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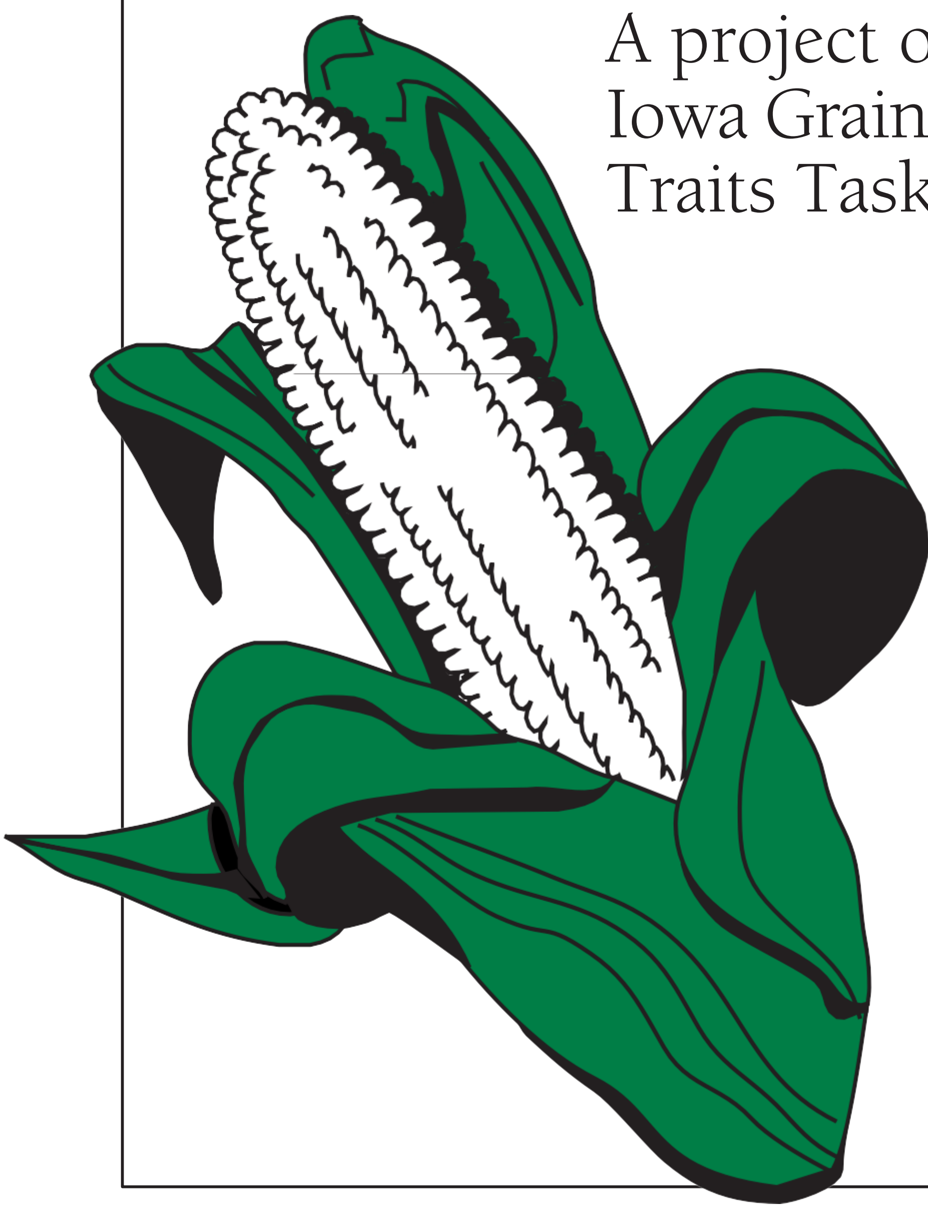

A project of the
Iowa Grain Quality Initiative
Traits Task Team

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Acknowledgment

This report is intended to provoke discussion and debate that will lead to a vision among researchers in public institutions, seed companies, and the starch processing and food industries for modifying corn traits for starch (and other complex carbohydrates) production to enhance utilization and profitability of growing corn. The report attempts to provide direction to farmer organizations and to the corn industry about potential targets for investing research funds. One should recognize that some of the modifications considered required speculation about functional properties and potential applications. Additional research on the relationship between the structures of starch and other complex carbohydrates and functionality in food and industrial applications may refute some of that speculation. Also, this document is a consensus report taking into account the recommendations and reviews of the consultants and advisors identified below.

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Executive Summary

Modified starches and other complex carbohydrates from genetically modified corn are intended to provide new functionalities that, in turn, make possible new products and markets for corn. Other important benefits include more uniform functionalities that are not possible with today's chemical modification routes, reduced processing costs, decreased or eliminated chemical modifications of the types resisted by consumers and environmentalists, and lower costs for users. Genetic modifications may result from traditional plant- breeding techniques or through biotechnology.

Specific goals for use of genetically modified corn to produce new starches and other complex carbohydrates are as follows: to improve gel properties; to improve viscosity and temperature stability; to reduce retrogradation and increase freeze-thaw and storage stabilities; to mimic properties of gelatin and fats; to improve flavor and flavor stability; to reduce or increase digestibility; to improve adhesion and film formation; and to achieve more efficient processing (e.g., milling and fermentation, reduced energy in cooking).

Twenty potential modifications (three high priority and 17 moderate priority, based upon potential gross added value) were identified and evaluated. The top seven market opportunities and related potential modifications are listed below.

Approximately 250 million bushels of corn is processed into starch products. Therefore, it is difficult to identify individual genetic modifications that will meet corn-producer targets for products that generate new demand of 100 million bushels or more. Industry has not seen starches or other complex carbohydrates with some of the functionalities considered in this report; therefore, it was not always possible to estimate with confidence the market potential and the impact on corn consumption. Many of the modifications may enable new "niche" markets with considerable reward to specific starch companies and to the few farmers who produce specialty corn for those companies.

Market Opportunity	Potential Modification	Gross Added Value[1] (million $/year)	Corn Consumed[1] (million bushels/year)	Average Added Value[1] ($/bushel)
Increase stability to acid and shear	Introduce aldehydes into starch	298	40	7.45
Improve wet mill yield of starch	Decrease or modify hard starch (horny endosperm)	280	1,140	0.25
Improve gel formation	Lengthen A and B_1 chains in amylopectin	208	7	29.70
Replace expensive chemical reaction	Introduce high levels of acetylation in starch	120	19	6.30
Reduce chemical modification	Introduce natural cross-linking in starch	60	3	20.00
Increase viscosity and water holding	Introduce cationic groups in starch	60	10	6.00
Improve flavor and improve paper manufacturing	Reduce starch lipids	50	46	1.09

[1]If all of the starch modifications could be achieved (some are mutually exclusive), the total gross added value would be about $1.25 billion, more than 200 million bushels of modified corn could be consumed, and the average added value across all modifications would be about $5.80 per bushel.

Introduction

Advances in biotechnology and improved understanding of biosynthesis of starch and other complex carbohydrates greatly increase the possibilities of developing new or modified corn products. Hereafter, the term "starch" will be used to denote both starch and other complex carbohydrates that are similar to starch but would not comply with the usually accepted terminology of starch. This report summarizes the authors' assessments, with input from industry consultants and advisors, of possible corn modifications to achieve new starches.

The purposes of the study were

- To identify and describe possible genetic modifications to corn that may have commercial value to the corn processing industry and to users of starch products;
- To estimate the gross added value (total value before costs or other market factors) that could be derived from each of the identified genetic modifications; and
- To rank specific genetic modifications for potential market impact, and thus prioritize for investing research funds.

The primary benefits of new starch products from genetically modified corn are

- New or improved functionalities (performance properties, such as greatly reduced cooking energy requirements) that make possible new products and markets for corn;
- More uniform functionalities that are not possible with today's chemical modification routes;
- Decreased processing costs for the starch industry;
- Decreased or eliminated chemical modifications that are resisted by consumers or that are subject to environmental constraints; and
- Lower costs for starch users.

Because management costs and production risks are higher for products from specialty or identity-preserved grains, the rewards must be sufficient to compensate all participating parties for their investments and risks.

Achieving new commercially viable starches by genetic modification of corn presumes knowledge about starch biosynthesis in the kernel, starch granule structure, the relationship of starch structure to functional properties, and plant viability and growth requirements. Although these subjects are not fully understood, starch modification research is still proceeding. Continued research in these areas is key to achieving long-term goals.

In considering genetic modifications of corn to produce new starches we included

- Modifications that are achievable through traditional and mutation breeding to alter gene expression;
- Modifications that can be achieved through transgenic means by which genes for new enzymes are introduced into corn from other plants, animals, and microorganisms; and
- Modifications that can be imagined from a starch structural viewpoint, but for which no known natural mechanism may exist today to achieve the modification (future findings may make these modifications possible).

Currently, our ability to envision the use of genetics and resultant enzymes to modify starch structure and functionality is limited by our understanding of enzymes. Of the more than 25,000 enzymes estimated to exist, only about 10% are sufficiently understood to be recognized by the International Union of Biochemistry (1). Scientists are making rapid progress in under- standing the function and location of enzymes that affect starch biosynthesis and the genes that encode them. Undoubtedly, enzymes not recognized today will be useful in the future to alter starch and to facilitate processing of corn into value-added products (2,3).

We recognized that some modifications may adversely impact the isolation of starch and wet milling of corn. These may not be attractive to today's corn processing industry. Some genetic modifications may require capital investments in new processing methods because the products of some modified starches may not exist as insoluble granules. Other changes envisioned in grain composition and endosperm structure could result in savings due to lower energy, utility and capital costs, and reduced use of processing chemicals.

Corn starch today is chemically altered for some food and industrial applications. The U.S. Food and Drug Administration requires the word "modified" to appear on food labels containing these starches. If corn could be genetically engineered to produce these modified starches in the kernel, foods containing these starches would not need to carry the "modified" designation in the ingredient listing under present labeling laws. These changes should be welcomed in the starch and food industries as well as by many consumers, although we also recognize growing consumer resistance to "genetically modified organisms." Processor savings from reduced chemical use or eliminated chemical processing are also important.

Methodology

In considering potential commercial values of new starches from genetically modified corn, three steps were undertaken:

1. Potential structural changes to starch were identified and how those changes might affect functionality were speculated; then
2. The applications and products in which the modified corn or starch might be useful were speculated; and finally
3. The functional properties and performance characteristics of competitive materials were compared to estimate potential market sizes and gross added values of the corn or starch modifications.

Additional research on the relationship between starch structure and function in food and industrial applications may refute some of that speculation.

A list of potentially useful modifications was first developed after several discussion sessions among Iowa State University scientists and staff. Ideas also resulted from a workshop meeting of public-sector and industry scientists. At the end of the report is the template of the analysis form that we used to evaluate functionality changes for each modification. The list of modifications was then provided to consultants and to industry scientists for comment and estimation of gross added value and consumption of the modified corn.

In some cases, we were able to identify strategies by which the desired modification could be achieved. However, we did not limit ourselves to modifications that could easily be achieved.

We also included descriptions of possible new materials (other complex carbohydrates) to replace typical corn starch in the endosperm and materials that could be useful in new applications.

In the real world, the actual sales volume for a new starch product from genetically modified corn is determined by overall supply and demand, and how closely the functional properties meet the application's requirements. When there is an existing commercial starch with properties similar to those of a new genetically modified starch, the sales volume can be more readily estimated. Accurate sales volumes of specific starch products are usually proprietary. The market values of starches with functional properties that are not fully defined, or for which no competing products with similar functionality are available for comparison, were difficult to forecast and subject to more error.

Glossary

For those unfamiliar with the detail of starch and polysaccharide chemistry, a glossary of terms commonly used in this report follows.

Alpha linkages – A specific type of linkage between glucose units as in normal starch

Absolute amylose – Amylose content as measured by newer and more precise methods

Apparent amylose – Amylose content as measured by older and less precise traditional methods

Beta linkages – A specific type of linkage between glucose units as in cellulose

Cross-linking – Bonds between linear starch chains that alter the physical and chemical behavior of starch

Degree of substitution (d.s.) – Average number of hydroxyl groups derivatized per anhydroglucose unit in a starch molecule

Functionality – performance property contributed by a specific ingredient, such as binding, water-holding capacity, film-forming, adhesion, gel stability, and viscosity

Enzyme – A protein having the ability to catalyze chemical reactions

Gelatinization – The melting of the crystalline regions of the starch granule

Paste – A dispersion of gelatinized starch

Pericarp – The outer layer surrounding the corn kernel

Polysaccharide – A polymer of sugars (e.g., starch, cellulose, etc.)

Retrogradation – Recrystallization of gelatinized starch as in staling of bread

Starch granules – Discrete bodies of starch, which, in their native form, are comprised of amylose and amylopectin, have large portions of crystallinity, and are insoluble in water

Viscosity – Fluidity of a liquid

Current Uses of Normal Corn Starch

Annual U.S. corn production is 9–10 billion bushels. During the 1997/1998 market year, 234 million bushels of corn was processed into starch, resulting in 7.4 billion pounds of starch products (4). Annual growth in U.S. corn starch production is expected to be 3.5% through the year 2010, unless genetic modifications cause major new processing plants to open. Corn is the most important and economical source of starch in the United States. Exports of corn starch account for less than 3% of total U.S. starch production.

Starch is the major carbohydrate storage product in corn kernels comprising 70–72% (dry basis) of the kernel. Starch exists as insoluble, partially crystalline granules that assume size and shape characteristics of the plant species. The amount and extent of crystallinity alter its physical properties and affect its ability to be chemically modified. Insolubility as granules is important to the current wet-milling process; modifications that change solubility may adversely impact starch recovery. Starch is made up of individual units of glucose, linked together in chains by *alpha* 1-4, and occasional *alpha* 1-6, linkages. The 1-4 linkages produce linear chains that primarily comprise molecules called “amylose,” whereas the *alpha* 1-6 linkages serve as branching points to produce branched-chain molecules called “amylopectin.”

The proportions of the two types of polymers comprising starch are established genetically. Normal corn starch contains about 27% “apparent” amylose, as determined by traditional measures (about 18% absolute amylose content). Amylose is a predominantly linear polymer (there may be minor amounts of very short branches) with glucose units linked by *alpha* 1-4 bonds. Amylopectin, a highly branched polymer, comprises the majority of the starch granule. Amylopectin has glucose units linked by *alpha* 1-4 and *alpha* 1-6 (branch points) bonds.

Plant geneticists have developed varieties of corn containing all amylopectin (waxy corn) and other varieties containing more than 70% amylose (high-amylose corn or amylo-maize) that are now grown commercially (a recent patent was awarded for corn containing starch with 85–95% amylose). Identity is preserved throughout production, processing, and marketing. Identity preservation and specialty grain production are not new concepts to many corn producers and the starch industry.

Native starch extracted from corn is a dry, soft, usually white powder. It is insoluble in cold water, alcohol, and most organic solvents. When the granules are heated in a water suspension, they bind water, increase in size, and lose their crystallinity, and the suspension becomes thicker until it forms a paste. This process is called gelatinization. The temperature at which the starch gelatinizes is an important functional property and often serves as a means of classifying starches from different sources.

The granular structure of starch is important to recovery processes and the abilities of commercial starches to fill specific product needs. The physical and chemical properties of starch make it useful in food and industrial applications as thickeners, suspension agents, emulsifiers, gels, adhesives, and films. Thickening properties are useful in puddings, gravies, sauces, pie fillings, and in some industrial applications (e.g., paper, adhesives) where viscosity is important. Starch pastes in foods can hold fat and protein particles in suspension to give desirable flavor, texture, and appearance; likewise, in paper coatings and in some adhesives, clay particles are suspended in starch pastes (5). Gel formation is important in puddings, salad dressings, and adhesives. When starch pastes are spread on smooth surfaces, the resulting strong, stable films are particularly useful in paper coatings and sizings, textile sizings, corrugated board, and adhesives.

Today's commercially important properties of starch often depend on the relative proportions of amylose to amylopectin, and tend to vary from one plant species to another. Once gelatinized, starches with high percentages of amylose form firm gels and strong, tough films. Waxy corn starches, which are nearly 100% amylopectin, gelatinize easily and yield nearly transparent, viscous pastes that will not gel. Behavioral properties of starches from different plants and modified starches usually fall between these two extremes.

Most corn starch is sold in the unmodified form to be used in paper and board production, adhesives, salad dressings, beer, canned foods, dry food mixes, molding starch, and laundry starch. A major deficiency of unmodified corn starch in many commercial uses is its extremely high viscosity (thickness of solution) when heated and its tendency to "retrograde" or "set-back" (recrystallize) at ambient or low temperatures. Retrogradation is a problem in many applications because the resulting gel becomes firm and tough, weeps moisture (syneresis), and may become brittle as it loses internal moisture and partially recrystallizes. Starches from genetically modified corn might be used to solve these types of practical problems facing industry and consumers.

Corn starch is plentiful and relatively inexpensive. Therefore, the U.S. starch industry has found ways to alter the properties of corn starch to fit processing and application needs rather than to substitute starches from other sources. Inherent properties of the corn starch granule can be altered by mild chemical and/or heat treatment to improve starch performance. Such modified starches and starch derivatives provide users with a range of products to fit individual processes and applications. However, modified and derivatized starches cost more than common corn starch and are required by law to be labeled as "Food starch – modified" on food product labels. The term "modified" used with a food ingredient is often perceived negatively by consumers, especially in some export markets (Asia and Europe).

Common treatments to reduce viscosity in corn starch pastes are acid modification, oxidation, and enzyme modification. These treatments split bonds between individual or groups of glucose units in starch chains. By carefully controlling the process, a starch chemist can produce starches with a wide range of viscosities. Derivatization techniques also may affect viscosity, but they usually are done to enhance or impart other functional behaviors, such as gel formation and solubility, that are different from those of the parent starch.

Cross-linked starches are those in which links are created between and among glucose chains, making them more stable to processing conditions such as heat, pH, and shear. These starches are important to the food industry because of great variation in cooking and storage temperatures (e.g., microwavable foods), processing equipment, and ingredient combinations. Stabilized starches, another group of starch derivatives, are specifically stabilized against gelling and may have other unique functional characteristics.

Hydroxyethyl and hydroxypropyl starches are starch derivatives used in paper and food manufacture, respectively, because of their abilities to form clear, stable pastes. Cationic starches (those that are chemically altered to carry a positive charge) are used in paper manufacture to impart strength and color retention by adding positively charged starch molecules to the negatively charged cellulose in paper pulp. Starch acetates are used both as textile sizings and as food thickeners. Starches often are first cross-linked to improve viscosity in processing, and then acetylated (chemical groups are added to starch chains) to prevent retrogradation of the starch paste.

Opportunities for New Starches from Genetically Modified Corn

The current market for corn starch products in food and industrial applications demands approximately 250 million bushels of corn; therefore, individual genetic modifications that will generate 100 million bushels or more of new demand are unlikely except for those modifications that enhance the milling process. However, several modifications will likely generate added economic impact equivalent to 100 million bushels of commodity corn. Some modifications provide starch functionalities that are available today, but only through chemical processes; other modifications may offer improvements over current starch products, or may provide new functionalities that industry has not seen. Many modifications could result in new niche markets and considerable reward for individual farmers who produce specialty corn for specific starch processors.

The modifications were ranked as follows based on estimates of commercial benefits (potential U.S. market impact) by the authors and industry consultants. Priority rankings were assigned based upon the amount of potential gross added value. High-priority modifications have potential added values exceeding $200 million per year, whereas those having less than $200 million per year but more than $2 million per year were judged to be moderate priority. Three modifications were judged to have high potential gross values and 17 were judged to have moderate potential gross added values. The moderate-priority modifications may have potential for specific companies in marketing specialty products, but the potential gross added value is probably not sufficiently large to impact large numbers of corn producers. Table 1 (pages 18- 22) provides more details on estimated market size, potential additional value per pound of starch, estimated corn consumption, and potential added value per bushel of corn for those modifications judged to be high or moderate priority.

High priority – Relatively high gross added value

- Introduce aldehyde groups into amylose and/or amylopectin
- Decrease, eliminate, or modify horny endosperm proteins for improved wet milling and increased starch yield
- Lengthen A and B_1 chains of amylopectin

Moderate priority – Modest gross added value

- Introduce high levels of acetylation into amylose and/or amylopectin
- Achieve natural cross-linking or enhance potential for cross-linking
- Introduce a cationic (positively charged) group into amylose and/or amylopectin
- Decrease starch lipids
- Alter all linkages from *alpha* to *beta* in amylopectin
- Introduce *o*-methyl, *o*-acetyl, *o*-succinyl, *o*-glycosyl, *o*-phosphatyl, or *o*-galactosyl groups into amylopectin and/or amylose
- Increase absolute amylose to >90%
- Reduce numbers of B_2, B_3, and B_4 chains in amylopectin
- Increase molecular weight of amylose
- Alter 1-4 linkages from *alpha* to intermittent *beta* in amylose and/or amylopectin
- Introduce an anionic (negatively charged) group into amylopectin and/or amylose
- Decrease absolute amylose to 5–10%
- Increase phytoglycogen to >90%
- Decrease molecular weight of amylose
- Replace starch with cyclodextrin
- Shorten A and B_1 chains in amylopectin
- Increase phytoglycogen to 25%

Other modifications judged to have little or no added values and thus would not be recommended targets are the following:

Low priority – Little gross added value

- Increase starch content
- Reduce pericarp thickness
- Introduce phosphate groups into amylopectin to simulate potato starch
- Introduce new *alpha*-(1-2) and *alpha*- (1-3) linkages into amylopectin
- Replace starch with polyhydroxybutyrate and/or polyhydroxyvalerate (biodegradable polymers produced today by fermentation)

Abandon – No gross added value

- Produce germless kernels to simplify milling
- Alter granule shape
- Increase granule mean size
- Decrease granule mean size
- Narrow granule size distribution
- Increase molecular weight of amylopectin without altering chain length
- Replace starch with levulan (otherwise known as fructan, a polymer of fructose; fructose could be produced by hydrolysis of fructan rather than isomerization of glucose)

If nearly all of the starch modifications identified (high and moderate priority) could be achieved, the total gross added value would be about $1.25 billion, over 200 million bushels of modified corn could be consumed, and the average added value across all modifications would be about $5.80 per bushel. However, some proposed modifications are mutually exclusive.

Market Needs for New Starches

The following is a more detailed discussion of the modifications judged to be important in food and industrial applications (potential modifications are shown in italics).

Food applications

About 100 million pounds (dry weight) of stabilized, cross-linked starches is used annually by the North American food industry. Prices of these starches range from $0.50/pound to $0.90/pound depending upon the specific modification and contract arrangements. These starches often are produced from waxy corn. The market for cross- linked waxy corn starch is about 30 million pounds with prices ranging from $0.50/pound to $0.75/pound (compared with $0.10–0.15/pound for normal corn starch).

Research areas considered to be useful were generally those that would reduce or eliminate the need to chemically treat corn starch to achieve desirable properties. Some goals that would be important to the food industry are

- Achieve natural cross-linking or enhance potential for cross-linking to improve paste stability to acid and shear (*e.g., introduce aldehyde or phosphate groups into amylopectin and/or amylose*)
- Mimic hydroxylated and acetylated starches (*shorten A and B_1 chains in amylopectin*)
- Bind cations and increase viscosity and water-holding capacity (*add an anionic [negatively charged] group*)
- Prevent retrogradation and reduce gelatinization temperature (*introduce o-methyl, o- succinyl, o-glycosyl, o-acetyl, o-phosphatyl, or o-galactosyl groups into amylose or amylopectin*)
- Improve wet milling and increase starch yield (*decrease amount of, eliminate, or modify horny endosperm proteins*)
- Improve flavor (*decrease starch lipid*)

Natural cross-linking might be achieved by introducing small amounts of diester cross-links in the granule by introducing diphosphate, diadipate, or disuccinate ester bonds by genetic modification. Naturally cross-linked waxy corn starch would be very useful to the food industry, both for its functional properties and absence of chemical modification. Naturally cross-linked starch or enhanced potential for cross-linking likely will be best accomplished on waxy corn that already contains mostly branched starch chains of amylopectin. *Introduction of groups, such as o-succinyl groups,* may provide interaction sites for cross-linking. Various levels of cross-linking are needed to provide products suited to a variety of applications. Perhaps this alteration could be accomplished by eliminating some cross-links from a highly cross-linked starch by using a simple treatment such as mild alkaline or enzymatic hydrolysis. Alternatively, *enhanced potential for cross-linking* might be achieved by genetic modification. Perhaps starch could be modified to contain glucuronic acid units, which might be induced to form intermolecular ester bonds by dry heat, thus producing cross-linking.

Shortening A and B_1 chains of amylopectin is one approach that would allow adequate sites for cross-linking but fewer long outer chains that could retrograde.

Addition of anionic moieties (i.e., glucuronic acid, phosphate, sulfate) also would provide electrostatic interaction among long chains of amylose and amylopectin that would reduce or prevent retrogradation and could give gum-like properties. Further interaction of negatively charged (anionic) groups with cations (di- and trivalent metal ions with positive charges) might lead to insolubilization, water-resistance, gel-formation, and chelation (binding of metallic ions) properties important in wastewater treatment, metal recovery, and wet-end paper manufacture.

Introducing o-succinyl or o-galactosyl substituents may provide enhanced potential for cross-linking as already discussed.

Introducing o-methyl or o-glycosyl groups should achieve low-temperature sol (colloidal suspension of solids in a liquid) stability. Interspersing single glucose units (*o*-glycosyl) along the chains of amylose would prevent hydrogen bond associations and retrogradation. This type of modification would provide high viscosity with low-temperature stability, lower gelatinization temperature, and possibly easier solubility in water. These properties would be particularly useful in high-amylose corn starch. This type of modification might fit into the biosynthetic pathway with less disruption of plant metabolic processes than would other approaches. Because starch composition would not change, this new starch would likely not require labeling as "modified food starch," and it should have no adverse effects if used as livestock feed.

Introducing low levels of acetylation, particularly in high-amylose corn starch, is another approach to achieve low-temperature stability, but the industrial method for achieving this modification is already inexpensive. Corn that produces starch acetate in granular form by genetic modification may allow more uniform substitution along starch chains. A wide range of food and industrial products could be developed based on starches of various degrees of acetylation.

Gelatin currently fills the large market for clear, thermo-reversible (gel when chilled, liquid when warm) gels in food production. Recent concern about "mad cow disease" could reduce gelatin use, but no good substitutes are available. The ability to produce similar gels with corn starch could result in a new market for starch, if a clear gel could be produced. An estimated 140 million pounds of gelatin is used in confectionery applications in the United States and Europe. Depending upon the grade, the price of gelatin currently is around $2.20/lb.

One possible approach for gaining the desired gel properties that may allow corn starch to compete with gelatin is to *lengthen A and B_1 chains in amylopectin*. Increased retrogradation and lack of clarity in the gel may result from this modification alone and would cause problems in some applications. However, these problems could be addressed with another chemical or genetic modification that attaches substituent groups along the starch chains (e.g., phosphate groups) to reduce retrogradation and provide clarity.

In addition to the above-mentioned modifications, two other modifications could improve corn starch for food applications. *Decreased starch lipid* and *decreased amount of, eliminated, or modified horny endosperm proteins* could improve gelling properties and reduce the typical "cardboard" flavor of corn starch. These modifications would be most useful in waxy corn starch, recognizing that one drawback would be poorer low-temperature stability.

Decreased, eliminated, or modified horny endosperm proteins should improve starch recovery during wet milling and may increase processing efficiency (but breakage susceptibility could increase). If coupled with *decreased starch lipid*, flavor and color also may improve. Impact on sales volume is not well defined. If accomplished on waxy corn starch, the market volume is estimated at 100 million pounds. Flavor removal and increased whiteness could expand the market for corn starch in both food and pharmaceutical areas.

Industrial applications

The demand for industrial corn starch in the United States is projected to rise 4.5% per year through the year 2000 when 7 billion pounds valued at $1 billion is expected to be produced. Indus- trial corn starch may account for an increasing portion of total U.S. corn starch use. Traditional applications, primarily adhesives, paper, and board, are expected to remain the dominant uses for corn starch. Adhesives and paper and paper- board production provide growing markets for modified starches, accounting for 47% of current total demand (4).

Approximately 1 billion pounds of hydroxyethyl starches is used in paper coatings and sizings. The current price of hydroxyethyl starch in large bulk quantities is $0.14/pound versus common corn starch at $0.09/pound. Industrial starch prices ranged from $0.05/pound to $0.18/pound over the period 1986–1996.

The demand for modified industrial corn starches is projected to expand 6.6% per year reaching 3.2 billion pounds by the year 2000 (6), although recent growth has been at a much lower pace. The demand for special types of starch used in the production of degradable plastics and super- absorbent polymers could rapidly grow. Corn starch supplied 60% of the starch used in degradable plastics in 1995 (175 million pounds at $0.15/pound) (6). Super-absorbent polymers are materials that can absorb several hundred times their own weight in water. Those super-absorbing polymers made from corn, used mainly in agricultural applications (e.g., seed coatings, fertilizer carriers), continue to be a small market for corn starch at 33 million pounds (at $0.12/pound) (6).

Traditional markets—paper and paperboard, adhesives, and textiles—will continue to provide the mainstay applications, jointly accounting for about 80% of total industrial starch sales. Growth will be aided by the increasing tendency of users in the paper and paperboard industry to purchase proprietary modified corn starches rather than to convert unmodified starches in-house (6).

New structures in the kernel that have possible competitive potential in industrial products in terms of functionality and economics include the following:

- Provide sites for cross-linking and improve paste stability to acid and shear (*achieve natural cross-linking or enhance the potential for cross-linking such as introducing aldehyde groups into amylopectin and/or amylose*)
- Decrease retrogradation rate and improve film formation (*increase the molecular weight of amylose*)
- Provide sites for attaching block co-polymers and improve paper coatings and adhesives (*introduce aldehyde groups*)
- Improve water resistance in adhesives *(introduce high levels of acetylation (d.s. 1-3) into amylose or amylopectin)*
- Bind anions, increase viscosity and water-holding capacity, improve gelling and flocculation (*introduce a cationic [positively charged] group into amylose*)
- Reduce reformed amylose particles (RAPS) (*decrease starch lipid*)
- Improve film and solution properties, and decrease retrogradation *(introduce linkages between glucose units other than alpha 1-4 and alpha 1-6)*
- Replace an expensive enzyme reaction in producing cyclodextrin *(replace starch with cyclodextrins)*

The benefits of *naturally cross-linked starches and enhanced potential for cross-linking* were discussed earlier with food applications in terms of viscosity stability under varying processing and storage conditions. These same properties also would be valuable in adhesives and coatings and would be in great demand in industrial applications if the cost was competitive. Approximately 1.2 billion pounds of starch is used in corrugating, 20% of which is in the carrier portion of the adhesive. The carrier cost is about $1.00 to $1.60 per dry pound. The bulk of the adhesive is unmodified corn starch. Requirements include a stable viscosity over fluctuating operating temperatures and during agitating and pumping in the adhesive application system. The final bond must show high tack to allow high machine speeds and also show high cohesive strength (fiber tear) and, in a number of applications, water resistance.

Introduction of aldehyde groups might achieve the desired levels of cross-linking by introducing substituent groups into linear amylose chains and linear sections of amylopectin. If these modifications could be made genetically, the placement of these additional side chains might be more uniform and better controlled than is possible with chemical modifications done today. Galactose oxidase, an enzyme, will catalyze the oxidation of the C-6 hydroxyl of galactose to an aldehyde. If a galactosyl starch can be made in the granule by genetic modification and genes to introduce and activate galactose oxidase action, aldehyde-containing starch could result.

Aldehyde groups also might be useful in further modifying starch by creating block copolymers (linkages with other polymers such as proteins and lipids), which are valuable in paper coating and sizing, textile sizing, and in paper wet-end manufacture. In this case, the aldehyde groups would need to be attached to the nonreducing ends of the starch molecule.

Introducing high levels of acetylation (d.s. 1-3) could provide polymers with water resistance and insolubility, which would improve adhesive properties of starch for corrugating applications. An unusual application of a naturally acetylated starch could be as a biodegradable hot-melt adhesive in repulping processes. Current methods for producing high levels of acetylation in starch are expensive and not in line with many potential applications.

Introduction of cationic groups (e.g., amine groups from glucosamine that give a positive charge to part of the molecule) is an important part of amphoteric (molecules with negative and positively charged portions) starches for paper manufacture and in wastewater treatment. The estimated market in the U.S. paper industry is about 300 million pounds in a price range of $0.15/pound to $0.30/pound.

Decreased starch lipid was mentioned above in terms of flavor and color removal for food and pharmaceutical applications. Naturally defatted starch also would solve a common problem in paper manufacture known as reformed amylose particles (RAPS), which are blamed on lipids associated with the amylose portion of starch. In fermentation processes, a naturally defatted starch would reduce the amount of sludge and related filtration problems.

Introduction of linkages other than alpha 1-4 and alpha 1-6 into starch might provide new and different properties for markets in which starch is not currently a player. Starch behavior is determined by the configuration of the molecule, so changes in position and type of glycosidic bonding are likely to change starch functional properties.

Creation of polymers with alternating spans of alpha 1-4 and beta 1-4 linkages might allow new abilities for the molecule to complex and associate with similar sections or with other molecules of natural and synthetic polymers. Such abilities may lead to more effective warp sizing of textiles, paper coating binders, paper sizing, and adhesives. A related modification, *insertion of beta 1-4 linkages intermittently in starch chains*, also would change molecular configuration, potentially improving film formation in coatings and adhesives.

Altering all alpha 1-4 and 1-6 linkages to beta linkages would yield polymers similar to cellulose. This modification would drastically decrease digestibility of the corn by humans and monogastric animals. Introducing new alpha linkages (i.e., 1-2, 1-3) into starch could produce a material that mimics dextrans (polysaccharides from yeasts and bacteria, which form highly viscous, slimy solutions) having possible applications in food and medical products.

A small market might be achieved by *replacing starch with cyclodextrin*. Cyclodextrins, like starch, are comprised of linkages between glucose molecules, but in a closed ring structure rather than in a linear chain. The hydrophobic (water-resisting) center of the ring is an effective encapsulation space for other small molecules, such as flavors, spices, and drugs. Cyclodextrins are currently used as flavor protectors in the food industry and are produced by a series of enzyme treatments to starch. Conceivably, cyclodextrins could be produced in the corn kernel if these enzymes were present and active there. The world market for cyclodextrins was estimated at 2–5 million pounds in 1993. The potential is considerably greater with more regulatory approvals and new uses (7). Current and potential markets are in foods and pharmaceuticals, but the current enzymatic production method is expensive. Transgenically moving cyclodextrinase into corn is attractive provided cyclodextrin can be recovered in meaningful quantities from corn through processing.

Biopolymers are organic substances consisting of repetitive linkages of similar molecules. Starch and cellulose are examples of biopolymers in which the repetitive unit is glucose; proteins are biopolymers of amino acids linked by peptide bonds. Synthetic structural materials, such as plastics, are polymers of petroleum-derived hydrocarbons. These polymers form rigid materials with many uses, but are often not biodegradable.

Manufacture of biodegradable films may benefit by *increasing the molecular weight of amylose.* This modification is likely to provide better film formation if better plasticizer systems are developed. Although retrogradation rate would be reduced, which would benefit most applications, the reduction would probably be insufficient to benefit food applications requiring low-temperature stability. This trait would be most useful in high-amylose corn starch.

Conclusions

This study identified a number of genetic modifications to corn for starch production that have value-added potential in specialty markets. Although no single corn or starch modification was identified that could increase corn consumption by 100 million bushels, several had high gross added values even if few additional pounds of starch were used. Modifications providing enhanced potential for cross-linking and modifications greatly improving freeze-thaw and storage stabilities and reducing retrogradation could have major market impact.

The properties of modified corn or starch suggested to have value potential are as follows (modifications to deliver the desired property are in italics):

- Provide sites for cross-linking, and improve paste stability to acid and shear (*introduce aldehyde groups into amylopectin and/or amylose*);
- Improve wet milling and increase yield of starch (*decrease, eliminate, or modify horny endosperm proteins*);
- Improve gel formation and mimic gelatin if a clear gel can be formed (*lengthen A and B_1 chains in amylopectin [further chemical treatment, such as phosphorylation, may be required]*);
- Improve water resistance in adhesives and enable hot-melt adhesives (*introduce high levels of acetyl into amylose and/or amylopectin*);
- Achieve natural cross-linking or enhance potential for cross-linking *(introduce aldehyde groups into either amylose or amylopectin);*
- Bind anions and increase viscosity and water-holding capacity (*introduce a cationic group into amylopectin and/or amylose*);
- Improve flavor and eliminate RAPS (*decrease starch lipid*);
- Decrease digestibility, water solubility, and retrogradation (*alter all linkages from alpha to beta in amylopectin*);
- Prevent retrogradation and reduce gelatinization temperature (*introduce o-methyl, o- acetyl, o-succinyl, o-glycosyl, or o-galactosyl groups into amylopectin and/or amylose*);
- Increase retrogradation and reduce digestibility (*increase absolute amylose to >90%*);
- Provide for easier cooking and improve freeze-thaw stability (*reduce number of B_2, B_3, and B_4 chains in amylopectin*);
- Decrease retrogradation rate and improve film formation (*increase molecular weight of amylose*);
- Decrease digestibility (*alter 1-4 linkages from alpha to intermittent beta in amylopectin*);
- Bind cations, provide sites for cross-linking (*introduce an anionic group into amylopectin and/or amylose*);
- Provide properties intermediate to normal and waxy starches (*decrease amylose to 5–10%*);
- Decrease paste viscosity, gel formation and retrogradation, and increase water-holding capacity (*increase phytoglycogen to >90%*);
- Increase retrogradation rate (*decrease molecular weight of amylose*);
- Replace the expensive reaction required to make cyclodextrin (*replace starch with cyclodextrin*);
- Mimic hydroxypropylated and acetylated starch (*shorten A and B_1 chains in amylopectin*); and
- Achieve a modest decrease in paste viscosity, gel formation, and retrogradation, and increase water-holding capacity (*increase phytoglycogen to >25%*).

If all of the starch modifications could be achieved the total gross value would be about \$1.25 billion, more than 200 million bushels of corn could be consumed, and the average added value across all modifications would be about \$5.80 per bushel. However, some of the modifications overlap or are mutually exclusive, so this total gross value would not be realized; but several modifications could potentially be stacked to provide a combination of benefits in one hybrid.

All of the above-mentioned modifications could reduce corn yields and/or adversely affect processing characteristics. These risks, as well as increased costs involved in preserving identity will reduce the total added values that were calculated in this report (net added values will be considerably less than the gross added values).

TABLE 1. Market Opportunities, Estimated Consumption and Gross Added Values for Various Genetic Modifications to Corn for Starch Production[1]

Market Opportunity	Possible Corn or Starch Modification to Deliver Desired Property	Gross Added Value (million $/year)	Projected Market Size (million pounds of starch/year)	Estimated Additional Value ($/pound of starch)	Projected Consumption of Modified Corn (million bushels/year)	Estimated Added Value ($/bushel)
High Priority						
Provide sites for cross-linking to improve stability to acid and shear; provide "natural" replacement for a common chemical reaction; replace formaldehyde in resins in corrugating and adhesives; provide sites for attaching block copolymers.	Introduce aldehyde groups into either amylose or amylo-pectin	282	1,200	0.07-0.40	38	2.21-12.60
Impart temporary wet strength to paper and prepare water-resistant paper coatings and water-resistant adhesives.		16	40	0.30-0.50	1.5	9.45-15.75
Decrease capital and operating costs for wet milling and starch recovery (increased starch yield); reduce steeping time; eliminate SO_2 and associated handling difficulties; lower protein content of starch to reduce off-flavors and colors.	Decrease, eliminate, or modify horny endosperm proteins	280	36,000 (potentially all starch and sugar, and some ethanol)	0.005-0.01	1,140	0.16-0.33
Improve gel formation; provide more stable viscosity; enable manipulation of structures to give a variety of properties; may provide a thermo-reversible clear gel that could substitute for gelatin; may retrograde faster unless an additional chemical treatment (e.g., phosphorylation) or genetic modification also is used.	Lengthen A and B_1 chains in amylo-pectin (realistic modification, progress already made but optimum not yet achieved	207	150	0.90-1.90	7	28.35-59.85
Useful in photographic film. Very clear film is needed, which will require an additional chemical treatment (e.g., possibly phosphyorylation or addition of other hydrophilic groups) or genetic modification.		0.8	0.8	0.90-1.10	0.03	28.35-34.65

Market Opportunity	Possible Corn or Starch Modification to Deliver Desired Property	Gross Added Value (million $/year)	Projected Market Size (million pounds of starch/year)	Estimated Additional Value ($/pound of starch)	Projected Consumption of Modified Corn (million bushels/year)	Estimated Added Value ($/bushel)
High Priority						
Replace a relatively expensive chemical reaction; provide “biodegradable hot-melt” adhesives with improved water resistance.	Introduce high levels (d.s. 1–3) of acetylation	120	600	0.15-0.25	19	4.73-7.88
Provide natural substitute for chemical cross-linking to inhibit granule swelling, resist breakdown, eliminate stickiness, improve acid and shear stability; eliminate need for a chemical reaction.	Achieve natural cross-linking or enhance potential for cross-linking (e.g., introduce o-succinyl groups)	60	40	0.40-0.80	3.2	12.60-25.20
Increase viscosity and water-holding capacity; bind electrolytes; improve gelling and flocculation; provide sites for cross-linking; may be useful in paper sizing, wastewater treatment, and protein interactions in foods and pharmaceuticals.	Introduce cationic groups (e.g., glucosamine) into either amylose or amylopectin)	60	300	0.15-0.30	10	4.73-9.45
Eliminate source of “cardboard” flavor and odor (especially in paper coatings and foods with high starch content).	Decrease starch lipid (especially in high-amylose starch)	8	50	0.10-0.20	1.6	3.15-7.20
Eliminate “reformed amylose particles” in paper manufacture that presently threatens starch in this market.		42	1,400	0.01-0.05	44	0.32-1.58
Decrease sludge in fermentation.		0	18,000	0.00	570	0.00

Market Opportunity	Possible Corn or Starch Modification to Deliver Desired Property	Gross Added Value (million $/year)	Projected Market Size (million pounds of starch/year)	Estimated Additional Value ($/pound of starch)	Projected Consumption of Modified Corn (million bushels/year)	Estimated Added Value ($/bushel)
High Priority						
Provide very different film and solution properties; decrease digestibility (weight control); decrease retrogradation; eliminate water solubility.	Alter all linkages (1-4 and 1-6) from *alpha* to *beta* in amylopectin	40	100	0.15-0.75	3.2	4.73-23.63
Possess cellulose-like properties. High priority cellulose is expensive and valuable to the chemical industry.		Undetermined	Undetermined. Potentially large	0.50-1.00	Undetermined	15.01-31.50
Prevent H-bond associations to improve cold-water solubility; prevent retrogradation; provide high-viscosity, low-temperature stability, low gelatinization linking, and may allow "natural" labeling.	Introduce *o*-methyl, *o*-acetyl, *o*-succinyl, *o*-glycosyl, *o*-galactosyl substituents into either amylose or amylopectin	35	100 (mostly waxy)	0.40-0.80	3.2	12.60-25.20
Provide more complete retrogradation and more "resistant" starch (to human digestion), which may be important in fat mimetics; improve granule integrity; improve film formation.	Increase absolute amylose to >90% (patent recently awarded)	33	50	0.15-1.15	1.6	4.73-36.23
Easier cooking, more opaque paste, and decreased gel strength; improve freeze-thaw stability and slower retrogradation.	Reduce number of B_2, B_3, and B_4 chains in amylopectin	26	75	0.20-0.50	2.4	6.30-15.75
Decrease retrogradation rate in food applications of high-amylose starch.	Increase molecular weight of amylose (realistic modification, already in progress)	8	100	0.05-0.10	3.2	1.57-3.15
Improve film formation in biodegradable plastics, corrugation, and adhesives.		18	175	0.08-0.12	5.6	2.52-3.78
Decrease digestibility; increase dietary fiber; reduce water solubility; could increase affinity with other substrates.	Alter 1-4 linkages from *alpha* to intermittent *beta* in amylopectin	20	50	0.30-0.50	1.6	9.45-15.75

Market Opportunity	Possible Corn or Starch Modification to Deliver Desired Property	Gross Added Value (million $/year)	Projected Market Size (million pounds of starch/year)	Estimated Additional Value ($/pound of starch)	Projected Consumption of Modified Corn (million bushels/year)	Estimated Added Value ($/bushel)
High Priority						
Increase viscosity and water-holding capabilities; provide sites for cross-linking to produce stabilized starches resistant to acid and shear for adhesives and coatings; may be useful in protein interactions in foods and pharmaceuticals.	Introduce anionic groups (e.g., glucuronic acid, phosphate) into amylose or amylopectin	7	100 (mostly waxy)	0.05-0.08	3.2	1.58-2.52
Bind electrolytes, as in wastewater treatment and metal recovery; provide sites for attachment of other polymers; eliminate one step in producing amphoteric starch.		7	50	0.12-0.15	1.6	3.78-4.73
Compete with potato starch.		6	100	0.04-0.08	3.2	1.26-2.52
Provide an intermediate amylose level between normal starch and waxy, giving properties intermediate to normal and waxy starch; unique gelation properties.	Decrease absolute amylose to 5–10%	16	50	0.15-0.50	1.6	4.73-36.23
Decrease gel formation and retrogradation; decrease viscosity; increase water-holding capacity.	Increase phytoglycogen to >90% (likely to be difficult to mill)	16	50	0.25-0.40	1.6	7.88-12.60
Increase digestibility, which may be important in all livestock feeds.			Not fed as starch	Not fed as starch	8,000	0.05-0.20
Increase retrogradation rate and rapid gelling in confectionery products; may be useful as "resistant" starches for reduced calorie foods; may be useful in corrugating carriers.	Decrease molecular weight of amylose	14	50	0.15-0.40	1.6	4.73-12.60
Replace an expensive enzyme reaction in producing cyclodextrin. Cyclodextrin provides stability to flavors and aromas, and provides a way to encapsulate ingredients and bind hydrophobic substances.	Replace starch with cyclodextrin (may be difficult to mill)	6	5	0.50-2.00	0.16	15.75-63.00

Market Opportunity	Possible Corn or Starch Modification to Deliver Desired Property	Gross Added Value (million $/year)	Projected Market Size (million pounds of starch/year)	Estimated Additional Value ($/pound of starch)	Projected Consumption of Modified Corn (million bushels/year)	Estimated Added Value ($/bushel)
High Priority						
Minimize low-temperature retrograding (especially useful in frozen and refrigerated foods); provide functionality of hydroxypropylated and acetylated starch; allow "natural labeling."	Shorten A and B_1 chains of amylopectin (realistic modification, work already in progress)	5	100 (mostly waxy)	0.04-0.06	32	1.26-1.89
Decrease gel formation and less retrogradation; decrease viscosity and increase water-holding capacity.	Increase phytoglycogen to >25% (may be difficult to mill because of increased water solubility)	2	50	0.03-0.05	1.6	0.95-1.58
Increase digestibility, which may be important in all livestock feeds.			Not fed as starch	Not fed as starch	8,000	0.05-0.20

[1]The methodology used to develop this table included the following steps: 1. Identifying potential structural changes to corn or starch (column 2) and speculating how those changes might affect their properties (column 1); 2. Speculating about applications and products in which the modified corn or starch might be useful; and 3. Comparing with the functional properties, performance characteristics, market sizes, and costs versus those of competitive materials in specific applications to arrive at a value for the starch (column 5) and an estimated market size (column 4) for the modified corn or starch.

References

1. Neidleman, S., Enzymology and Food Processing, in Biotechnology in Food Processing, edited by S.K. Harlander and T.P. Labuza, Noyes Publications: Park Ridge, NJ, pp. 37–56 (1986).

2. Wasserman, B.P., C. Harn, C. Mu-Forster, and R. Huang, Progress toward genetically modified starches, *Cereal Foods World* 40:810–817 (1995).

3. Mu-Forster, C., R. Huang, J.R. Powers, R.W. Harriman, M. Knight, G.W. Singletary, P.L. Keeling, and B.P. Wasserman, Physical association of starch biosynthetic enzymes with starch granules of maize endosperm, *Plant Physiol.* 111:821–829 (1996).

4. U.S. Department of Agriculture, Economic Research Service, Feed Outlook, March (1999).

5. Corn Refiners Association, Corn Starch, Corn Refiners Assn.: Washington, DC (1986).

6. The Freedonia Group, Industrial Corn Starch, in Industrial Starch and Other Corn Chemicals to 2000, Report 843, Freedonia Group: Cleveland, OH (1996).

7. Duxbury, D.D., Cyclodextrins: Opening up worldwide markets, *Food Processing*, pp. 88-90 (April 1993).

Template Used to Evaluate Genetic Modifications

Category Title

Compositional/structural change or genetic modification:

Anticipated benefits/applications:

Potential problems:

Relative feasibility:

Estimated commercial significance:

Anticipated changes in starch functionality:

- Granule properties:
  - Dusting characteristics -
  - Coating properties -
  - Flow properties of dry starch -
  - Cold-water solubility -
  - Granule integrity -
  - Digestibility -
- Gelatinization properties:
  - Gelatinization temperature -
  - Gelatinization range -
  - Gelatinization enthalpy (energy, difficult to cook) -
- Paste characteristics:
  - Pasting temperature -
  - Hot-paste viscosity -
  - Cold viscosity -
  - Resistance to shear thinning -
  - Paste clarity -
  - Amount of lipid binding -
- Gel properties:
  - Gel strength -
  - Gel clarity -
  - Freeze-thaw stability -
  - Water-holding capacity -
  - Susceptibility to starch-degrading enzymes -
  - Retrogradation rate -
- Films, plastics, and binders:
  - Film formation -
  - Water resistance -
  - Tensile strength -
  - Adhesion -
- Other:
  - Color -
  - Flavor -

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