2015 marks 100 years of AACC International members working together to share cereal grain science. The Centennial Committee, with the help of many expert members, is creating activities to celebrate achievements and look to the future of our science. The Scientific Milestones Sub-committee is coordinating a series of summary highlights—each focusing on an important area of cereal grain science. Experts in each area have identified key breakthroughs over the last 100 years, provided brief descriptions of the discoveries, and given examples of how these breakthroughs led to changes in our cereal foods. The experts also provide a few ideas on where future research may lead us. These brief highlights are meant to provide an overview and cannot be inclusive of the exhaustive research in these areas.

Centennial Scientific Milestones Sub-committee: Lauren Brewer, Rachel Prososki, and Steven Nelson.

Carbohydrates

David R. Lineback, James N. BeMiller, and Paul A. Seib

Introduction

Carbohydrates are the most abundant biological materials in cereal grains, in the plant kingdom, and throughout nature. Carbohydrates are important in human nutrition and for imparting various functionalities to foods. When the American Association of Cereal Chemists (now AACC International or AACCI) was founded in 1915, milling of grains into flours, meals, and other products and consumption of whole grains, such as rice, had been occurring since antiquity. However, in 1915, there was almost no processed food industry—only small commercial production of starch, no commercial production of crystalline dextrose/glucose, only primitive production of starch dextrin or starch-based sweeteners, no chemically modified starches, only a cursory understanding of the structures of amylose and amylopectin and the architecture of starch granules, and no knowledge of genetics of cereal grains, the biosynthesis of sugar or starch, what constitutes dietary fiber, the structures of the polysaccharides classified as dietary fiber, or the importance of dietary fiber in the human diet. Since then, a huge starch industry that includes chemically, physically, and genetically modified starch, conversion products, and coproducts for use in food and nonfood products has developed; the genetics, enzymes, and biochemical pathways related to the biosynthesis of sugar and starch have been established; and research into the roles of starch and polysaccharidic dietary fiber has begun.

AACCI was formed 100 years ago because the milling industry needed to standardize products and methods. At that time, wheat was mostly milled by relatively small mills to produce flours for households and neighborhood bakeries. Today, in the United States, approximately 920 million bushels of wheat are milled each year to produce more than 21 million tons of flours for a variety of bakery and pasta products. The corn wet-milling industry annually produces 2.9 million tons of corn starches and modified corn starches, primarily for the paper and food industries; almost 15 million tons of syrups and maltodextrins for the food industry; and 7.7 million tons of coproducts, such as corn oil and corn gluten feed. Rice growers produce about 9.5 million tons of rice, and annual sales of breakfast cereals top $13 billion.

Over its first century, AACCI has witnessed outstanding progress in cereal starch science. This involves the key discoveries listed in the timeline, but their importance goes well beyond this. Developments derived from these discoveries and the associated increase in knowledge concerning cereal starches have come to be of great importance in furthering our understanding of the structures, properties, functionality, and utilization of individual starches. They contribute to the daily lives of Americans through industrial food and commercial products, the roles of cereal dietary fiber and products in diet and health, and generation of challenges for the further research that is needed.

1925–1927 Dr. Carl Alsberg investigated the role of starch in bread staling

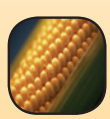
1926

U.S. Mills introduced first raisin bran on the market

1930s Starch products began to be developed as ingredients

1935 Bread dough "strengthened" by low levels of vitamin C

1940s Waxy maize starch was introduced



1940s–1950s Most of the modified food starches were developed

1942 Dr. Thomas J. Schoch separated amylose and amylopectin from starch

1958 Commercialization of the first high-amylose maize hybrid

Key Discoveries

- In the 1920s and 1930s, it was realized that wheat starch granules can be damaged by milling and that the degree of starch damage is important to baking quality. Development of various methods to measure the degree of starch damage followed. It also was realized that starch plays a role in bread staling. Dr. Carl L. Alsberg, who is honored by the AACCI Alsberg-Schoch-French Lectureship, conducted pioneering research on the role of starch in milling and bread staling (Alsberg, *Cereal Chem* 4:485-492, 1927). In 1930 the Amylograph was introduced by CW Brabender in Germany. The Amylograph and similar instruments are widely used to measure the pasting properties of flours and starches.

- In 1935 H. Jorgensen (*Biochem Z* 280:1-37, 1935) made a surprising discovery in Copenhagen. Low levels of vitamin C or L-ascorbic acid mixed into a bread dough did not weaken the dough as expected for a strong reducing agent. Instead, L-ascorbic acid strengthened the dough and increased loaf volume by some 20%—the same increase observed when adding the oxidant potassium bromate. L-Ascorbic acid is included with carbohydrates because it is produced from a 6-carbon sugar by oxidizing two of its hydroxyls to carbonyls. Bakers around the world consider vitamin C to be crucial to the production of yeast-leavened bakery foods, even though the total tonnage used for this function is a small fraction of the total.

- Before 1940, the processed food industry was very small and little starch was added as an ingredient in food formulations. Around that time, starch ingredients were beginning to be developed for the rapidly growing processed food and beverage industries. However, some commercial products containing carbohydrates were already available, e.g., Baby Ruth® candy bar (1920), Wonder® bread (1920), Yoo-Hoo® chocolate drink (1923), Wheaties® cereal (1924), Hostess® cakes (1927), and Kool-Aid® (1927). Uncle Sam® cereal was first introduced in 1908; and Skinner's® Raisin Bran was the first raisin bran on the market and introduced in the United States in 1926 by U.S. Mills.

- Most of the modified food starch products were developed and introduced in the 1940s and 1950s.Waxy maize starch was introduced in the 1940s. A starch that thickens without gelling had been sought for years. U.S. patent 2,328,537 was granted to Herman H. Schopmeyer and George E. Felton in 1943 for the commercial production of waxy maize starch. Over the ensuing years other waxy cereals were developed, including waxy sorghum, rice, barley, and wheat.

> ***"While fully aware of the great advances that have been made in our knowledge and understanding of cereal starches during this past century, I am constantly reminded of how little we really know and the challenges requiring future research in this area."***
>
> – Lineback

- In the 1940s, Dr. Thomas J. Schoch separated amylose and amylopectin from starch, the most abundant components of cereal grains. This work proved that normal starch is composed of amylose, a practically linear polymer, and amylopectin, a branched polymer. L. Maquenne and E. Roux are said to have earlier defined the fractions amylose and amylopectin.

- While some research was begun in the 1940s, the 1950s and 1960s produced research on the various genes and enzymes involved in starch biosynthesis, and the pathway of starch biosynthesis was elucidated. With that, the 1950s also provided an understanding and identification of enzymes that hydrolyze starch in specific patterns. Key studies noted that both different amylases and the same type of amylase (for example: α-amylase from different sources, including different microbial sources) hydrolyze starch in specific patterns unique to the particular enzyme. Such enzymes have been the key reagents in determining what we now know about the molecular structure of starch. Also, those same enzymes are essential to brewing and to the conversion of starch into maltodextrins, resistant starch, and sweeteners. Amylolytic enzymes include α-amylase, β-amylase, glucoamylase, pullulanase, and isoamylase.

1966
AACCI Carbohydrate Division was established

1967

First commercial shipment of fructose corn syrup produced in the U.S.

1967–1973
Maltodextrins were developed as well as cyclodextrins. "Cluster" model of amylopectin proposed by Z. Nikuni and by D. French

1970s–1980s
Dr. Denis Burkitt proposed that the consumption of dietary fiber from cereals promotes human health. Fiber in cereal grain includes β-glucan, xylans, cellulose and resistant starch.

1980s
Drs. Harry Levine and Louise Slade developed concepts surrounding interactions of water in cooked cereal products

1990s
Dr. Hans Englyst and coworkers coined the terms rapidly digested starch and resistant starch (a part of dietary fiber)

- High-amylose maize/corn starch was introduced in the 1950s. In 1958, Bear Hybrids Corn Company, in cooperation with American Maize Products Co. and National Starch and Chemical Co., commercialized the first high-amylose maize hybrid.

> ***"I am confident that, throughout history, the 20th century will be regarded as the golden age of cereal carbohydrate chemistry and biochemistry because of the tremendous advances made—both in understanding the natures and origins of the carbohydrate components in cereals and in putting them to food and industrial use."***
>
> – BeMiller

- High-fructose syrups were developed between 1957 and 1984. Glucose isomerase technology grew in the mid-1950s with the discovery that xylose isomerase could convert D-glucose to D-fructose. U.S. patent 2,950,228 was granted to R. O. Marshall in 1960 for the isomerization of glucose to fructose using an enzyme preparation that contained xylose isomerase. The first commercial shipment of fructose corn syrup produced in the United States was made by the Clinton Corn Processing Company in 1967. Research on glucose isomerase technology and its application was not pursued by the industry until the mid-1960s, when the science provided for the affordability and commercial feasibility of the process.

- Maltodextrins were developed between 1967 and 1973. Maltodextrins are widely used to encapsulate flavors and oils, to replace fat, and as bulking agents. Cyclodextrins form strong complexes with flavor agents.

- In 1977 investigators at the USDA Agricultural Research Service showed that a portion of high-amylose corn starch is indigestible in humans (Wolf, Khoo, and Inglett, *Staerke* 12:401-405, 1977). This observation, and those of others in the early 1980s, led Hans Englyst and coworkers to coin the word "resistant starch" (Englyst, Wiggins, and Cummings, *Analyst* 107:307-318, 1982). Thus, resistant starch is that carbohydrate-derived fraction in food that is not digested in the small intestines, but partially or completely fermented in the large intestine. The resulting products are thought to provide health benefits.

- In the 1970s and 1980s, Dr. Denis Burkitt put forth the proposition that the consumption of dietary fiber from cereals promotes human health by ameliorating heart disease, colon cancer, and obesity. This hypothesis was based on his nutritional studies in parts of Africa, where grain sorghum and millet were heavily consumed. He compared the pattern of diseases in African hospitals with Western diseases and concluded that many Western diseases, which were rare in Africa, were the result of diet and lifestyle. The cell walls of cereals are composed principally of arabinoxylan, β-glucan, and cellulose.

> ***"After air and water the third 'most-limiting nutrient' for human life is food energy. Food energy powers our brain and nerve activities, organ function, tissue repair, digestion, temperature control, and muscular movement. For economic reasons, carbohydrate from plants constitutes the major source of food energy. Even so, indigestible carbohydrate or dietary fiber in food, albeit at a somewhat lower level, contributes to health by ameliorating cardiovascular disease and colon cancer."***
>
> – Seib

- Beginning in 1979 (Donovan, *Biopolym* 18:263, 1979), the gelatinization of starch mixed with varying amounts of water was determined by differential scanning calorimetry, and soon thereafter three component mixtures were studied, such as starch-water-sugar and starch-water-salts. Today isolated starch would be subjected to DSC to determine its gelatinization properties. The results of DSC studies indicate how starch behaves when processing a cereal food.

- In the 1980s, Drs. Harry Levine and Louise Slade developed the concepts surrounding the interactions of water, glass transition temperature, and food texture. They recognized that water in cooked cereal products controls storage stability and eating texture. Water is the natural plasticizer of starch molecules, and starch often constitutes the continuous phase of a cooked cereal. When the starch molecules are "lubricated" with water, the starch molecules can move past one another whenever a force, such as biting or even gravitation, is applied. Cooked cereal products containing concentrated, hydrated starch molecules with a low glass transition temperature will likely have a soft and tender bite, such as a pudding or noodle. As the moisture in the cooked cereal product falls below approximately 15% and the glass transition temperature of the continuous starchy phase rises, the eating texture becomes rubbery to leathery. When moisture content reaches approximately 2–3%, the product becomes hard, but if thin, it is crispy.

- The structure/organization of the starch granule and the properties of its two component polymers (amylose and amylopectin) were heavily investigated in the 1970s and 1980s. However, the structure/organization of the starch granule has been and continues to be a major, complex problem. The realization that the amylose component, traditionally considered to be a linear polymer, contains a limited number of branches was first reported in 1981 (Hizukuri, Takeda, Yasuda, and Suzuki, *Carbohydr Res* 94:205, 1981) and elaborated in subsequent studies from that laboratory. The currently accepted cluster model for amylopectin with many starch chains wound into a double-helix was first proposed independently in 1969 and1971 (Nikuni, *Chori Kagaku* 2:6, 1969; French, *J Jpn Soc Starch Sci* 19:8, 1971) and further developed (Robin, Mercier, Charbonnière, and Guilbot, *Cereal Chem* 51:389, 1974; Hizukuri, *Carbohydr Res* 147:342, 1986). These studies originated the models that have been and continue to be refined and expanded through continuing investigations on cereal starches in many laboratories. The structure/organization of the granule is a complex issue resulting from the enzymatic synthesis of starch in cereals. The structure/organization is responsible for the properties and functionalities of the various cereal starches.

- Modernization of the corn wet-milling industry to produce a wide array of useful modified starches occurred between 1935 and 1995. The main development was a method to react starch in aqueous slurries while maintaining the granule integrity so that the modified starch product can be recovered by filtration or centrifugation. This same filtration or centrifugation also removes the reaction by-products.

- In the 1990s, largely through the efforts of Hans Englyst and associates in Cambridge, U.K., carbohydrate in foods is now classified nutritionally as rapidly digested, slowly digested, or resistant (Englyst, Kingman, and Cummings, *Eur J Clin Nutr* 46(Suppl 2):S33-S50, 1992). Dietary fiber is currently defined as the sum of nonstarch polysaccharides, resistant starch, and resistant oligosaccharides.

Summary

The past 100 years has seen

- Development of many new starch products, both those from new corn cultivars and via chemical modifications
- Expansion and improvement of a variety of glucose and high-fructose syrups
- Extensive modernization of the corn wet-milling industry
- Considerable use of enzymes in producing starch conversion products
- Lengthy advancement in understanding the natures of starch polymers and granules and the physicochemical characteristics of starch granules and their pastes

As to the future, the near future is in carbohydrate nutrition, the distant future is in breeding cereals for consumer-valued properties, and beyond that is in the hands of the up-and-coming scientists in our field.

References

BeMiller, H. N. One hundred years of commercial food carbohydrates in the United States. J. Agric. Food Chem. 57:8125-8129, 2009.

Bundy, B. *The Century in Food: America's Fads and Favorites*. Collectors Press, Portland, OR, 2002.

Burkitt, D. *Don't Forget Fibre in Your Diet: To Help Avoid Many of Our Commonest Diseases*. Martin Dunitz Ltd., London, 1979.

Englyst, H., Wiggins, H. S., and Cummings, J. H. Analyst 107:307-318, 1982.

Kimmerle, B. *Candy: The Sweet History*. Collectors Press, Portland, OR, 2003.

Levine, H., and Slade, L. A food polymer science approach to structure-property relationships in aqueous food systems: Non-equilibrium behavior of carbohydrate water systems. Pages 29-102 in: *Water Relationships in Foods: Advances in the 1980s and Trends for the 1990s*. H. Levine and L. Slade, eds. Plenum Press, New York, 1991.

Maquenne, L. Über den Rückgang des Stärkekleisters. Compt. Rend. 137:88-90, 797-799, 1903.

Marshall, R. O. Enzymic conversion of dextrose to fructose. U.S. patent 2,950,228. 1960.

Parker, P. M., ed. *Maltodextrin: Webster's Timeline History 1970–2007*. ICON Group International, San Diego, CA, 2010.

Schoch, T. J. Physical aspects of starch behavior. Cereal Chem. 18:121-128, 1941.

Schoch, T. J. The fractionation of starch. Adv. Carbohydr. Chem. 1:247-277, 1945.

Schopmeyer, H. H., and Felton, G. E. Waxy starch product and method of making. U.S. patent 2,354,838. 1944.

Trager, J. *The Food Chronology: A Food Lover's Compendium of Events and Anecdotes, from Prehistory to the Present*. Owl Books, New York, 1995.

Wolf, M. J., Khoo, U., and Inglett, G. E. Staerke 12401-405, 1977.

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