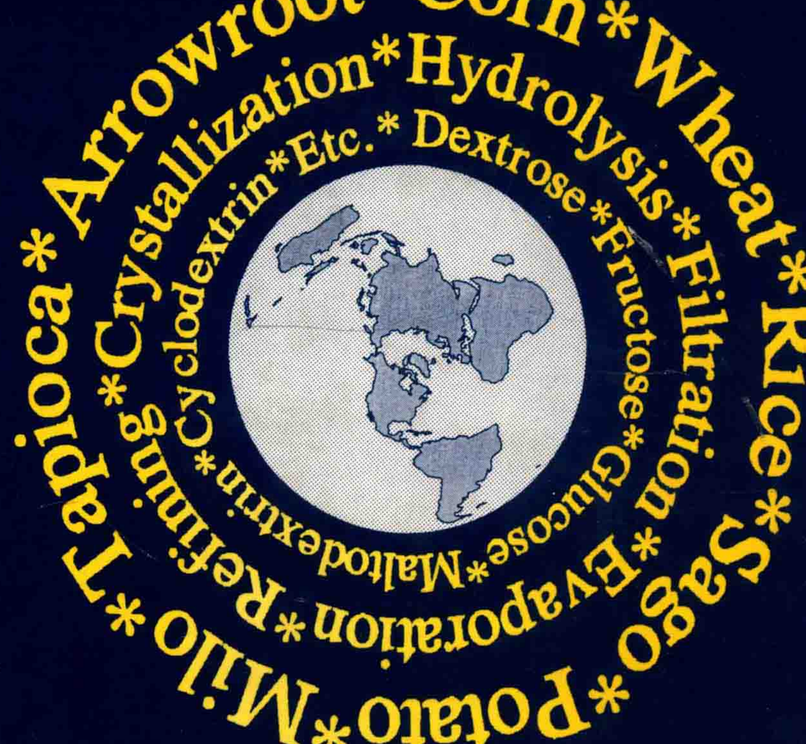
STARCH HYDROLYSIS PRODUCTS

WORLDWIDE TECHNOLOGY PRODUCTION AND APPLICATIONS

FRED W. SCHENCK • RONALD E. HEBEDA



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Worldwide Technology, Production, and Applications

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Series Foreword

This book begins the Food Science and Technology series to be published by VCH Publishers, Inc. It is a pleasure to have Fred Schenck and Ron Hebeda as editors as they are thoroughly familiar with the subject of starch hydrolysis products that are made and used around the world. Although many journal articles and books have been written on the individual aspects of this subject, no single volume has provided such comprehensive coverage before. To help the users of this book, it includes a directory of some of the many companies that offer applicable products and services.

Over the next several years, VCH Publishers, Inc. will be releasing new titles in food science and technology covering such topics as dairy science and technology, food biotechnology, food enzymes, food proteins, table olives, herbs and spices, seafood quality evaluation, analytical methodology, and molecular genetics. If you are in any discipline within the broad field of food science and technology and wish to join these authors and editors, please write me. New subject proposals are always welcome.

Y.H. Hui
Editor
Food Science and Technology Series

Introduction

Hydrolysis products, primarily sweeteners, are the largest end use of starches. Many books have been written about specific hydrolysis products, manufacturing processes, and the equipment used for production. No single volume, however, has attempted to provide the reader with complete coverage of all facets of this complex industry. This book is a first!

Within these covers, the reader will find material on aspects of the production, technology, and applications for starch hydrolysis products produced around the world. This volume gives details of factory design and construction, product applications, analysis, quality control, waste treatment, legal aspects, metabolism, and industry economics. Also included is a worldwide list of starch hydrolysate producers (numbering more than 200), a list of fructose-bearing syrup manufacturers (including estimated tonnage produced), and a directory of suppliers of equipment, ingredients, and technology.

The chapter authors are experts in their respective fields. Drawn primarily from the starch hydrolysis industry around the globe, they provide a practical real-world viewpoint of this fascinating subject. Chapter-end reference sections offer many citations for further reading.

Units of measurement are metric, with most conforming to SI (Système International) international system of units. License has been taken with some units for the sake of familiarity and dimension. While the SI unit for temperature is the kelvin, the more familiar Celsius scale has been used. Where long periods of time are expressed, minutes or hours are used instead of the SI standard, seconds. Also, large volumes are given in cubic meters as opposed to liters.

The book begins with a history of starch hydrolysate production. From the first syrup produced from arrowroot starch in ninth century Japan, the reader is led toward the present-day industry, which has succeeded in creating products with sucrose-like sweetness through enzyme-catalyzed isomerization and chromatographic separation.

The second chapter discusses the subject of starch sources and the production of modified starches is discussed. The third chapter covers the enzymes used to convert the starch molecule into the wide array of specialized products available for industrial, pharmaceutical, and food uses. And the fourth chapter details the processes and equipment used in the hydrolysis of starch.

The individual products of starch hydrolysis are dealt with in the next seven chapters. Chapter 5 covers crystalline and liquid dextrose products. Chapters 6 and 7 detail the production, properties, and applications of liquid and crystalline fructose. Chapters 8 and 9 deal with the larger saccharides, covering maltodextrin and glucose syrups, respectively. Chapters 10 and 11 discuss the specialized hydrolysis products, cyclodextrins and oligosaccharides.

Chapter 12 deals with the analytical methodology of starch hydrolysates and includes the necessary information for setting up a modern analytical laboratory for process and quality control. Chapter 13 discusses the metabolism of starch hydrolysates, while Chapter 14 delves into the legal aspects of their production and sale, covering the governmental regulations that make these products uniform around the world.

The next seven chapters take the reader through the production steps in great detail. Chapter 15 covers the economic aspects of manufacture. Chapter 16 details the design, control, and construction of a typical facility. Chapters 17–20 describe the equipment used for clarification, concentration, refining, and chromatographic separation. The most up-to-date aspects of these operations are provided, including membrane separation for both clarification and concentration, as well as total resin refining. Chapter 21 describes the treatment of waste streams using methods ranging from ground disposal to tertiary treatment.

Appendix I is a worldwide list of suppliers of equipment, ingredients, and services. This is a list of respondents to a questionnaire ONLY; inclusion on this list does *not* indicate any sort of endorsement of the products or services, nor are negative implications attached to absence.

Appendix II is a glossary of terms that may be unfamiliar to the reader from outside the industry.

The contents of this volume in the Food Science and Technology Series edited by Dr. Y. H. Hui form a complete book on the subject of starch hydrolysis, one that you will refer to for many years.

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Starch Hydrolysis Products:

An Introduction and History

Fred W. Schenck and Ronald E. Hebeda

1.1. Introduction

Hydrolysis products, primarily sweeteners, are the largest end use of starches. A large variety of starches are used for their production around the world. This chapter gives the history of starch hydrolysate production, beginning in ninth century Japan and continuing through the development of glucose isomerization, which allows starch sugars to replace sucrose in liquid applications. The less common hydrolysate products are briefly discussed. Also included is a worldwide list of producers (numbering more than 200). Possibilities for the future of this industry are also explored. For readers from outside the industry, a glossary of selected terms used in this book is provided in Appendix II [1].

1.2. History

1.2.1. Starch Source

Regardless of botanical source, all starches are polymers consisting of α-linked anhydroglucopyranose units. Hydrolysis products made from various starch sources are virtually identical in terms of chemical, physical, and organoleptic properties. As a result, starch hydrolysis products are manufactured from a wide variety of raw materials throughout the world.

In Asia, it is not uncommon for a factory to use sago, tapioca, or maize (corn) starch for glucose production, depending on availability and price. The starch source and purity have an influence on the manufacturing requirements, but a variety of starches are used successfully.

In Thailand, for example, a syrup called "Chinese maltose" is produced from wheat and glutinous rice. In Pakistan, broken rice is used to produce 42% fructose and enzyme–enzyme glucose syrups having qualities comparable to products made from maize starch.

Starches from barley, sago, sorghum, wheat, rice, potato, tapioca, and other grains and roots serve as raw materials for the making of hydrolysis products around the world. But, the unsurpassed productivity of the maize plant has made it the leading source of starch for conversion [2]. Nearly 100% of the glucose-based sweeteners produced in the United States and 84% of the production in Japan are from maize. The use of wheat starch (as a coproduct of vital gluten production) is significantly increasing in Europe. Yet, most glucose-containing sweeteners produced there still originate from maize starch, much of it grown in France.

About 70% of the world production of maize starch is converted to glucose-containing sweeteners. Starch hydrolysis products are as old as life itself. When starch is eaten, acid and enzymatic processes convert these macromolecules to glucose. This digestion process is similar to the commercial manufacture of starch-based sweeteners today.

1.2.2. Early History

The first sweetener created from starch was a syrup produced in Japan during the ninth century by the action of malt on arrowroot starch (it is still produced today as a "traditional" sweetener) [3]. Glucose was first obtained in pure form from grape juice by the German chemist, A. S. Marggraf, in the middle of the seventeenth century [4]. By 1781, it was known that starches could be treated with acids to produce a soluble, sweet-flavored substance [5]. This knowledge was little more than a laboratory curiosity until the Napoleonic wars, when the blockade of cane sugar imports from the West Indies provided an incentive for the development of alternative sweeteners.

One of the first of these was the preparation of a α-D-glucose crystals from grape juice by Proust in 1801 [6]. The synonym for D-glucose, grape sugar, owes its origin to this process. In 1811, G. S. C. Kirchoff, who was searching for a substitute for gum arabic (used in the manufacture of porcelain), overcooked a mixture of potato starch and sulfuric acid [7]. The sweet, syrupy substance that resulted earned him a lifetime pension of 5000 rubles per year and the Order of St. Anne, Second Class from the Russian emperor on January 29, 1812 [8].

Although others disputed his claim [9], Kirchoff recognized the commercial potential of his discovery and proceeded to improve the process.

He succeeded in preparing a syrup that crystallized upon standing and from which a solid product (D-glucose) was obtained by pressing the mass in cloth sacks. This solid material contained large quantities of uncrystallized syrup and was quite impure. Nonetheless, serious attempts were made to manufacture the product on a large scale. But after the defeat of Napoleon at Waterloo, cane sugar became available again and the venture was abandoned.

While the commercial production of starch sweeteners suffered a temporary setback, scientific investigation of the process continued. The French chemist Saussure determined the acid conversion of starch to be a hydrolysis reaction in which the link between two anhydroglucopyranose units is severed while one molecule of water is added. Carried to the limit, starch hydrolysis produces the basic building block, D-glucose. Starch sweeteners have unique functionality in the manufacture of candies. The result was development of a great industry in Europe (especially in Germany) and in the United States [10].

Early efforts to improve the quality of "starch sugars" were directed at controlling the nonspecific nature of the acid hydrolysis. The market signaled a need for purer forms, but early commercial production (1880–1920) of crystalline glucose required either repeated crystallization steps or crystallization from nonaqueous solvents. The only solid form of glucose available in quantity at low price at that time was a cast product. Starch was acid converted to the highest degree possible, evaporated to a thick syrup, and poured into molds where it hardened into solid blocks. Subsequently, it was removed from the molds, chipped into small pieces, and sold.

Chip sugars were the invention of Arno Behr, who also patented a process (US 259,794) for the manufacture of anhydrous dextrose by quiescent crystallization and centrifugal separation. A refinement of the chip sugar process, similar to the Kirchoff process for solid starch sugar, was developed by Charles W. Post of breakfast food fame. It involved grinding the partially crystallized hydrolysate, placing it in presscloths, and squeezing it in a hydraulic press. Post called the mother liquor removed by this process hydrol, a name that has persisted for corn sugar molasses ever since [11].

Chip sugars can also be thought of as the forerunners of total sugars. These products comprise 60% of the crystalline glucose produced in Korea and more than one-third of the solid glucose sold in Japan. While total sugars have a large share of the solid glucose market in the Orient, their success in the Western Hemisphere has been less spectacular. This is in spite of many patented processes for their manufacture [12–21]. Except for a spray-dried hydrolysate having the name Cantab (Penford Products Co., United States), pure glucose crystals are preferred in the Americas and in Europe.

The process for economically producing pure crystalline glucose, the invention of William Bentley Newkirk, resulted in an astronomical increase in crystalline glucose sales. What is more amazing is that only 3 years elapsed between Newkirk's employment by the Corn Products Refining Company and the construction of the first crystalline monohydrate dextrose production facility at Argo, Illinois. Development costs were a mere $150,000—even in the 1920s, a small amount for such a monumental development [11].

By carefully controlling the conditions during the crystallization step, large, easily separable crystals could be produced economically. The first experimental product of satisfactory purity was produced in 1921. In 1923 Bill Newkirk received a patent for developing a commercially feasible process for the production of pure crystalline glucose [22]. This patent was one of the rare instances of a crystral structure being the subject of a patent claim. That year, 50 metric tons of Cerelose brand monohydrate dextrose were sold. Soon after, the Argo refinery was expanded to a daily capacity of 225 metric tons. By 1940 the annual production in the United States had reached 320,000 metric tons and today stands at 500,000 metric tons! Consumption of dextrose in the United States has grown by a factor of TEN THOUSAND TIMES in the past 70 years as a result of Newkirk's invention.

The strength of the Newkirk patent was upheld in the courts [23], providing Corn Products with virtual control of the crystalline dextrose market for many years. It took nearly 10 years to develop processes sufficiently unique to allow the emergence of license-free competition [24]. The advent of an economical process for the production of high purity crystalline glucose was one of but a few developments that resulted in substantial growth of the starch hydrolysis industry.

1.2.3. Enzymatic Conversion

Ironically, while the first starch hydrolysate product was produced enzymatically, acid hydrolysis had become the predominant conversion process in the early twentieth century. Acid conversion is a random-action mechanism that results in remarkably reproducible saccharide compositions for any given degree of hydrolysis. This reproducible composition is also a limitation. The manufacturer lacks ways of influencing the saccharide distribution for a given degree of conversion. This is important in some applications of glucose syrups.

Additionally, acid syrups having a dextrose equivalent (DE) below about 30 will tend to cloud upon standing, as a result of a precipitation (retrogradation) of the longest chain linear polymers. And, while acid hydrolysis to DE values in the high 80s is possible, the extreme conditions required to produce DE values greater than about 55 promote the formation of excessive amounts of glucose degradation products (e.g., 5-hydroxymethylfurfural, HMF) that are difficult to remove during refining. These color precursors cause eventual product yellowing. The most common acid glucose product has a DE value of about 40–45 because of these upper and lower conversion limitations.

The limitations at both the low and high ends of the conversion spectrum, coupled with the inflexible saccharide distribution resulting from acid hydrolysis, led manufacturers to investigate enzymatic hydrolysis for making improved glucose-containing syrups.

Enzymatic starch hydrolysis had been observed in 1833 by Payen and Persoz [25] when an unknown material in a precipitated malt extract was found to convert starch to sugar. However, the phenomenon of "separating" a soluble dextrin from starch was not attributed to the action of amylase enzymes at the time. The mysterious material was called "diastase" from the French word meaning separation. "Diastase" eventually became a generic word for all amylases. As specific enzymes were later discovered, they were named by adding "-ase" to the substrate used by the particular enzyme. Amylase, for instance, was derived from "amyl" (starch) plus "ase."

Later in the nineteenth century, Jokichi Takamine developed the first industrial production systems for fungal amylases [26]. In 1896, a crude mixture of *Aspergillus oryzae* enzymes (Takadiastase) was first marketed outside the Orient. This type of preparation was later used for removal of starch in the production of pectin [27].

A fungal amylase preparation was first employed for commercial syrup manufacture in 1938 [28]. The enzyme preparation contained a mixture of glucoamylase and α-amylase and was used to convert a 45–50 DE acid hydrolysate to a 65 DE product. Compared to acid syrups, the new product was sweeter, less bitter, more fluid, and less likely to crystallize. The process for manufacturing the new syrup was licensed throughout the industry, and corn syrup consumption increased by 86% between 1940 and 1942 [29].

During this period of time, studies were initiated in an attempt to find a source of mold enzyme that could replace malt used to generate fermentable sugars in the manufacture of grain alcohol. Takamine had suggested this application for mold enzymes as early as 1914 [30]. But the need did not develop until production of synthetic rubber during World War II increased the demand for alcohol and sufficient malt was not available. Subsequent studies showed that enzyme mixtures from fungal strains of *Aspergillus* and *Rhizopus* could replace malt [31,32]. An *A. oryzae* mold bran was eventually used in alcohol production near the end of the war [33].

Studies were continued after the war in an attempt to develop a fungal enzyme product that could be used as a substitute for acid hydrolysis in starch saccharification. Work as early as 1913 had suggested that a dextrose-producing enzyme was present in fungal enzyme mixtures [34]. Later studies indicated that the same enzyme was present in preparations used for syrup production [35,36]. *Aspergillus* strains were studied as a source for this enzyme in the late 1940s [37–39]. It was found that the enzyme preparations contained a mixture of the dextrose producing enzyme, glucoamylase, along with α-amylase [40]. In 1951, glucoamylases from both *A. niger* [41] and *R. delemar* [42,43] were characterized. The enzyme from the

Rhizopus strain was called gluc amylase and the *Aspergillus* enzyme amyloglucosidase. Both terms are still in use today although the offical trivial name for the enzyme is glucoamylase.

The *Rhizopus* enzyme was selected for extensive study in Japan because it did not contain the contaminating enzyme transglucosidase (TG). This side activity, present in *Aspergillus* enzyme preparations, was responsible for lowering dextrose yield during saccharification by the formation of reversion products. The *Rhizopus* enzyme, however, was produced in low yields and exhibited a lower optimum temperature and narrower pH range than the *Aspergillus* enzyme. As a result, the *Rhizopus* enzyme was never used extensively in commercial operations. Investigation of *A. niger* glucoamylase was continued in the United States. Several techniques were eventually developed to remove TG including precipitation, absorption, temperature/pH treatment, and strain mutation. A suitable glucoamylase product was tested in pilot plant facilities in Germany in 1957 [44] and commercial operation was initiated by 1960.

The coupling of a secondary enzymatic hydrolysis to a preliminary acid thinning allowed producers to expand the range of DE values both up and down. It also provided control over the saccharide distribution by enzyme selection. At first, enzyme conversion was used to extend the degree of conversion upward, primarily to maximize glucose production for the manufacture of crystalline glucose and for the production of sweeter, less viscous glucose-containing syrups. It also made possible the selective production of more maltose or more glucose, depending on the enzyme chosen.

Having reached commercial success with enzymatic saccharification, the next goal was to replace acid hydrolysis totally by developing a high temperature amylase that could efficiently liquify starch. Thermostable bacterial α-amylase had been developed in the early 1900s by Boidin and Effront [45,46]. The enzyme was used commercially for starch hydrolysis in several different industries [47]: in the brewing industry for liquefaction of corn, rice, and wheat; in the textile industry for removing starch from woven fibers (desizing) to permit uniform bleaching and dying; and in the paper industry for preparing paper coatings and sizes from starch pastes. The α-amylase had also been suggested for use in baking as an antistaling agent [48] and for reducing viscosity in chocolate syrup by hydrolysis of cocoa starch [49].

So, it was a logical extension of known technology to use the heat-stable α-amylases derived from the bacterium *Bacillus subtilis* for starch liquefaction. Commercial processes were implemented in the early 1960s, resulting in a total enzyme process. This further expanded control of saccharide range and distribution. A total enzymatic conversion process eliminated the need for preliminary acid hydrolysis. On the high end of the glucose conversion scale, a totally enzymatic conversion greatly increased the yield of glucose while decreasing the refining requirements.

By allowing the economic production of much purer starch hydrolysates