The Evolution of Enzyme-Treated Starches from Sweeteners to Healthy Ingredients

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Over recent decades the role of food starch has expanded from that of an energy source to a texturizing ingredient. The texture of a food depends on the properties of the starches present, as well as changes in these properties during processing. To positively influence both aspects of food starches, many starch derivatives have been developed using chemical and enzymatic treatments. Today, a wide variety of starches can be found in markets and on food labels, ranging from highly degraded starch polymers (i.e., maltodextrins) to highly crosslinked starches that form large networks.

Beneficial Starches

Maltodextrins with a wide range of dextrose equivalents (DEs) can be produced by controlled hydrolysis using acids and/or α-amylase. In practice, acid treatments alone can produce large amounts of free glucose, whereas less-hydrolyzed, low-DE treatments produce large linear maltodextrins that have a strong tendency to reassociate with each other (retrograde). As a result, some maltodextrins are produced from starch using hydrolytic enzyme treatments, in particular α-amylases. Hydrolytic enzyme treatments are more controllable, and specific hydrolysis can be easily performed in water and under very mild conditions (3). Enzyme-hydrolyzed products are used in fillings and as sweeteners in beverages (e.g., soft drinks). However, both consumers and the food and beverage industries are looking for innovative product solutions and ingredient options because these hydrolyzed products simply do not possess sufficient end-product functionality.

The obesity epidemic (20) and its associated diseases, such as type 2 diabetes, have highlighted the consequences of dietary patterns that include high levels of fat and sugar. More than 30% of Americans are obese, which increased health care costs in 2010 by $3,500/year/person, for a staggering total of $316 billion (5). In addition, there is increasing interest in "clean label" foods (e.g., foods containing ingredients that do not have E numbers [6]), and ingredients such as low-DE maltodextrins do not have E numbers that must be included on food labels. The combination of questions concerning health outcomes and the perception of health benefits provided has forced the food ingredient industry to develop new types of starches with better nutritional properties.

Fat Replacement. In the field of carbohydrate-based fat replacement (1) early attempts to create texturizing, fat-replacement starches through enzymatic modification were based on the use of α-amylase as the predominant hydrolytic enzyme. Over the last 10 years additional specific and nonhydrolytic starch-active enzymes have been developed that have more specific activities. These include branching enzymes and 4-α-glucanotransferase. These enzymes hydrolyze starch polymers differently than do α-amylases; instead, α-glucanotransferases remodel parts of the amylose and amylopectin polymers by cleaving and reforming α-1,4- and α-1,6-glycosidic bonds (18). As described by Van der Maarel et al. (19) and Kaper et al. (11) the enzyme amylomaltase converts the amylose and amylopectin of normal starches into an amylopectin with elongated chains (Fig. 1). Amylomaltase (e.g., Etenia, Avebe) produces starch that forms strong thermoreversible gels in water. In this respect the resulting system resembles other hydrocolloids. The mode of action of amylomaltase in products such as low-fat yogurts is unique (2,10). Upon setting of the yogurt, the amylomaltase action results in small gel particles in the protein flocs that resemble droplets of fat and create textures similar to those of full-fat equivalents (2,4). In Europe amylomaltase carries no E number and is considered label friendly.

Glucose Control and Dietary Fibers. As discussed by Kendall et al. (12), interest in blood glucose control and the effects of fiber on the gut microbiome and health is a recent and continuing trend that has drawn a lot of attention. Consumers, especially in the United States, are demanding food products that provide improved control of blood sugar levels, provide balanced delivery of energy, and aid in weight management (i.e., products [ingredients] with a low glycemic index or slow glycemic response). Initially, the development of new ingredients resulted in slowly digestible carbohydrates (e.g., isomaltulose) and dietary fibers (e.g., resistant starches, inulin, and polydextrose) (15).

Other transferase enzymes can be employed to create slowly digestible (low-DE) starches for food applications. Once gelatinized, unmodified starches are rapidly degraded by the digestive system but can be converted into slowly digestible starches by the actions of branching enzymes. Van der Maarel et al. (17) showed that the branching enzyme of the bacterium *Deinococcus radiodurans* (16) converts amylopectin into a branched maltodextrin with a side-chain distribution dominated by side chains shorter than those produced by other branching enzymes. In vitro digestion analysis revealed that the resulting starch had a slower glucose release when incubated with a pancreatic amylase preparation. Further improvement in the results can be achieved by combining branching and maltogenic α-amylase treatments, as described by Hansen et al. (8). The result is a starch with a decrease in the longest glucose chains and an increase in shorter chains, as well as a more compact structure that is less accessible by pancreatic amylases. Using a somewhat different approach Kajiura et al. (9) created a "cyclic cluster dextrin" (CCD) or highly branched cyclic dextrin. Character-

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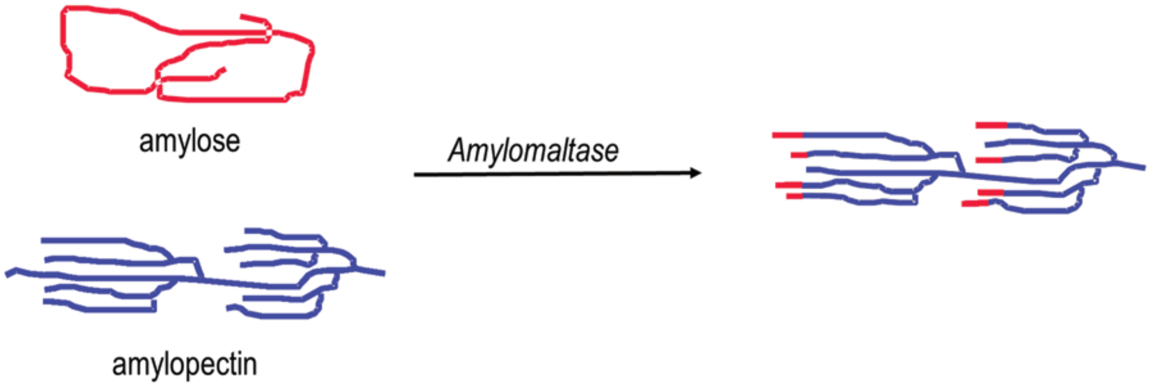

Fig. 1. The conversion of amylose and amylopectin by amylomaltase (e.g., Etenia, Avebe).

ized as having a slow glycemic response, it is claimed to provide improved sports performance by, for example, producing faster gastric emptying. Recently, an isomalto-oligosaccharide (Vitafiber, BioNeutra) has been introduced for this purpose.

Soluble Fiber. Another important field for further development of healthy starches is in the area of soluble food fibers. The first successful food fiber obtained from starch and enzymes was an indigestible dextrin (FiberSol) developed by Matsutani Chemical Industries Co., Ltd. in the late 1980s (14). In this case, a yellow dextrin is treated with α-amylase, and the remaining high molecular weight fraction acts as a food fiber. In the past decade new methods and fibers have been developed. For example, a water-soluble dietary fiber (Fibryxa, Hayashibara Co., Ltd.) has been introduced that is made using a special α-4-6 transferase. Enzyme action yields a mix of isomalto-maltose oligosaccharides. Isomalto-oligosaccharides can be produced using maltose and transglycosylating enzymes, and products based on this process have been introduced. In all of these cases, the resulting materials behave as soluble food fibers. Recent trends in improvement of the health benefits of ingredients have resulted in the development of isomalto/malto-polysaccharides. As described by Leemhuis et al. (13) these are actually dextrans. The fraction rich in α-1-6 linkages easily passes through the small intestine and remains undigested in the large intestine. Fermentation of the product is relatively slow in the large intestine and stimulates the growth of beneficial microbiota, such as *Lactobacillus* and *Bifidobacterium* (7). In vitro experiments showed that high amounts of short-chain fatty acids, in particular acetic acid and succinic acid, were produced.

Conclusions

In recent decades, the role of starch in foods has expanded from that of an energy source to a food texturizer, and, most recently, to a health-promoting ingredient. There are several new routes through which health-promoting starches can be developed. One method utilizes specific enzymes with specific modes of action to create starches that are slowly digestible or nondigestible and that still have texturizing properties. In the coming years, many innovations in ingredients will be developed to meet consumer demands, using faster changing technologies than ever before. Utilizing new enzymes to modify starches, innovative starches with health benefits will be introduced, such as carriers for medicines and smart starch–protein combinations with improved nutritional values!

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Lizette Oudhuis obtained her Ph.D. degree in the field of polymer chemistry at the Groningen University and started working in this field at Avebe in 1996. From 2006 till 2012 Lizette was a senior scientist at TNO (Dutch organization for applied scientific research) with a focus on carbohydrates and food. Her main interest is structure–function relationships and the study of food as a complex polymer system. At the moment her focus is on nutrition, especially on the digestibility of starches and proteins in relation to health. Lizette is working as team lead nutrition in the Avebe R&D Department and two days a week as a professor of food physics at the University of Applied Science Van Hall Larenstein (Leeuwarden, The Netherlands). Most recently she is working in close collaboration with SMEs (micro-, small-, and medium-size enterprises) and students and through lectures to explore new technologies, such as 3D food printing, for opportunities to create innovative healthy food concepts that can support long-life healthiness from childhood through old age.

Piet Buwalda's passion is understanding how nature works. Starch is just a small part of it, but it is very important for food products and other applications. What intrigues him the most is the relationship between the properties and backbone of the carbohydrate. The new enzymatic method enables starch to enter new fields of application. Piet obtained his Ph.D. degree at the Groningen University and started working in this field in 1989. Currently he is the starch technology officer at Avebe (a large potato starch producer), and he is also working one day a week as an associate professor at the Wageningen University, working on carbohydrate conversions.

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