

FUNDAMENTAL SCIENCES

*Chemistry*

# CELLULOSE SCIENCE AND TECHNOLOGY

---

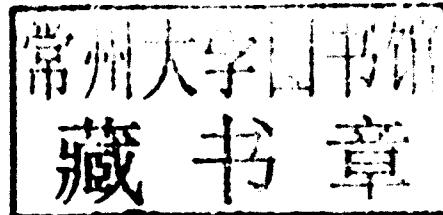
Jean-Luc Wertz, Olivier Bédué and Jean P. Mercier



EPFL Press

Distributed by CRC Press

CELLULOSE SCIENCE  
AND TECHNOLOGY





FUNDAMENTAL SCIENCES

*Chemistry*

# CELLULOSE SCIENCE AND TECHNOLOGY

---

Jean-Luc Wertz, Olivier Bédué and Jean P. Mercier

EPFL Press

A Swiss academic publisher distributed by CRC Press



**CRC Press**  
Taylor & Francis Group

**Taylor and Francis Group, LLC**  
6000 Broken Sound Parkway, NW, Suite 300,  
Boca Raton, FL 33487

**Distribution and Customer Service**  
[orders@crcpress.com](mailto:orders@crcpress.com)

**[www.crcpress.com](http://www.crcpress.com)**

Library of Congress Cataloging-in-Publication Data  
A catalog record for this book is available from the Library of Congress.

This book is published under the editorial direction of  
Professor Hubert Girault (EPFL).

Cover photos of breadfruit, papaya, seagrape and palm plants  
by Olivier Bédué.



is an imprint owned by Presses polytechniques et universitaires romandes, a  
Swiss academic publishing company whose main purpose is to publish the  
teaching and research works of the Ecole polytechnique fédérale de Lausanne.

Presses polytechniques et universitaires romandes  
EPFL – Rolex Learning Center  
Post office box 119  
CH-1015 Lausanne, Switzerland  
E-mail: [ppur@epfl.ch](mailto:ppur@epfl.ch)  
Phone: 021/693 21 30  
Fax: 021/693 40 27

**[www.epflpress.org](http://www.epflpress.org)**

© 2010, First edition, EPFL Press  
ISBN 978-2-940222-41-4 (EPFL Press)  
ISBN 978-1-4200-6688-3 (CRC Press)

Printed in Italy

All right reserved (including those of translation into other languages). No part  
of this book may be reproduced in any form – by photoprint, microfilm, or any  
other means – nor transmitted or translated into a machine language without  
written permission from the publisher.

---

# First Foreword

It is a common statement to say that cellulose is the world's most abundant polymer. In view of its importance to mankind, an enormous research effort, substantiated by myriads of reports and patents, has been devoted to this biopolymer in the last 150 years. The periodical appearance of textbooks presenting in perspective the major developments of the science of cellulose is therefore crucial for those who want to stay abreast, without being submerged by the overwhelming primary literature.

It is in this context that *Cellulose Science and Technology* is written, summarizing some of the major progress of cellulose science in the last 20 years. During this period, significant advances that are reviewed have been made in the understanding of the biological role of cellulose in nature, either in the deciphering of its biosynthesis mechanism or in following the path of its bio-degradation. Other major advances have been obtained in the structural definition of cellulose at the molecular and supramolecular level. Such a definition, which is comprehensively described, has fundamental implications in every aspect of cellulose science. Throughout the chapters that successively present the biology, chemistry, physics and technology of cellulose, one of the merits

of this book is to account for the special morphology of cellulose and its implication in the various processes that are reviewed.

There is no doubt that this book will serve as a reference for those who are already active in the field of cellulosics as well as for those who are interested in biomass utilization and/or in the production of eco-friendly materials from sustainable non-food resources.

Henri Chanzy  
Honorary Scientist  
CERMAV-CNRS

February 2009

---

## Second Foreword

Biomass has provided for many centuries a major contribution to human development, both for food (humans and animals) and non-food supplies (buildings, ships, textiles, papers, energy...).

Biomass is even at the origin of oil, gas and coal; now, many stakeholders would like to release this dependence on these fossil fuels, replacing part or all of them by renewable sources of energy.

Biomass could be one of those renewable sources for energy, but it brings its own dilemmas; if biomass combustion is known from the early stages of humanity, still providing one tenth of primary energy supplies, it is too often at the cost of non-sustainable deforestation practices; if biofuels can be manufactured from sugars, starch, vegetable oils, they could readily enter in direct competition with food markets if they develop without all the necessary cautions.

This is why energy players devote so much attention now to ligno-cellulosic materials, and its possible transformation in modern energy vectors, especially motor fuels or chemicals. But all the specialists know this is not an easy issue;

if cellulose is the most abundant biopolymer, it has been made very stable by Nature, and therefore not so easy to de-structure.

This is why I do welcome *Cellulose Science and Technology*, by Jean-Luc Wertz, Olivier Bédué, Jean P. Mercier, all Total Group colleagues during their careers, providing us with an in depth understanding of this extraordinary bio-polymer, cellulose. No doubt their book will be considered as a reference, both for energy and materials applications of cellulose.

Jean-Michel Gires,  
Executive Vice President  
Sustainable Development and Environment,  
Total

April 2009

---

# Table of contents

<b>First Foreword .....</b>	<b>5</b>
<b>Second Foreword .....</b>	<b>7</b>
<b>Preface .....</b>	<b>19</b>
<b>Chapter 1</b>	
<b>Introduction .....</b>	<b>21</b>
<b>1.1 The cellulose molecule .....</b>	<b>21</b>
<b>1.1.1 Molecular structure.....</b>	<b>21</b>
<b>1.1.2 Glucose chemistry.....</b>	<b>23</b>
<b>1.1.3 Related di- and polysaccharides .....</b>	<b>25</b>
<i>Disaccharides .....</i>	<b>25</b>
<i>Polysaccharides.....</i>	<b>26</b>

<b>1.2 Structure of the book .....</b>	<b>30</b>
<b>1.3 References.....</b>	<b>31</b>

## Chapter 2

<b>Biosynthesis of Cellulose .....</b>	<b>33</b>
<b>2.1 Introduction.....</b>	<b>33</b>
<b>2.2 Selective principles of botany .....</b>	<b>34</b>
<b>2.2.1 Classification of green plants .....</b>	<b>34</b>
<b>2.2.2 Plant cells .....</b>	<b>36</b>
<b>2.3 Cellulose-related biology .....</b>	<b>38</b>
<b>2.3.1 From genes to proteins .....</b>	<b>38</b>
<b>2.3.2 DNA cloning and PCR.....</b>	<b>41</b>
<b>2.4 Terminal complexes.....</b>	<b>41</b>
<b>2.5 Glucose polymerization by cellulose synthases.....</b>	<b>46</b>
<b>2.5.1 Cellulose synthase substrate .....</b>	<b>46</b>
<b>2.5.2 Cellulose synthases.....</b>	<b>47</b>
<i>Processive <math>\beta</math>-glycosyltransferases.....</i>	<b>47</b>
<i>Conserved motifs.....</i>	<b>48</b>
<i>Cellulose synthase family.....</i>	<b>49</b>
<b>2.5.3 Polymerization models .....</b>	<b>51</b>
<b>2.5.4 Polymerization of cellulose in <i>Acetobacter xylinum</i> .....</b>	<b>54</b>
<i>Biosynthetic pathway of cellulose.....</i>	<b>54</b>
<i>UniProt description .....</i>	<b>57</b>
<i>Other bacteria .....</i>	<b>57</b>
<b>2.5.5 Polymerization of cellulose in plants .....</b>	<b>58</b>
<i>Genes encoding cellulose synthases.....</i>	<b>58</b>
<i>Korriagan .....</i>	<b>64</b>
<i>Sitosterol-<math>\beta</math>-glucoside primer .....</i>	<b>66</b>
<i>Other non-catalytic molecules.....</i>	<b>67</b>
<b>2.6 Chain assembly into microfibrils .....</b>	<b>68</b>
<b>2.6.1 Chain assembly in <i>Acetobacter xylinum</i> .....</b>	<b>69</b>

<b>2.6.2</b>	Chain assembly in plants.....	70
<b>2.7</b>	<b>Status of non-in-vivo cellulose synthesis .....</b>	<b>75</b>
<b>2.7.1</b>	In vitro synthesis.....	75
	<i>Synthesis by bacterial synthases</i> .....	75
	<i>Synthesis by plant synthases</i> .....	75
	<i>Enzymatic polymerization</i> .....	76
<b>2.7.2</b>	Chemical synthesis.....	79
<b>2.8</b>	<b>References.....</b>	<b>80</b>

## Chapter 3

**Structure and Properties of Cellulose .....** **87**

<b>3.1</b>	Introduction .....	87
<b>3.2</b>	<b>Supramolecular structure .....</b>	<b>88</b>
<b>3.2.1</b>	Crystallinity of cellulose materials.....	88
<b>3.2.2</b>	Crystal polymorphs.....	89
<b>3.2.3</b>	Coordinate system.....	90
<b>3.2.4</b>	Cellulose I.....	90
<b>3.2.5</b>	Cellulose II.....	101
<b>3.2.6</b>	Cellulose III and IV.....	105
<b>3.2.7</b>	Soda celluloses.....	107
<b>3.2.8</b>	Summary of crystal structures .....	108
<b>3.3</b>	<b>Morphological structure .....</b>	<b>109</b>
<b>3.3.1</b>	Introduction.....	109
<b>3.3.2</b>	Microfibrils.....	110
	<i>Types of microfibrils</i> .....	110
	<i>Crystalline features</i> .....	111
	<i>Chain polarity and biosynthesis</i> .....	117
	<i>Amorphous domains</i> .....	117
<b>3.3.3</b>	Plant cell walls .....	118
	<i>Extracellular matrix</i> .....	118
	<i>Primary cell wall</i> .....	119
	<i>Microtubules</i> .....	121

<i>Wall proteins</i> .....	122
<i>Pores</i> .....	123
<i>Biosynthesis</i> .....	123
<i>Representative examples</i> .....	124
<b>3.3.4 Bacterial cellulose.....</b>	<b>127</b>
<b>3.4 Properties.....</b>	<b>130</b>
<b>3.4.1 Mechanical properties .....</b>	<b>130</b>
<i>Theoretical values</i> .....	130
<i>Experimental values</i> .....	130
<b>3.4.2 Physical properties and liquid crystals .....</b>	<b>132</b>
<i>Thermal, electrical and optical properties</i> .....	132
<i>Liquid crystals</i> .....	134
<b>3.4.3 Environmental properties.....</b>	<b>137</b>
<b>3.4.4 Nanocomposites .....</b>	<b>138</b>
<b>3.5 References.....</b>	<b>140</b>

## Chapter 4

<b>Swelling and Dissolution of Cellulose .....</b>	<b>147</b>
<b>4.1 Introduction .....</b>	<b>147</b>
<b>4.2 Intercrystalline swelling.....</b>	<b>148</b>
<b>4.2.1 Water .....</b>	<b>148</b>
<i>Water sorption isotherms</i> .....	149
<i>Bound water</i> .....	151
<i>Water retention value, fiber saturation point and solute exclusion</i> .....	153
<i>Cellulose plasticization with water</i> .....	155
<b>4.2.2 Organic liquids .....</b>	<b>156</b>
<i>Interaction of cellulose with organic liquids</i> .....	156
<i>Inclusion compounds</i> .....	158
<b>4.3 Intracrystalline swelling.....</b>	<b>158</b>
<b>4.3.1 Alkali metal hydroxides .....</b>	<b>159</b>
<i>Mercerization</i> .....	159
<i>Alkali celluloses</i> .....	159

<i>Changes in fiber dimensions on swelling .....</i>	161
<i>Supramolecular and morphological structure.....</i>	162
<i>Mechanism of swelling by alkalis.....</i>	164
<b>4.3.2 Inorganic acids and salts .....</b>	167
<b>4.3.3 Amines .....</b>	170
<i>Swelling of cellulose by amines.....</i>	170
<i>Effect of amines on cellulose properties.....</i>	172
<b>4.3.4 Ammonia .....</b>	173
<i>Swelling of cellulose by liquid ammonia .....</i>	173
<i>Effect of liquid ammonia on cellulose properties.....</i>	174
<b>4.3.5 Hydrazine.....</b>	175
<b>4.4 Dissolution .....</b>	175
<b>4.4.1 Non-derivatizing solvents .....</b>	176
<i>Aqueous solutions of transition metal complexes .....</i>	176
<i>Non-aqueous LiCl/DMA system .....</i>	177
<i>Organic amine oxides .....</i>	178
<i>Aqueous sodium hydroxide .....</i>	188
<i>Ionic liquids.....</i>	192
<b>4.4.2 Derivatizing solvents .....</b>	194
<i>Viscose process.....</i>	196
<i>N2O4/DMF system .....</i>	200
<i>DMSO/paraformaldehyde system.....</i>	201
<b>4.5 References.....</b>	201
<hr/>	
<b>Chapter 5</b>	
<b>Enzymatic Hydrolysis of Cellulose .....</b>	209
<b>5.1 Introduction .....</b>	209
<b>5.2 Cellulases.....</b>	210
<b>5.2.1 Organism source.....</b>	210
<b>5.2.2 Endo- and exo-action .....</b>	210
<b>5.2.3 Modular structure .....</b>	211
<i>Catalytic module .....</i>	211
<i>Carbohydrate-binding module.....</i>	213

5.2.4 Mechanism.....	217
5.2.5 Nomenclature .....	218
<b>5.3 Noncomplexed cellulase systems.....</b>	<b>219</b>
<b>5.3.1 Solubilization of native cellulose .....</b>	<b>219</b>
<b>5.3.2 <i>Trichoderma reesei</i> (<i>Hypocrea jecorina</i>) .....</b>	<b>220</b>
<i>Cel7A</i> .....	221
<i>Cel6A</i> .....	222
<i>Endoglucanases</i> .....	226
<i>CBMs</i> .....	226
<b>5.3.3 <i>Humicola insolens</i> .....</b>	<b>228</b>
<i>Cel7A</i> .....	228
<i>Cel6A</i> .....	229
<i>Endoglucanases</i> .....	229
<i>Cellulose digestion</i> .....	231
<b>5.3.4 Kinetics and activity .....</b>	<b>232</b>
<b>5.3.5 Synergism.....</b>	<b>233</b>
<b>5.4 Multienzyme complexes.....</b>	<b>234</b>
<b>5.4.1 The cellulosome concept .....</b>	<b>234</b>
<b>5.4.2 Types of cellulosome .....</b>	<b>234</b>
<b>5.4.3 Scaffoldin carbohydrate-binding modules .....</b>	<b>235</b>
<b>5.4.4 Cohesin-dockerin interaction .....</b>	<b>236</b>
<b>5.4.5 Representative examples of cellulosome.....</b>	<b>240</b>
<i>Clostridium cellulolyticum</i> .....	240
<i>Clostridium thermocellum</i> .....	241
<i>Acetivibrio cellulolyticus</i> .....	245
<i>Ruminococcus flavefaciens</i> .....	246
<i>Bacteroides cellulosolvens</i> .....	247
<b>5.4.6 Designer cellulosomes.....</b>	<b>247</b>
<b>5.5 References.....</b>	<b>248</b>

## Chapter 6

**Non-Biological Degradation of Cellulose..** 257

<b>6.1 Introduction .....</b>	<b>257</b>
-------------------------------	------------

<b>6.2 Acid hydrolysis .....</b>	258
<b>6.2.1 Mechanism and kinetics.....</b>	258
<b>6.3 Alkaline degradation .....</b>	260
<b>6.3.1 Action of alkalis on monosaccharides.....</b>	260
<b>6.3.2 Action of alkalis on cellulose.....</b>	261
<i>Endwise degradation (peeling) .....</i>	261
<i>Alkaline hydrolysis .....</i>	262
<b>6.4 Oxidative degradation .....</b>	263
<b>6.4.1 Oxidation by sodium hypochlorite.....</b>	264
<b>6.4.2 Oxidation by atmospheric oxygen         and by hydrogen peroxide .....</b>	265
<b>6.5 Thermal degradation .....</b>	266
<b>6.6 Mechanical and radiation degradation .....</b>	268
<b>6.6.1 Mechanical degradation.....</b>	268
<b>6.6.2 Radiation degradation.....</b>	270
<i>IR, visible and UV radiation .....</i>	270
<i>High-energy radiation .....</i>	271
<b>6.7 References.....</b>	272

---

## Chapter 7

<b>Cellulose Derivatives.....</b>	275
<b>7.1 Introduction .....</b>	275
<b>7.2 Esterification.....</b>	277
<b>7.2.1 Inorganic cellulose esters.....</b>	277
<i>Cellulose nitrate .....</i>	277
<i>Cellulose nitrite .....</i>	278
<i>Cellulose sulfate .....</i>	279
<i>Phosphorus-containing cellulose derivatives.....</i>	279
<i>Cellulose borates .....</i>	280
<i>Deoxycelluloses .....</i>	280
<i>Esters of carbonic acid derivatives .....</i>	281
<b>7.2.2 Organic cellulose esters .....</b>	282

<i>Cellulose formate</i> .....	282
<i>Cellulose acetate</i> .....	282
<i>Esters of higher aliphatic acids</i> .....	284
<i>Cellulose carbamates</i> .....	286
<i>Cellulose sulfonates</i> .....	286
<b>7.2.3 Summary</b> .....	287
<b>7.3 Etherification</b> .....	287
<b>7.3.1 Alkyl ethers of cellulose</b> .....	288
<b>7.3.2 Carboxymethylcellulose</b> .....	289
<b>7.3.3 Hydroxyalkyl ethers of cellulose</b> .....	290
<b>7.3.4 Cyanoethylcellulose</b> .....	293
<b>7.3.5 Other ethers of cellulose</b> .....	293
<b>7.3.6 Summary</b> .....	294
<b>7.4 Crosslinking of cellulose</b> .....	295
<b>7.4.1 Chemical finishing of textiles and paper</b> .....	295
<b>7.4.2 Crosslinking agents</b> .....	296
<b>7.5 Grafting of cellulose</b> .....	298
<b>7.6 References</b> .....	299

## Chapter 8

# Fuels and Chemicals from Biomass ..... 303

<b>8.1 Cellulosic biomass for renewable energy and products</b> .....	303
<b>8.1.1 Biomass</b> .....	303
<b>8.1.2 Biorefinery and global warming</b> .....	304
<b>8.1.3 Bioethanol and biodiesel</b> .....	305
<b>8.1.4 Conversion pathways</b> .....	306
<b>8.2 Biochemical conversion of cellulosic biomass</b> .....	307
<b>8.2.1 Enzymatic hydrolysis</b> .....	308
<b>8.2.2 Acid hydrolysis</b> .....	312
<i>Dilute acid hydrolysis</i> .....	312