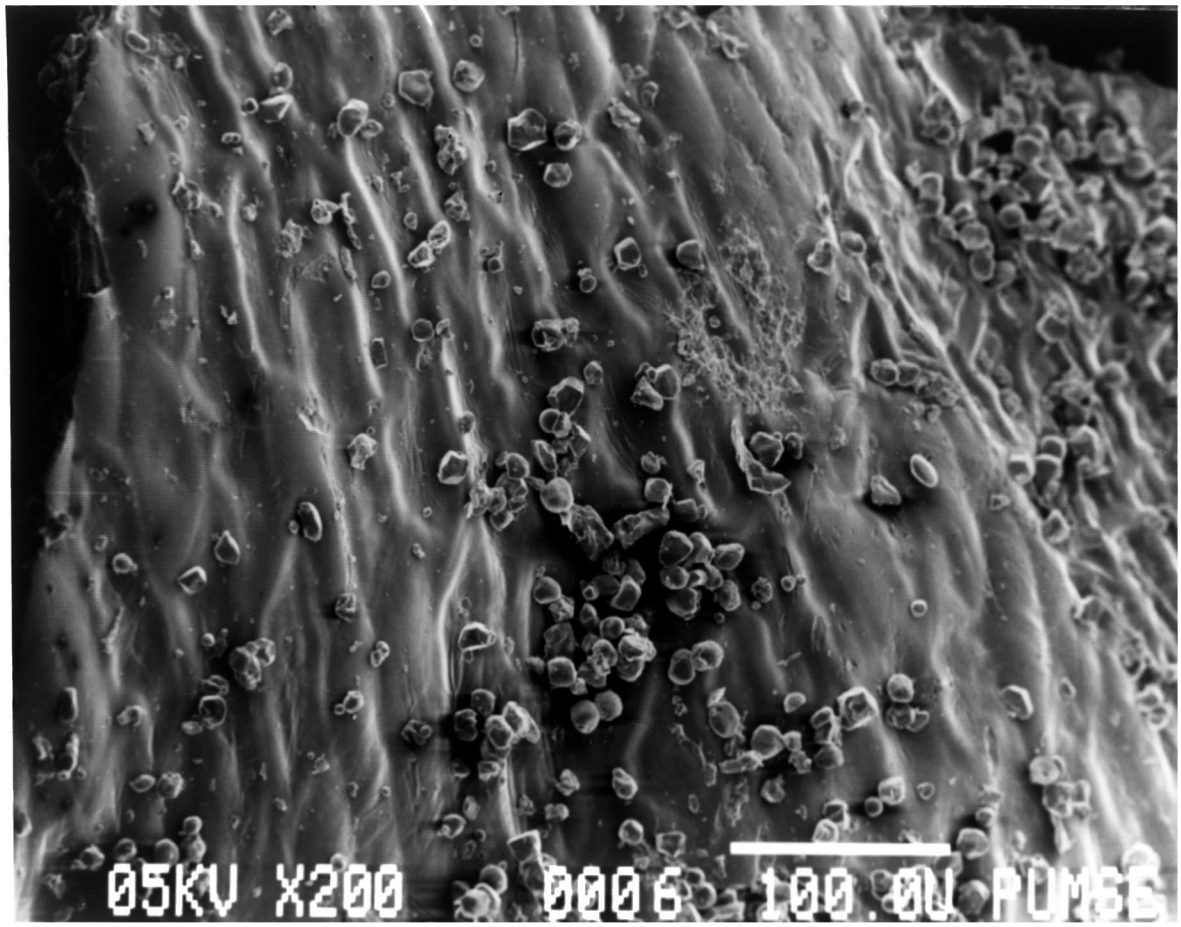


Figure 6. A scanning electron microscope image of the horny endosperm. Note the mostly smooth surface (bar represents 100.0 μm length).

be used as replacements for industrial desiccants, the characteristics of the resulting grits would need to be defined. The determination of the characteristics was accomplished by testing the modified corn grits as a "drop in" replacement in the Skarstrom cycle pressure swing dryer, and by examining the grits in a scanning electron microscope. The operational adsorptive capacity would be determined by the dew point of the product air from the PSA system, and the macrostructure of the surface would be determined by the scanning electron microscope. A drop-in replacement requires defined properties such as a minimum particle size, physical and chemical stability, and operational capacity. A desiccant with these properties will have the advantages of a low pressure drop through the PSA system column, resistance to degradation and fouling, and an operational adsorptive capacity needed for producing low dew point product air from the PSA system.

The operational characteristics of this novel adsorbent in a Skarstrom cycle pressure swing adsorption system are described, and possible mechanisms of sorption are proposed.

Materials and Methods

Pressure Swing Dryer

The device used to dry air, by using corn grits as a desiccant, was the Skarstrom cycle pressure swing dryer (Puregas Model HF 200A106-M30, General Cable Co., Westminster, CO). The apparatus consisted of two desiccant beds and two three-way valves. The operation of the PSA occurred in the following manner:

1. Compressed, moist air at 308 kPa (30 psig) was fed to the first column (with previously dried corn grits)

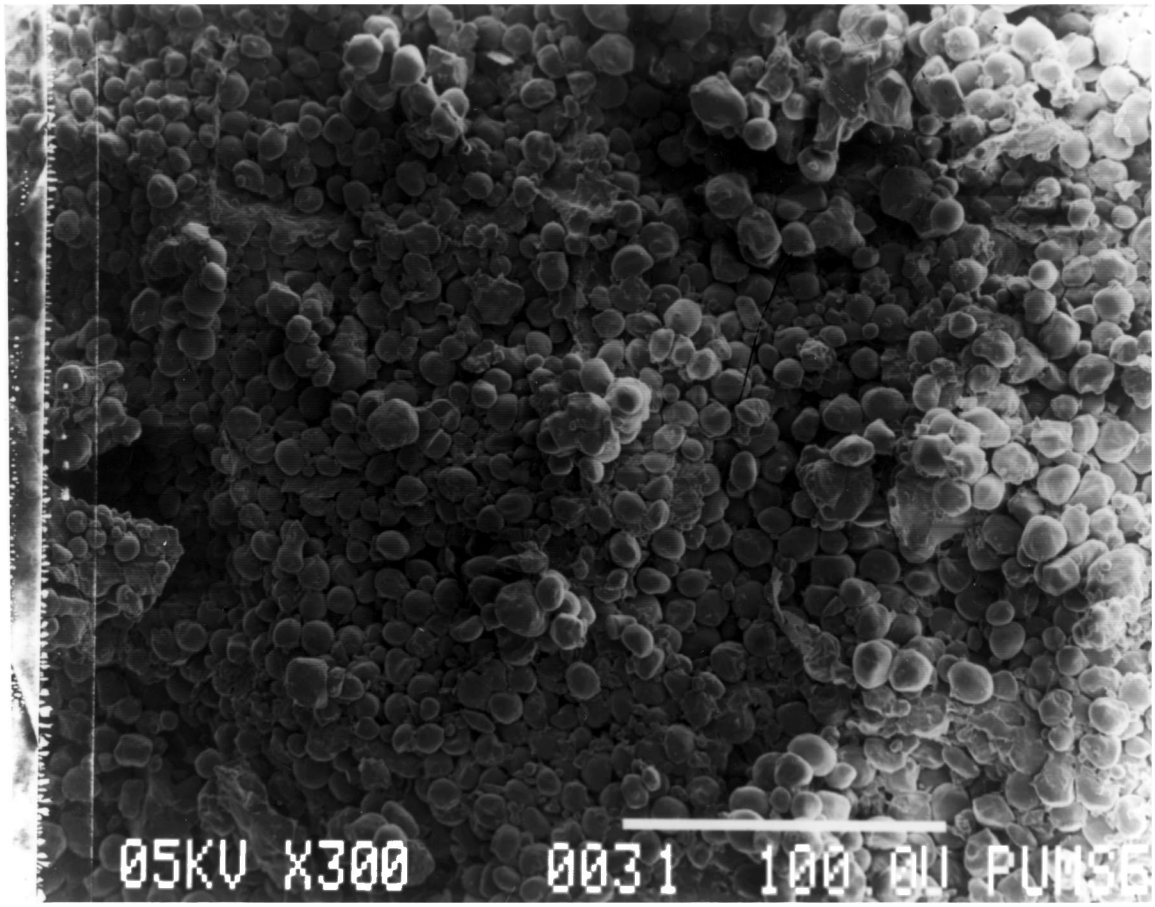


Figure 7. A scanning electron microscope image of the floury endosperm. Note the starch granules covering the surface (bar represents 100.0 μm length).

and the corn grits adsorbed the water, giving dry product air, which was vented to the atmosphere.

2. A portion of the dry air was decompressed to atmospheric pressure and sent through the second column (previously used). The decompression caused the volume of dry air to expand, which meant that a large volume of dry air flowed over the used desiccant. Since most of the adsorbed water was on the surface, this enabled the dry air to carry the moisture from the surface of the corn grits out of the column. This moist gas was the purge gas, which was vented to the atmosphere.
3. Every 30 seconds the valves switched and the process began again.

The conditions at which the pressure swing dryer was run were modified so that the system could be used as an evaluation tool to quickly assess the adsorptive capacity of the corn grits. Consequently, the ratio of the volume of purge gas to feed gas (at their respective pressures) was 2.6 : 1, which is relatively high. Operational ratios for inorganic desiccants generally range from 1.1 to 2.0 (Skarstrom, 1972). Optimization of this desiccant, and a complete comparison of it to molecular sieves also requires that different ratios of purge to feed gas be examined, with the goal of reducing this ratio.

Modification Methods

Several methods were tested to determine if the grits could be successfully modified to increase the specific surface area. The reagents and enzymes used were selected because they would either break down the protein matrix or make the starch more porous. Hydrochloric acid and sulfuric acid act by hydrolyzing starch, which could cause pores in the surface of

the corn grits. Sodium hydroxide disrupts the crystalline areas of the corn grits by causing swelling, which could make the surface area more accessible. Two enzymes were used: α-amylase and cellulase enzyme. Maxaliq® S α-amylase (Bacterial Source: *Bacillus licheniformis*; Lot S F4269, Gist-Brocades International B.V., Charlotte, NC) was utilized because it is an endo-acting enzyme that breaks α-1,4 glycosidic bonds randomly on the amylose and amylopectin chains (Shuler and Kargi, 1992; Ladisch et al., 1983). Cellulase (Cytolase CL; Fungal Source: *Trichoderma longbrachiatum*; Genencor, Inc., San Francisco, CA) was used because it was found to have cross activity on starch (Gulati, 1995). Cellulase is a mixture of three major types of enzyme components consisting of randomly acting endoglucanase (1,4-β-D-glucan glucanohydrolase); exoglucanase (β-D-glucan cellobiohydrolase), which hydrolyzes cellulose from the reducing end with cellobiose as the primary product; and β-glucosidase (cellobiase), which hydrolyzes cellobiose to glucose (Ladisch et al., 1981).

General Modification Procedures

In the initial modification method, 10–12 ml of the diluted modifying agent were added to 1 gram of the 2.16 mm size corn grits in a test tube. The mixture was shaken for 5 seconds in a vortex mixer and then placed aside for 48 hours to 8 days, depending on the modification agent. After the time had elapsed, the solution was discarded and the grits were rinsed repeatedly with water and then dried in an oven. The structural integrity was initially tested by attempting to crush the grits between the fingers. If they did not break apart, then that specific modification was scaled up for the preparation of 300 grams for acid modified or 400 grams for enzyme modified corn adsorbent for testing in the PSA system.

Modifying Agents

Acid and Base. Hydrochloric acid was used in nine different concentrations: 0.05, 0.1, 0.2, 0.5, 1, 2, 3, 4, and 6 N. Sulfuric acid was used in concentrations of 1.5, 3, 6, and 9 N. Twelve milliliters of each acid concentration was added to 1 gram of the corn grits, shaken, and then left to sit for 60 hours (for the HCl) and 70 hours (for the H_2SO_4). Sodium hydroxide was tested in six different concentrations: 0.02, 0.05, 0.1, 0.2, 0.5, and 2 N. Ten milliliters of the basic solutions were added to 1 gram of corn grits, shaken, and set aside for 48 hours.

Cellulase. The enzyme treatment was slightly different. For the cellulase enzyme three solutions were prepared, an undiluted strength, a 1/10 dilution, and a 1/101 dilution of cellulase to water. The solutions were buffered at pH 4.8 with citrate buffer, and warmed to 50°C. Ten milliliters of each cellulase solution were added to 1 gram of corn grits and the mixtures were kept at 50°C in a water bath. Sodium azide (EM Science, Cherry Hill, NJ) was also added as an anti-microbial agent.

Amylase. The α-amylase solution was prepared by adding the enzyme in a 1/50 dilution to phosphate buffer at a pH of 6.9. The buffer was prepared by combining water that had been treated by reverse osmosis and deionization with 2.4 g/l of sodium phosphate (monobasic, NaH_2PO_4; Sigma Chemical, St. Louis, MO) and 0.3915 g/l of sodium chloride (Mallinckrodt, Paris, KY). The pH was then adjusted to 6.9 with aqueous sodium hydroxide (Mallinckrodt, Paris, KY). Sodium azide was also added as an antimicrobial agent. Ten milliliters of the diluted enzyme solution were added to 1 gram of corn grits at room temperature. The enzyme-grit solution was soaked for 8 days and then dried in an oven for 24 hours at 40°C.

Preliminary Determination of Effects of Modification Procedures

From the initial structural integrity results (crushing by hand), 0.1 N sodium hydroxide, 3 N and 1 N hydrochloric acid, and 3 N sulfuric acid were selected for modifying the larger amount of corn grits for testing in the PSA system. The enzyme dilutions for the bench scale procedure were selected based on the extent of conversion to glucose obtained from the test tube runs. A 10% conversion by weight of starch to glucose and maltose was the desired goal, because it was estimated that by removing this amount, the desired porosity would be gained without a significant decrease in structural integrity or size.

After soaking the corn grits in the enzyme solution, samples of the solution were taken to determine the percent hydrolysis of the grits. The samples were spun

Table 3. Effect of enzyme dilution on glucose formed from corn grits after 150 hours at 50°C. Data from Gulati (1995).

Enzyme	Dilution	Activity	pH	% Conversion[a]
Amylase	50×	115 TAU/ml[b]	6.9	14.3
Cellulase	None	59 FPU/ml[c]	4.8	13
Cellulase	10×	5.9 FPU/ml	4.8	1.5
Cellulase	101×	0.58 FPU/ml	4.8	4

[a] Defined as (gram glucose formed/gram starch initially present × 1.11) × 100.
[b] TAU = thermostable amylase unit = one unit is the amount of enzyme needed to completely dextrinize one milligram starch/minute at pH 6.6 and 30°C.
[c] FPU = filter paper units = relates amount of glucose formed from filter paper by the cellulase enzyme.

down in a centrifuge to obtain solid-free liquid. The percent conversion of the starch was found for the cellulase enzyme by injecting 10 μl of the liquid from the corn grit/enzyme solutions into a Beckman Glucose Analyzer 2 (Fullerton, CA), which measured the glucose concentration. To determine the conversion due to the α-amylase, a 50 μl sample of the corn grit/enzyme solution was injected into a Bio-Rad (Hercules, CA) HPX-87C liquid chromatography column to determine glucose and maltose content. The HPX-87C column is the calcium form of sulfonated divinyl benzene styrene copolymer and can separate carbohydrates. The mobile phase was 0.2 μm filtered, degassed, deionized water at 85°C and a flow rate of 0.6 ml/min. A Waters differential refractometer (Model R401, Milford, MA) was used as the detector. The highest percent conversions were for the 50 times diluted amylase and the undiluted cellulase. The percent conversions of starch for the enzymes after 150 hours of soaking are shown in Table 3.

Scale-up of Modification Procedures

The scale-up to 300 or 400 grams of the grits occurred simply by making 1 liter of the specific solution and placing the desired amount of corn grits in the solution. The corn grits were soaked for the specified amount of time with sodium azide added as an antimicrobial agent at a concentration of 0.02 g/100 ml of solution. After being soaked, the grits were washed and rinsed several times over a few days, then dried in an oven for 24 hours at 40°C. After this process, the grits were tested in the PSA system.

Sieve Analysis

The particle sizes of the grits before and after enzyme treatment were examined using a sieve size analysis shaker (Fritsch Analysette, Germany). The sieve sizes used were 0.150, 0.180, 0.250, 0.355, 0.500, 0.710, 0.850, and 1.18 mm.

Scanning Electron Microscope

The corn grits were examined using a JEOL T300 Scanning Electron Microscope. First, the dried material was coated with gold/palladium for conductivity using an Anatech LTD Hummer 6.2 sputter coater. The samples were examined at operating voltages of 5 kV, 15 kV, or 20 kV.

Surface Area Measurements

The specific surface areas of the corn grits were determined by the BET method (Brunauer et al., 1938). The apparatus used was a Quantasorb adsorption device (Quantachrome Corporation, Syosset, NY). The specific surface area was determined by immersing a sealed tube of dried grits in liquid nitrogen at 77 K and passing a stream of gaseous nitrogen over it. The nitrogen adsorbed onto the surface to form a monolayer, and when the tube was taken out of the liquid nitrogen, the monolayer desorbed from the corn grits and was measured. This measurement was used to calculate the monolayer surface area, which was divided by the mass of the sample to give specific surface area.

Attrition

During an extended test period of the unmodified corn grits in the pressure swing dryer, over a total of 88 days, or 250,000 cycles, the weight loss by attrition was found to be less than 1% (Westgate and Ladisch, 1993b). This result initiated interest in testing the attrition resistance of the modified grits. The grits were also tested, for comparison purposes, against molecular sieves (3A, Aldrich Chemical Co., Inc., Milwaukee, WI) and silica gel (14–20 mesh, Aldrich Chemical Co., Inc., Milwaukee, WI) using a Crescent Dental Mfg. Co. Wig-L-Bug Amalgamator (Lyons, IL). A 0.5 gram sample of the material was placed in the cylindrical, stainless steel sample holder (3 cm long × 1 cm diameter), which also held a single 0.5 cm stainless steel

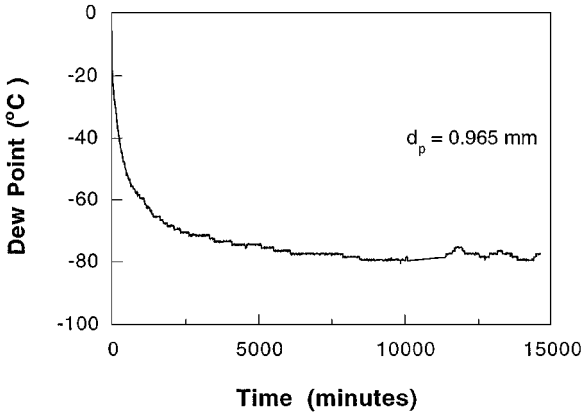


Figure 8. Plot of dry-down rate using modified grits.

ball, and set to shake for 2.5, 5, or 10 seconds. The sample was removed from the holder and sieved using a 0.075 mm sieve size. The final weight of the material retained on the sieve was obtained. The initial weight minus the final weight divided by the initial weight gave the percent fines.

It is interesting to note that the operational capacity did not decrease over the 88 days. There are no filters in the system except for oil droplet traps, so any contaminants contained in the air compressor inlet stream that might adsorb onto the corn grits do not cause a decay in their performance as a desiccants.

Results and Discussion

All of the modified corn grits were tested in the pressure swing dryer for improvements in product air dew point. The acid and base modified and the cellulase modified corn grits increased the product air dew point. The α-amylase modified corn grits were the only material that showed a decrease in the product air dew point.

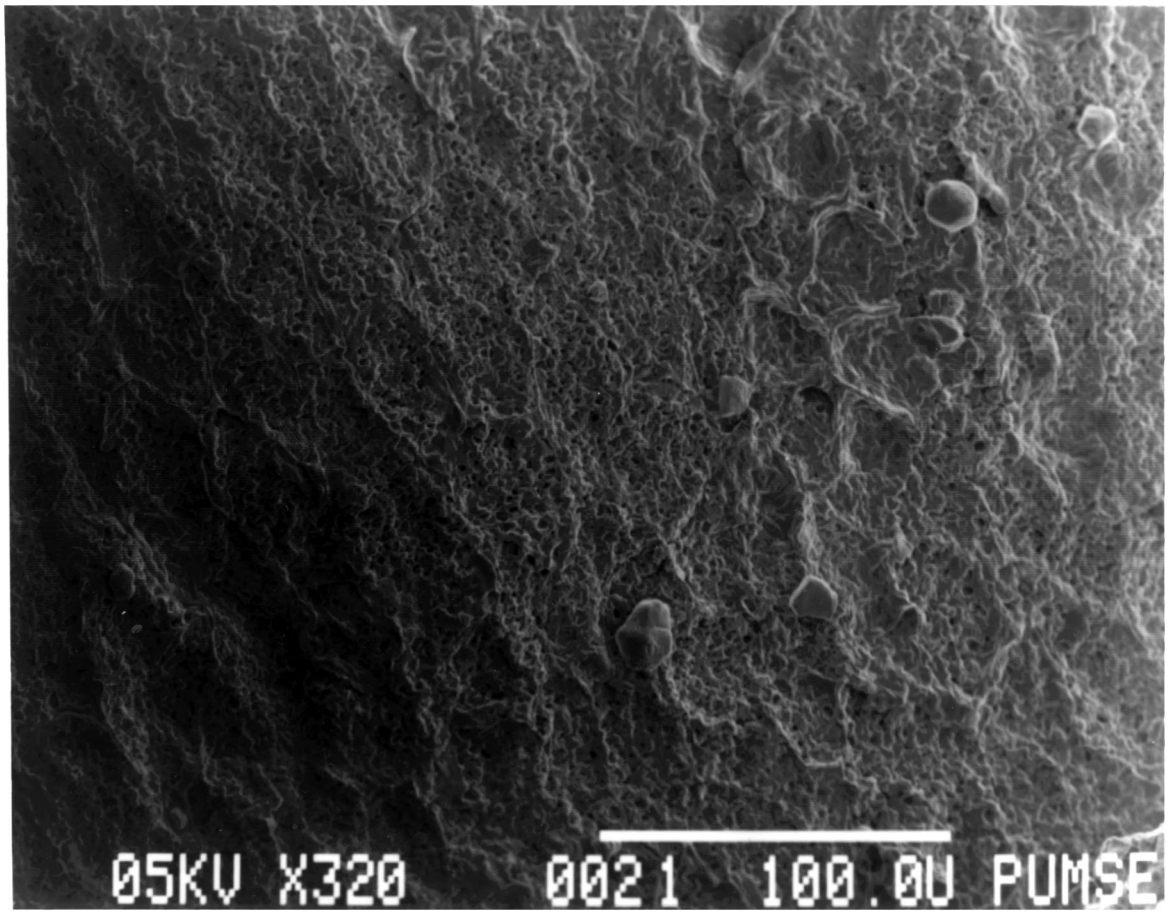


Figure 9. A scanning electron microscope image of the α-amylase modified horny endosperm (bar represents 100.0 μm length). Note pits and pinholes in comparison to unmodified horny endosperm (Fig. 6).

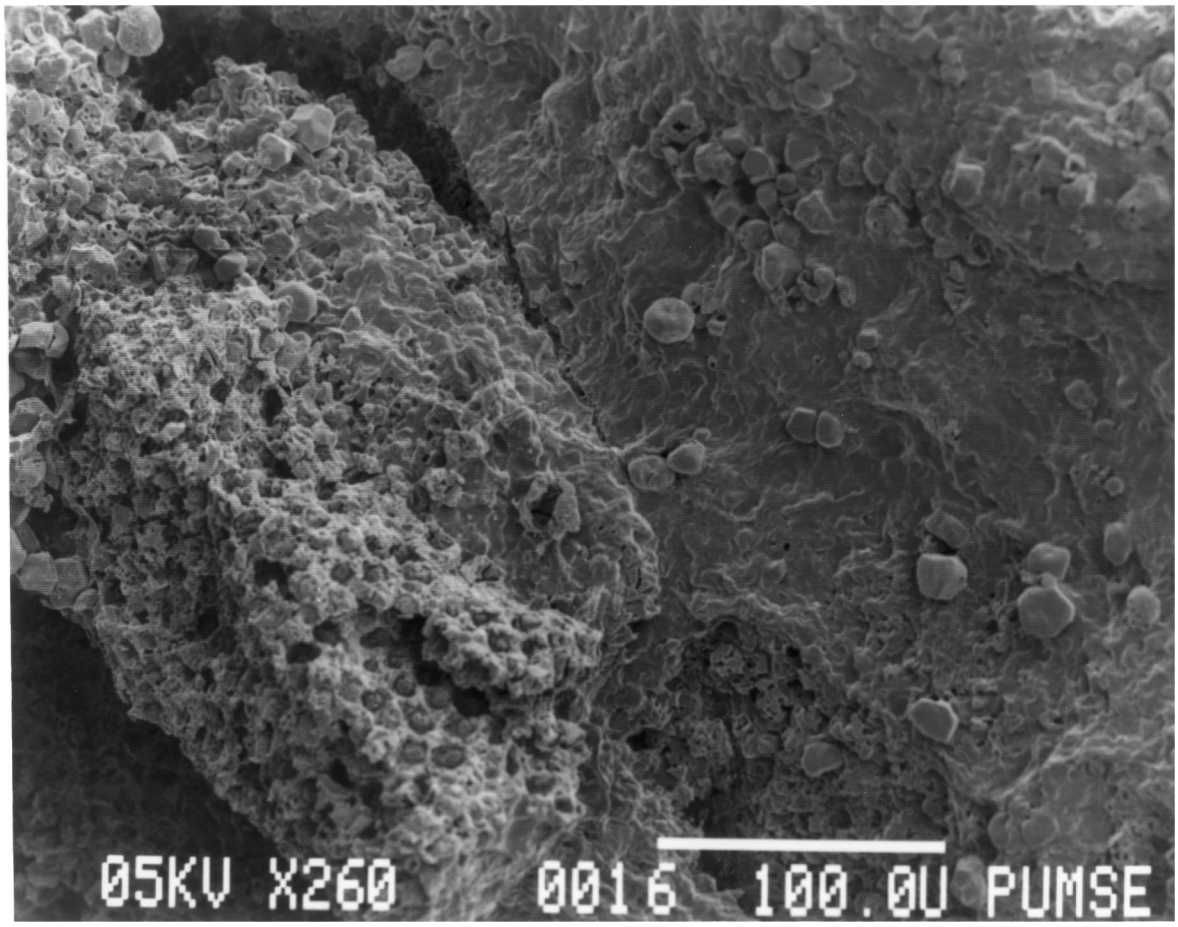


Figure 10. A scanning electron microscope image of the α-amylase modified floury endosperm (bar represents 100.0 μm length). Compare to unmodified floury endosperm (Fig. 7).

α-Amylase Modified Corn Grits

Since only the grits soaked in α-amylase had some improvement in dew point after being modified, they are the focus in this section. The sieve size analysis showed that the size of the grits changed from a 2.16 mm mean unmodified size to a 2.12 mm mean modified size. A 0.978 mm mean size of corn grits was also modified and the mean final size was 0.965 mm. The change in diameter was less than 2% for both sizes, so the size reduction was small.

The 2.12 mm corn grits were able to dry moist air to a -56°C dew point and the 0.965 mm corn grits to a -80°C dew point, which was the detection limit of the hygrometer. A sample dry down of the product air over time using the modified 0.965 mm corn grits in the PSA is shown in Fig. 8. The dew point of the product air rapidly dropped at first and then slowly attained steady state at -80°C.

Scanning electron microscopy showed that the action of the α-amylase enzyme was to create pinholes and pitting in the starch. An SEM image of the horny endosperm is shown in Fig. 9 and it is easy to see (comparing to Fig. 6) the holes that the enzyme created in the previously smooth surface. Figure 10 shows an SEM image of the floury endosperm. The surface appears radically changed in comparison to the unmodified structure (Fig. 7). Figure 11, a magnified view of the same area, shows that the enzyme stripped away layers of starch.

SEM images of cellulase treated grits show that the enzyme mixture acted differently on the corn grits than the α-amylase. Figure 12 shows an area of the corn grits where the starch granules have been hollowed out.

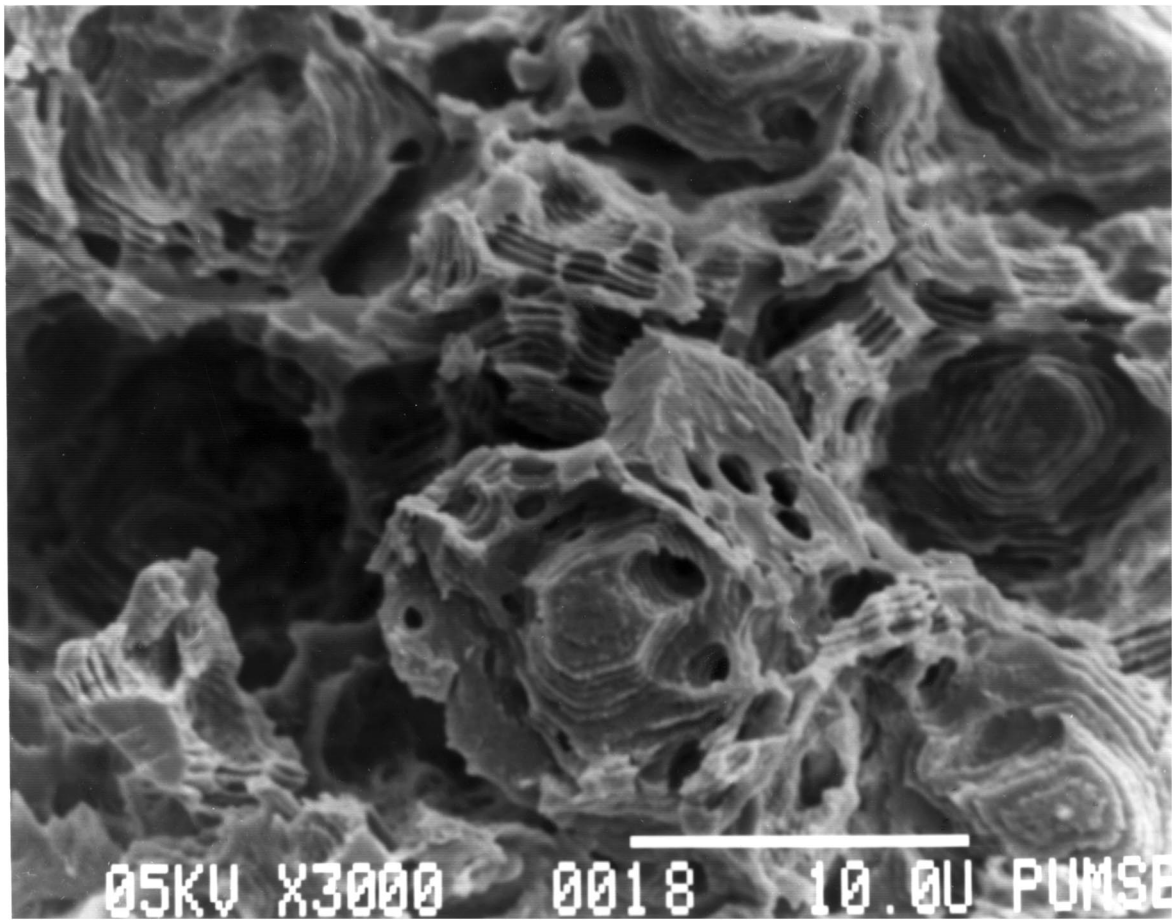


Figure 11. Higher magnification scanning electron microscope image of the α-amylase modified floury endosperm (bar represents 100.0 μm length).

This is different from the pits and pinholes caused by the α-amylase. The action of the cellulase seems to hydrolyze the remaining starch. However, this does show that the cellulase may have cross-activity on starch. It is also possible that this cellulase preparation may contain amylolytic enzymes, although, if present, these enzymes exhibit a different pattern of action than that of α-amylase, shown in Figs. 9 and 10. It is also interesting to note that straight visible lines are clear in the picture, indicating where the cellulase removed the cell walls. Figure 13 shows another area of the cellulase treated corn grits where it appears that the cellulase has removed enough of the protein that holds the starch granules together to allow entire cells to fall off.

The specific surface area was measured by BET adsorption of a nitrogen monolayer onto the corn grits. Figure 14 shows a graph of the BET specific surface area versus steady-state dew point of the product gas. It can be seen for the two larger sizes of corn grits, the native 2.16 mm size and the modified 2.12 mm size, that neither the particle diameter nor the BET specific surface area changed much; however, there was a large change in the steady-state dew points. The native 0.976 mm and modified 0.965 mm sizes had a more noticeable difference in both specific surface area and in steady-state dew point.

The small change in specific surface areas indicates that the large change in steady-state dew point was not just due to the creation of pores and variations in surface texture. Possible explanations for the improved performance of the modified grits are that scission of the starch chains on the surface occurred without deep pores being formed, a disruption of the crystallinity occurred due to the extended soaking of the corn grits or possibly to the action of the α-amylase, or that during the soaking period, hydroxyl groups changed

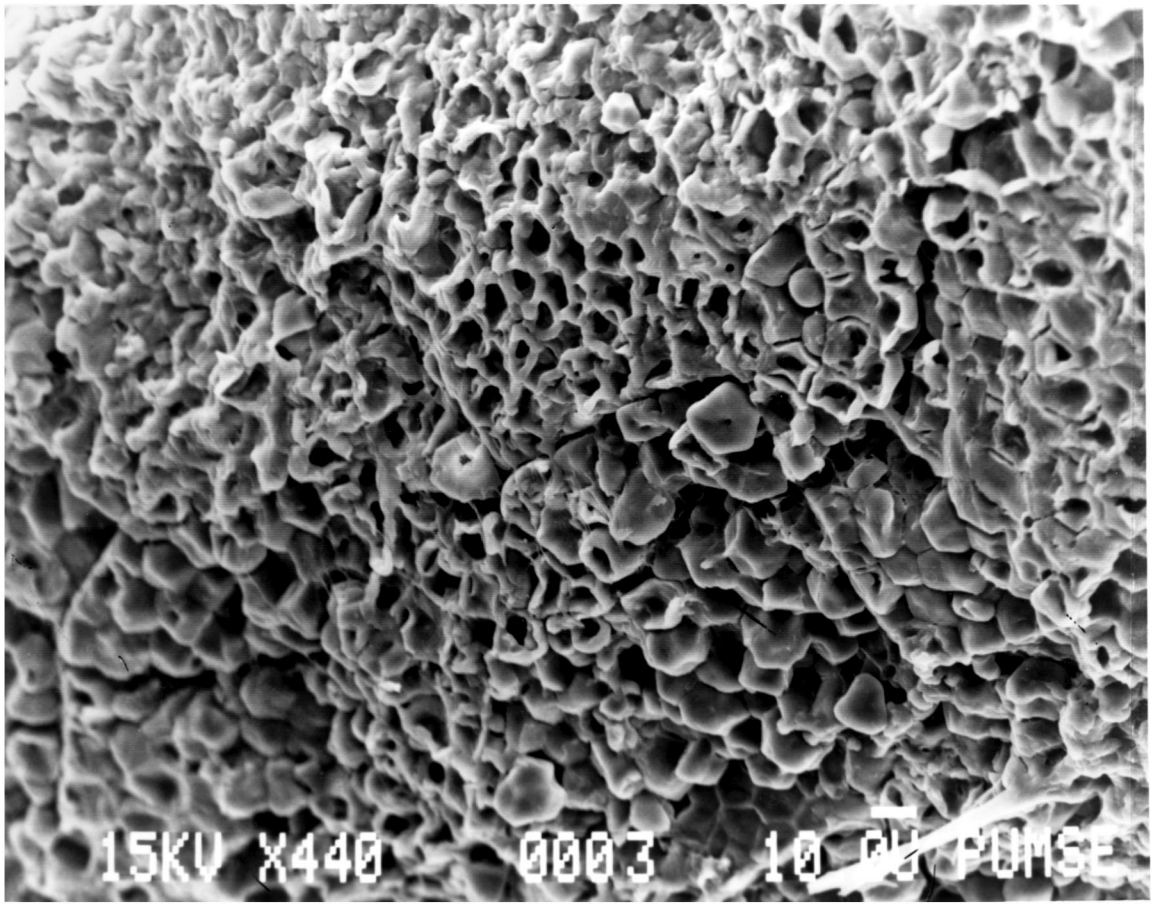


Figure 12. A scanning electron microscope image of the cellulase modified corn grits. Note the hydrolyzing action of cellulase (bar represents 100.0 μm length).

their orientation to become more accessible to the water molecules. For each scission that the α-amylase makes in the starch chain, two new hydroxyl groups are formed. This is a small percentage, however, of the hydroxyl groups already present on a 20 to 200 glucose unit long starch chain. If the crystallinity were disrupted during the modification, the hydroxyl groups that were associated with hydrogen bonds would be free for water adsorption sites.

The individual effects might not make a large difference in the product air dew point, but could exhibit a synergistic effect. All of the previous mechanisms would allow more ─OH groups to become available for adsorption of water without a marked change in the surface area.

In the PSA system, the loading/regeneration cycles are only 30 seconds, therefore only a fraction of the equilibrium water sorption capacity is utilized. A quantitative value for the equilibrium water sorption capacity was found by applying the potential theory using data from Westgate et al. (1992) (Table 4). The potential theory equation for the volume of adsorbed phase (W) for large pore materials is

$$\ln W = \ln W_o - (\kappa_2/\beta)[RT \ln(P_o/P)]$$

This gives an equilibrium loading capacity of $W = 0.054$ gram water/gram corn grits at 25°C. However, the operational capacity of the corn grits in the pressure swing dryer is much lower. For example, the 0.965 mm corn grits had an operational capacity of 0.000045 grams of water/gram of corn grits for each 30 second cycle, less than 0.1% of equilibrium moisture.

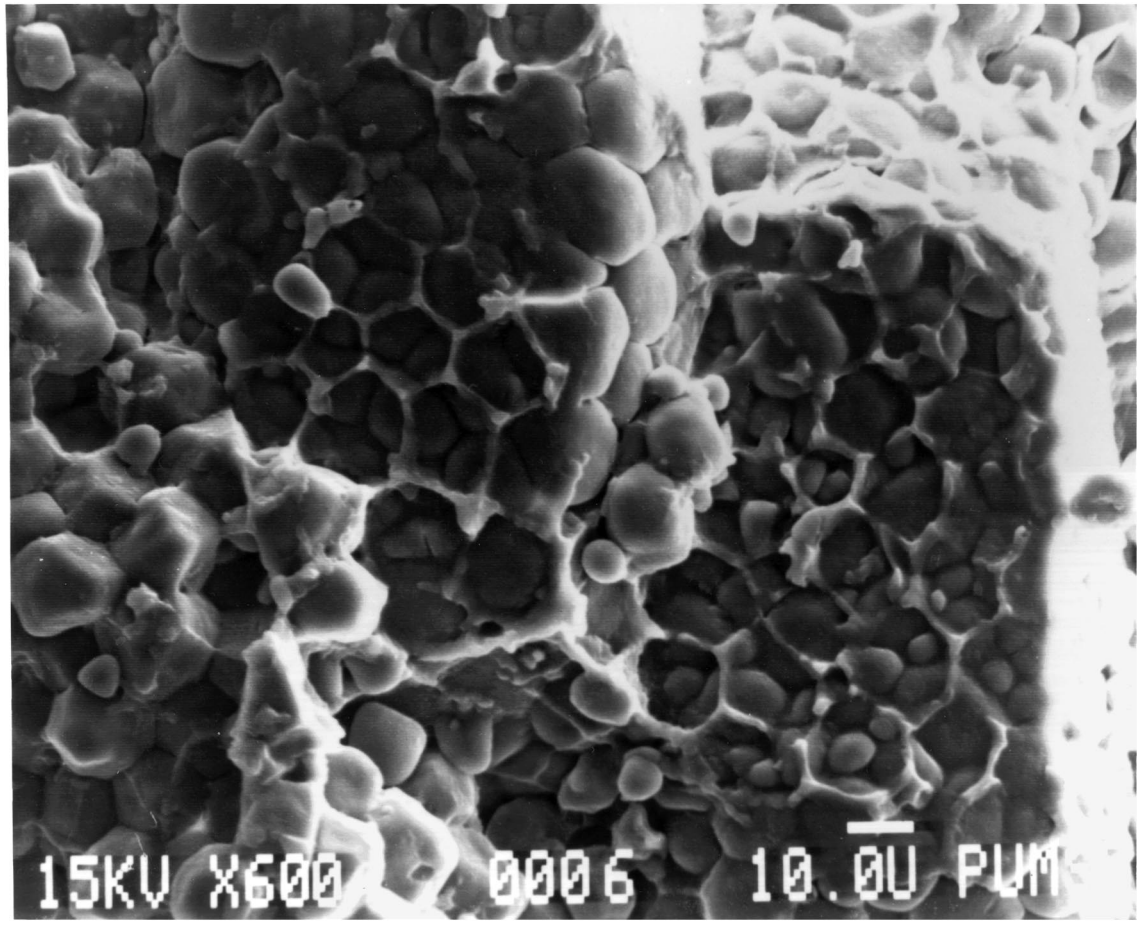


Figure 13. A scanning electron microscope image of the cellulase modified corn grits. Note the flat edges and remaining protein on the endosperm cells (bar represents 100.0 μm length).

The steady-state drying capacity of the native corn grits was a function of the total specific surface area, as shown by the difference in the final dew points of the

Table 4. Values of variables in the potential theory (at 37.5°C and 25°C inlet air). Data from Westgate et al. (1992).

Variables	Value
W_o	$W'_o \exp(A_2/T)$
W'_o	0.019
A_2	695
R	8.31451 J/mol K
T	310.5 K
P_o/P	$(0.1268)^{-1}$
κ_2/β	0.000224

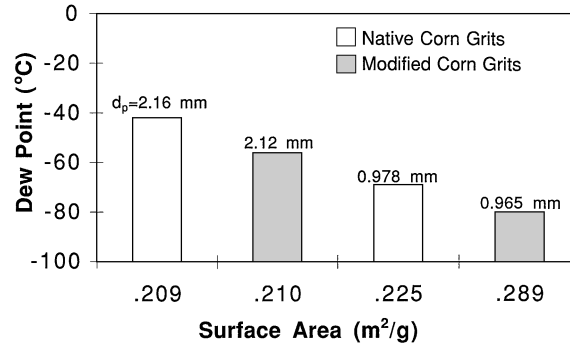


Figure 14. Pressure swing dryer: Outlet dew points vs. specific surface area.

2.16 mm and 0.978 mm sizes (Fig. 4). However, since the particle diameters did not differ greatly between the native and modified corn grits, the packing densities of

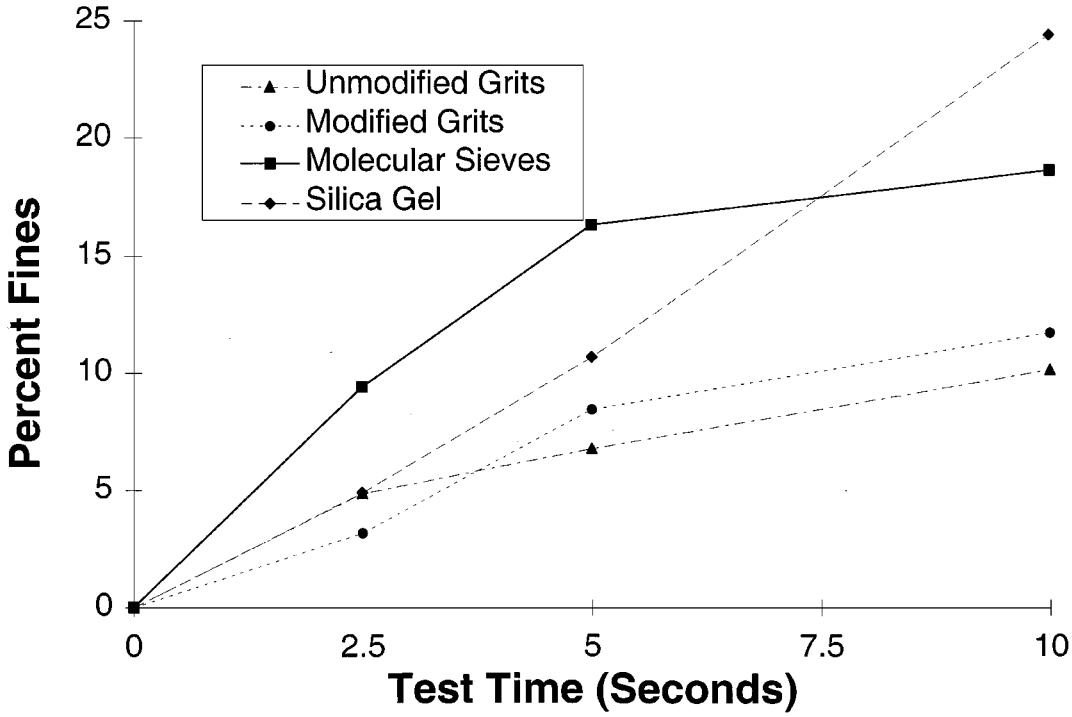


Figure 15. Attrition tests for various desiccants showing resulting fines as test time increases.

the native and modified grits were determined. It was found that the density of the native grits was higher than that of the modified grits even though the specific surface area remained similar between the modified and native grits. Table 5 shows the packing density of each type of corn grits. It is clear that the difference in specific surface area cannot be the only factor causing the change in adsorptive capacity between the native and modified grits.

The attrition test was designed as an accelerated test to estimate how the grits would degrade mechanically over long periods of use in the pressure swing dryer. The results for unmodified grits, modified grits, molecular sieves, and silica gel are shown in Fig. 15. The sizes of all are within the same range of 0.965 to 1.18 mm. It can be seen that the grits had lower attrition than both the silica gel and molecular sieves.

The next steps for the modified corn grits will be to test them for an extended length of time in the pressure swing dryer and other testing. The other testing methods would include determination of equilibrium adsorption capacity of water vapor, fixed bed operational capacity from atmospheric pressure air, and adsorption of water from water-ethanol vapors.

Table 5. Packing densities of the different sizes of native and modified grits.

	Packing density (g/ml)
0.978 mm Native	0.73
2.16 mm Native	0.76
0.965 mm Modified	0.63
2.12 mm Modified	0.68

Conclusions

The pressure swing adsorption system relies on the water adsorbing capability of the surface of the corn grits. The modification of grits with α-amylase allowed the grits to adsorb more water. Electron microscopy provides evidence this was due to pores that were created by enzyme modification and which increased the specific surface area. The enzyme activity may also have enhanced accessibility of $-$OH groups on the surface. Effects other than specific surface area must be

considered since the dew point of the product air decreased for the larger size of corn grits while the specific surface area stayed approximately the same.

The data from the pressure swing dryer show that a starch-based adsorbent is a possible drop-in replacement for currently used industrial desiccants, under the same purge to feed gas ratio as used in this work. The potential benefits of a starch-based desiccant are that it is inexpensive (corn costs approximately $0.10 per pound), renewable, resistant to attrition, biodegradable, and avoids expensive disposal costs.

Nomenclature

W	$N \times V$ = volume of adsorbed phase	cm^3/g
W_o	Limiting volume of adsorbed space micropore volume	cm^3/g
W'_o	Preexponential constant in the expression for W_o	cm^3/g
R	Gas constant	J/mol K
T	Temperature K	
(P_o/P)	Relative humidity	—
A_2	Constant reflecting temperature dependence of W_o	K
nm	Nanometers = 10 Å	
κ_2	Large pore constant	$(J/mol)^{-1}$
β	Affinity coefficient that characterizes the polarizability of the adsorbate (dimensionless)	—

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References

Anderson, L.E., M. Gulati, P.J. Westgate, E.P. Kvam, K. Bowman, and M.R. Ladisch, "Drying of Gases Using a New Polysaccharide Based Adsorbent," *Ind. Eng. Chem. Res.*, **35**, 1180–1187 (1996).

Brunauer, S., P.H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).

Bushuk, W. and C.A. Winkler, "Sorption of Organic Vapors on Wheat Flour at 27°C," *Cer. Chem.*, **34**, 87 (1957).

Chung, D.S. and H.B. Pfost, *Trans. ASAE*, **10**, 549 (1967).

Goetz, R.J., "Change in the Air," *Forefront*, **6**, 2 (1995).

Gulati, M., "Studies on Methods for Lowering Fuel Alcohol Production Costs," Master's Thesis, Purdue University, West Lafayette, Indiana, 1995.

Gulati, M., P.J. Westgate, M.A. Brewer, R.L. Hendrickson, and M.R. Ladisch, "Sorptive Recovery of Dilute Ethanol from Distillation Column
Bottoms Stream," *Appl. Biochem. Biotechnol.*, **57/58**, 103–119 (1996).

Hong, J., M. Voloch, M.R. Ladisch, and G.T. Tsao, "Adsorption of Ethanol-Water Mixtures by Biomass Materials," *Biotechnology and Bioengineering*, **24**, 725 (1982).

Kerr, R.W., *Chemistry and Industry of Starch*, p. 36, Academic Press, Inc., New York, 1950.

Ladisch, M.R. and K. Dyck, "Dehydration of Ethanol: New Approach Gives Positive Energy Balance," *Science*, **205**, 898 (1979).

Ladisch, M.R., J. Hong, M. Voloch, and G.T. Tsao, "Cellulase Kinetics," *Trends in the Biology of Fermentations for Fuels and Chemicals*, 55–83 (1981).

Ladisch, M.R., K.W. Lin, M. Voloch, and G.T. Tsao, "Process Considerations in the Enzymatic Hydrolysis of Biomass," *Enzyme Microb. Technol.*, **5**, 82–102 (1983).

Ladisch, M.R., M. Voloch, J. Hong, P. Bienkowski, and G.T. Tsao, "Cornmeal Adsorber for Dehydrating Ethanol Vapors," *Ind. Eng. Chem. Process Des. Dev.*, **23**, 437–443 (1984).

Lee, J.Y. and M.R. Ladisch, "Polysaccharides as Adsorbents," *Biochemical Engineering V*, M.L. Shuler and W.A. Weigand (Eds.), The New York Academy of Sciences, New York, 1987.

Neuman, R., M. Voloch, P. Bienkowski, and M.R. Ladisch, "Water Sorption Properties of a Polysaccharide Sorbent," *I&EC Fundamentals*, **25**, 422 (1986).

Rebar, V., E.R. Fischbach, D. Apostolopoulos, and J.L. Kokini, "Thermodynamics of Water and Ethanol Adsorption on Four Starches as Model Biomass Separation Systems," *Biotechnology and Bioengineering*, **26**, 513–517 (1984).

Rodriguez-Arias, J.H., W.W. Hall, and F.W. Bakker-Arkema, *Cereal Chemistry*, **40**, 676 (1963).

Shuler, M.L. and F. Kargi, *Bioprocess Engineering*, pp. 94–95, Prentice-Hall, Inc., New Jersey, 1992.

Skarstrom, C.W., "Heat Loss Fractionation of Gases Over Solid Adsorbents," *Recent Developments in Separation Science.* Vol. II, N.N. Li (Ed.), CRC Press, Cleveland, 1972.

Westgate, P.J. and M.R. Ladisch, "Sorption of Organics and Water on Starch," *Ind. Eng. Chem. Res.*, **32**, 1676–1680 (1993a).

Westgate, P.J. and M.R. Ladisch, "Air Drying Using Corn Grits as the Sorbent in a Pressure Swing Adsorber," *AIChE Journal*, **39**, 720–723 (1993b).

Westgate, P., J.Y. Lee, and M.R. Ladisch, "Modeling of Equilibrium Sorption of Water Vapor on Starch Materials," *Transactions of the ASAE*, **35**, 213–219 (1992).

Zobel, H.F., "Molecules to Granules: A Comprehensive Starch Review," *Starch*, **40**, 44–50 (1988).