STARCH CONVERSION TECHNOLOGY

Edited by

G.M.A. VAN BEYNUM J.A. ROELS

STARCH CONVERSION TECHNOLOGY

any form or by any means, electronic or mechanication, because the

Edited by

G.M.A. VAN BEYNUM J.A. ROELS

Gist-brocades Delft, The Netherlands

MARCEL DEKKER, INC.

New York and Basel

Library of Congress Cataloging in Publication Data Main entry under title:

Starch conversion technology.

ISBN 0-8247-7194-X

(Food science and technology; 14) Bibliography: p. Includes index.

1. Starch. I. Beynum, G. M. A. van, [date].
II. Roels, J. A. III. Series: Food science and technology
(Marcel Dekker, Inc.); 14.
TP415.S73 1985 664'.2 85-6894

COPYRIGHT © 1985 by MARCEL DEKKER, INC. ALL RIGHTS RESERVED.

Neither this book nor any part may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, microfilming, and recording, or by any information storage and retrieval system, without permission in writing from the publisher.

MARCEL DEKKER, INC. 270 Madison Avenue, New York, New York 10016

Current printing (last digit): 10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

STARCH CONVERSION TECHNOLOGY

FOOD SCIENCE AND TECHNOLOGY

A Series of Monographs and Textbooks

Editors

STEVEN R. TANNENBAUM

Department of Nutrition and Food Science Massachusetts Institute of Technology Cambridge, Massachusetts

PIETER WALSTRA

Department of Food Science Wageningen Agricultural University Wageningen, The Netherlands

- 1. Flavor Research: Principles and Techniques, R. Teranishi, I. Hornstein, P. Issenberg, and E. L. Wick (out of print)
- 2. Principles of Enzymology for the Food Sciences, John R. Whitaker
- 3. Low-Temperature Preservation of Foods and Living Matter, Owen R. Fennema, William D. Powrie, and Elmer H. Marth
- 4. Principles of Food Science
 - Part I: Food Chemistry, edited by Owen R. Fennema
 Part II: Physical Methods of Food Preservation, Marcus Karel, Owen R.
 Fennema, and Daryl B. Lund
- 5. Food Emulsions, edited by Stig Friberg
- 6. Nutritional and Safety Aspects of Food Processing, edited by Steven R. Tannenbaum
- 7. Flavor Research: Recent Advances, edited by R. Teranishi, Robert A. Flath, and Hiroshi Sugisawa
- 8. Computer-Aided Techniques in Food Technology, edited by Israel Saguy '
- 9. Handbook of Tropical Foods, edited by Harvey T. Chan
- 10. Antimicrobials in Foods, edited by Alfred Larry Branen and P. Michael Davidson
- 11. Food Constituents and Food Residues: Their Chromatographic Determination, edited by James F. Lawrence
- 12. Aspartame: Physiology and Biochemistry, edited by Lewis D. Stegink and L. J. Filer, Jr.
- 13. Handbook of Vitamins: Nutritional, Biochemical, and Clinical Aspects, edited by Lawrence J. Machlin
- 14. Starch Conversion Technology, edited by G. M. A. van Beynum and J. A. Roels
- 15. Food Chemistry: Second Edition, Revised and Expanded, edited by Owen R. Fennema

Other Volumes in Preparation

此为试读,需要完整PDF请访问:www.ertongbook.com

PREFACE and has derete and often delicated and the total and has been produced and the second an

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 14.106 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 × 109 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.

nology that strandsted as to come as this world in which we have to

tendered of the (Charles (Charles (Charles and any short short

of new processes and their products, which may result from aconomic,

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.

G . M. A. van Beynum G . M. A. Roels

CONTRIBUTORS Series T to transpired red

W. A. van Beynum Gist broades Delt. The Netherlands

S. J. Truesdell of the tree, Croton Calaertan

B. L. Dasinger Pfizer Inc., Groton, Connecticut

D. M. Fenton Pfizer Inc., Groton, Connecticut

Guy Fleche Roquette Freres S. A., Lestrem, France

Carroll R. Keim Consultant, Stamford, Connecticut

A. P. G. Kieboom Delft University of Technology, Delft, The Netherlands

John E. Long Archer Daniels Midland Corporation Decatur, Illinois

R. P. Nelson Pfizer L.c., Groton, Connecticut

Peter J. Reilly Iowa State University, Ames, Iowa

F. F. Roberts Pfizer Inc., Groton, Connecticut

J. A. Roels Gist-brocades, Delft, The Netherlands

Rodney L. Simms Deci Corporation, Decatur, Illinois

J. J. M. Swinkels AVEBE, Veendam, The Netherlands

- x / Contributors
- S. J. Truesdell Pfizer Inc., Groton, Connecticut
- R. van Tilburg Gist-brocades, Delft, The Netherlands
- H. van Bekkum Delft University of Technology, Delft, The Netherlands
- G. M. A. van Beynum Gist-brocades, Delft, The Netherlands
- K. Venkatasubramanian H. J. Heinz Company, Pittsburgh, Pennsylvania

Cuy Fixire Requeste brares S. ... Lestron, Tunce Cuy Fixire Requeste brares S. ... Lestron, Tunce Consultant, Stanford, Comperficut

A. C. Klebosza Delft University of Redmology Delf Nethon Long Archer Danies Million Corporation Decimal Consultant Long Archer Danies Million Corporation Decimal Long Archer Million Corporation Consultant Long State Consultant Con

New Standels 42

CONTENTS

Preface iii

Contributors ix

| 1. | The Multidimensionality of Starch Conversion Technology | |
|----|---|--|
| | G. M. A. van Beynum and J. A. Roels | |

- I. Introduction 1 artim & secreted state to gottoubor 42 11
- II. Industrial Applications of Raw Materials 1
- III. Economical, Political, and Technological Aspects of Substitution Options 5
 - IV. Products that Potentially Can Be Prepared from Starch 11
 References 13
- 2. Sources of Starch, Its Chemistry and Physics 15
 - J. J. M. Swinkels and A Magna I have appropriately and the second and the second
 - I. Introduction 15
 - II. Sources of Starc 17
 - III. Chemical Composition and Structure 24 10 1000/A 11
 - IV. Physical Properties 30
 References 45

wi / Contents

| 3. | The Technology of Corn Wet Milling 47 |
|----|---|
| | Rodney L. Simms |
| | I. Introduction 47 II. Wet Milling Process 47 |
| | III. Corn Sweetener Process 56 IV. Dry Starch 62 |
| | V. Plant Layout and Control 67 |
| | 그는 맛없다고 그릇 병에 있었습니다는 바람이 바람이 하다면 다니다. |
| 4. | Chemical Modification and Degradation of Starch 73 |
| | Guy Fleche |
| | I. Introduction 73 II. Why Modify Starch? 74 |
| | III. General Principles of Starch Chemistry 78IV. Depolymerized Starches 85 |
| | V. Cross-linked Starches 91 VI. Starch Esters and Ethers 92 References 97 |
| | 그 그녀들이 얼굴한 경험이라고 있다. 사람들은 사람들이 하다 |
| 5. | Enzymic Degradation of Starch 101 |
| | Peter J. Reilly |
| | I. Introduction 101 II. Production of Low Dextrose Equivalent Syrups with |
| | α-Amylase 102 III. Production of High Dextrose Equivalent Syrups with Glucoamylase 114 |
| | IV. Use of Isoamylase and Pullulanase for Debranching 124 V. Production of High-maltose Syrups with Fungal α-Amylase and β-Amylase 127 References 134 |
| | lic anenges 13 |
| 6. | Starch and Energy: Technology and Economics of Fuel Alcoho Production 143 |
| | K. Venkatasubramanian and Carroll R. Keim |
| | I. Introduction 143 II. Background 144 III. Alcohol Production Technology 158 |

Summary and Conclusions 171

References 172

| | | Contents | / vi |
|----|-------|---|------|
| 7. | Enzym | nic Isomerization of Corn Starch-based Glucose Syrups | 175 |
| | R. va | n Tilburg | 01 |
| | I. | Introduction 175 | |
| | II. | Glucose Isomerase: Sources and Properties 176 | |
| | III. | Immobilized Glucose Isomerase 183 | 9.1 |
| | IV. | Enzyme Kinetics and Thermodynamics 193 | |
| | V. | Productivity Model for Isomerization in Packed Bed | |
| | | Reactors 200 | |
| | VI. | The Conversion Process in Packed Bed Reactors 209 | |

VII. Process Optimization 214

VIII. Pressure Drop 219

High-fructose Corn Syrups and Their Applications Nomenclature 229 References 231

Enzymic and Microbial Processes in the Conversion of Carbohydrates Derived from Starch 237

B. L. Dasinger, D. M. Fenton, R. P. Nelson, F. F. Roberts, and S. J. Truesdell

I. Introduction 237

Carbon Substrates 237

III. Organic Acids 239

IV. Penicillins 244

V. Enzymes 246

VI. Amino Acids 249

VII. Microbial Polysaccharides

Additional Fermentation Products from Starch: Future VIII. Fermentation Trends 254 References 258

Chemical Conversion of Starch-based Glucose Syrups

A. P. G. Kieboom and H. van Bekkum

I. Introduction 263

II. Isomerization 265

III. Hydrogenation 278

IV. Oxidation 284

Enantioselective Synthesis

Miscellaneous Reactions and Products VI.

VII. Conclusions 323 References 324

United States Markets for Starch-based Products 335 John E. Long I. Introduction 335

Additional Leagueston Products from Starch. Fut

McConversion of Starch-based blucose Sycups

102 Interest of the Synthogian Control A sabo I bea acoltosofi atrounsilosofia

introduction

Wet Milling Volumes 336 11.

Corn Sweeteners 337 III.

343 Starch IV.

344 most rel labout virvitaubors Maltodextrins V.

VI. Dextrins 345

345 VII. Ethanol

347 Miscellaneous VIII. References Regardantone Corn Strans and

349 ndex

THE MULTIDIMENSIONALITY OF STARCH CONVERSION TECHNOLOGY

G. M. A. van Beynum and J. A. Roels Gist-brocades, Delft, Ine Netherlands

I. INTRODUCTION strategies around the best sport and man in the same

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.

gas or appathe. These faedatocles can be used as energy sources

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.

H. 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

contempora longite is the contemporary in 1987 shanes are contemporary

Table 1 World Starch Production and Amount of Processed Starch

| Source | Annual world production (109 ton)a | on Amount of processed starch (10 ⁶ ton) |
|---------|------------------------------------|---|
| Corn | ±1000 | ON A STREET NOTES TAYOO |
| Wheat | | C. M. A. van Beynus weg I. A. Re |
| Potato | ** ±100 | Glat hen otes, Delit, tee Metherlin |
| Tapioca | 100 | 0.5 |
| Total | 1100 | 14 (1.3%) |

^aSee 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

mounts of therebes produced and proceeded and the resuct

| ms. L political, and beh | Amounts (U.S. figures) | | s lemetem som s andre Then se draw som |
|-----------------------------|------------------------|------------|---|
| Products ybassis | 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, thicken- er, stabilizer |
| Modified starches | 1.8 | 22 | Coating, adhesive |
| Maltodextrins | 0.045 | 0.5 | Food additive |
| Dextrins | 0.045 | 0.5 | Food additive |
| Ethanol | 1.1ª | 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 imes 10¹² 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 |
| Arteian irren ek a | | an no commentation y | 11 (Chap. 6) |
| Molasses | Renewable . | Ethanol | 11-17 |
| Wood | Renewable | Ethanol | 22 |
| Cellulosic wastes | Renewable | Ethanol | 13 |
| Wood | Renewable | Methanol | 14 |
| of the introversible | TO STAND AND STANDS | As is | 2 |
| Coal ' | Fossil fuel | Methanol | 8 |
| Coal | Fossil fuel | As is | 2 |
| Crude oil | Fossil fuel | As is | 5 (\$35 per barrel) |
| tree, the lipid | magn a so horo | Gasoline | ing on a public of a second |
| also are some | AVER BUILDING | 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