STARCH CONVERSION TECHNOLOGY

Edited by

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PREFACE

Starch is a well-known and abundant source of renewable raw material. Its yearly production level is surpassed only by the formation of (ligno-)cellulosis. An amount of more than 14.10^6 tons of starch is processed yearly by industry. Corn is the most important source for this raw material but potato also is of significant importance. Minor quantities are derived from wheat and tapioca. The total starch production in agriculture is of course much larger; for instance, the total world starch production is estimated to have been at least 1.1×10^9 ton in 1978. So, nowadays only 1% of the total starch production is further processed (converted). The overwhelming majority of the agricultural production of starch containing crops is used as a feed or a food.

Starch has been well known for more than 2000 years and although most starch is used as such in several food and feed applications, there have always been processes by which starch is converted to a form which makes it more suitable for other applications. Starch conversion technology is thus of about the same age as starch itself, and during the last 100 years this technology has been the subject of several more-or-less extensive publications. Nevertheless, there is need for another collection of papers on this subject. In the last 10–20 years important new starch conversion processes and their technologies have been developed which added new starch-based products to the existing list. To cite an important number of examples, these are: high fructose corn syrups (HFCS), glucose syrups, dextrose, modified starches, (malto)dextrins, and ethanol. It is remarkable that such recent developments as HFCS and ethanol already account for more than 50% of the total.

What we would like to stress in this Preface is that the development of new processes and their products, which may result from economic, political, and/or technological developments, may already have an important impact on the balance between starch and its various modified products as well as on the balance between the various starch-based products. It is this mixture of economic, political, and technological influences that make a book concerning starch conversion technology a rather complex one. Besides technological developments, political and economic considerations have formed the basis for the development of processes for high fructose corn syrups and gasohol. Obviously, starch reaches a new stage of its life the moment that it turns out to be a competitor to sucrose or crude oil.

Thus it is the multidimensional complexity of starch conversion technology that stimulated us to compose this work in which we have tried to bring together chapters of both technological and economic/political natures. The reader will find in the book rather classic chapters on starch covering its structure and properties (Chapter 2) and physical and chemical modifications of starch (Chapter 4), as well as other chapters which deal with current subjects such as enzymatic degradation of starch (Chapter 5) and the use of starch and starch-based products in the fermentation industry (Chapter 8). The chapters on gasohol (Chapter 6) and high fructose corn syrups (Chapter 7) describe important technological developments of recent date, while Chapter 9 looks at the starch conversion processes from a completely different point of view, that of the synthetic organic chemist. Chapter 10 is dedicated to economic and political considerations in the United States and other chapters (6 and 7) also deal with these aspects of the subject; much to our surprise, however, we were unable to find any person willing to write a similar chapter on the European (EEC) situation. An overview of the total refinery operation from corn to "feed stocks," the corn wet milling process (Chapter 3), completes this work. *Starch Conversion Technology* should interest people who are engaged in academic or industrial research on raw applications of starch or in the development of new chemical or biochemical processes to be used in starch conversion technology. It is also suited for use in advanced university courses or postgraduate courses.

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THE MULTIDIMENSIONALITY OF STARCH CONVERSION TECHNOLOGY

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I. INTRODUCTION

In this introductory chapter, we will first look at starch as an important raw material for industrial use. Tables 1 and 2 give information about the amounts of starches produced and processed and the variety of starch-based products and their volumes that are yearly produced in the United States.

Then we bring to the reader's attention the various aspects that make a raw material suitable for certain applications.

Then, we draw some attention to the economical, political, and technological aspects and mixtures of these that play a role, when starch and its products are considered as substitutes for already existing products derived from other sources. The chapter concludes with a list of products that can be prepared from starch.

II. INDUSTRIAL APPLICATIONS OF RAW MATERIALS

A. The Debate on Fossil or Renewable Resources

The present-day energy supply and chemical industries are almost wholly based on fossil sources of raw material, that is, oil, natural gas, and, to a probably increasing extent in the near future, coal, are the main sources of energy and organic chemical raw materials. The fossil *resources* are processed to *feedstocks*, such as synthesis

Table 1 World Starch Production and Amount of Processed Starch

Source	Annual world production (10^9 ton)[a]	Amount of processed starch (10^6 ton)
Corn	±1000	11
Wheat		0.5
Potato	±100	2
Tapioca		0.5
Total	1100	14 (1.3%)

[a]See Ref. 1.

gas or naphtha. These feedstocks can be used as energy sources as such or can be processed into more sophisticated energy carriers, such as gasoline. Alternatively, the feedstocks can be processed into primary chemicals, such as ammonia, methanol, propylene, ethylene, and benzene, from which intermediate chemicals, the starting

Table 2 Starch-Based Products and Applications

Products	Amounts (U.S. figures) 10^6 ton	% of total	Application
High-fructose corn syrup	2.9	35	Food sweetener
Glucose syrups	2.0	24	Sweetener, raw material
Dextrose	0.45	5	Sweetener, thickener, stabilizer
Modified starches	1.8	22	Coating, adhesive
Maltodextrins	0.045	0.5	Food additive
Dextrins	0.045	0.5	Food additive
Ethanol	1.1[a]	15	Beverages, ethanol
Total	8.3	100	

[a]Estimated amount of starch used in 1982 ethanol production.

point of the versatility of fossil-based organic chemistry, are produced. The synthesis routes thus result in the production of increasingly complex *performance chemicals*, of which polymeric materials, detergents, pharmaceuticals, pigments, and dyes are examples.

In the debate on the competition between a fossil and a renewable resource-based society, at present slackening due to decreasing oil prices, starch-containing crops could be considered to an alternative resource. The first very impressive fact is the awareness that our society uses an energy equivalent of close to 10 TW (10×10^{12} W) of fossil resources, but the total annual starch production is equivalent to about 0.5 TW. There is a clear and dramatic mismatch between the availability of starch and the demand for energy by society. The picture becomes somewhat less sombre if the total availability of starch is compared to the demand for fossil resources in the chemical industry, that is, excluding the resources used for the production of energy carriers. This is only about 7% of the total demand and equivalent to 0.7 TW in energy equivalents. These values offer a clear indication that the large-scale application of starch as a source of energy for society is not really possible. Even its application to the supply of bulk chemicals seems to be questionable.

If starch-containing crops are considered as a resource, the lipid, protein, and starch fractions could be considered feedstocks, the glucose syrups could be considered primary chemicals, and compounds such as ethanol, lactic acid, levulinic acid, and fructose could be considered key intermediates or *performance chemicals*.

B. Performance Characteristics of Performance Chemicals

Performance chemicals have properties that constitute their value in the application. The performance characteristics can be of a number of different natures. The following distinctions are possible.

Performance as an energy carrier. In this case, the energy content of the substance considered is of course an important characteristic, but also additional value may derive from the fact that it can be used in special applications. Of course, the costs of a Penlite battery is, in terms of energy equivalency, much higher than the price of wood or cow dung for heating purposes. Table 3 gives an overview of the costs per unit extractable energy of a variety of substances that can be used as energy carriers. The values given are only rough estimates. Starch has recently penetrated the position of a raw material for the production of an energy carrier, as it can be fermented to ethanol, which can be used as a gasoline extender (see Chap. 6) in gasohol. In gasohol, ethanol gets an additional value because of its properties as an octane booster.

Table 3 Costs of Various Energy Carriers If Produced from Various Raw Materials

Raw materials	Type	Energy carrier	Production costs ($/GJ)
Sugar beet	Renewable	Ethanol	16.5
Sugarcane	Renewable	Ethanol	15
Corn	Renewable	Ethanol	16
			11 (Chap. 6)
Molasses	Renewable	Ethanol	11–17
Wood	Renewable	Ethanol	22
Cellulosic wastes	Renewable	Ethanol	13
Wood	Renewable	Methanol	14
		As is	2
Coal	Fossil fuel	Methanol	8
Coal	Fossil fuel	As is	2
Crude oil	Fossil fuel	As is	5 ($35 per barrel)
		Gasoline	7
		Ethanol	16

Source: From Ref. 2.

Performance in terms of feed or food value. In this case the nutritive qualities of the oils, fats, or amino acids constitute the value of the derived product or the crude resource. A typical value of proteins in feed and/or food applications can be derived from that of the competing soy bean proteins; these had a value of $300/ton in 1979. Of course, a large amount of the starch-containing agricultural resources exists in the carbohydrate fraction, which definitely has a much lower value. A figure of $125/ton can be considered typical of the price of integral corn, but the protein feed, which is derived from it after ethanol production, attains a value of $282/ton (see Chap. 6), that is, close to the value of soybean protein.

Performance in terms of chemical properties. A number of starch-derived products obtain performance qualities from their chemical properties as such. The antibiotic properties of the antibiotic penicillin, which can be obtained by fermentation (see Chap. 8), and the use of starch-derived polyols in polyurethanes can be considered examples of such chemical performance applications.

Performance in terms of physicochemical properties. In this case the interaction between the physical and chemical characteristics