

Table of Contents

1	Introduction	1
	References	3
2	Nature of Cellulosic Material	5
2.1	Components of Cellulosic Materials	5
2.1.1	Extraneous Materials	5
2.1.2	Polysaccharides	6
2.1.3	Lignin	8
2.2	Composition of Wood and Straw	11
2.3	Structure of Plant Cell Walls	11
2.4	Structure of Cellulose	14
2.4.1	Chemical and Molecular Structure of Cellulose	14
2.4.2	Structure and Morphology of Cellulose Fibers	16
	References	19
3	Enzymatic Hydrolysis	21
3.1	Nature of Lignocellulosic Structural Resistance	21
3.1.1	Degree of Water Swelling of Cellulose Fiber	21
3.1.2	Crystallinity of Cellulose	22
3.1.3	Molecular Structure of Cellulose	23
3.1.4	Extraneous Material – Lignin	24
3.1.5	Presence of Substituent Groups	26
3.1.6	Capillary Structure of Cellulose	26
3.2	Properties and Mode of Cellulase Biodegradation	29
3.2.1	Effect of Cellulase on some Properties of Cellulose Fibers	39
3.2.1.1	Fragmentation of Cellulose Fibers	39
3.2.1.2	Swelling of Cellulose Fibers and the Swelling Factor	40
3.2.2	Mode of Action of the Cellulase	41
3.2.2.1	(C_1-C_x) Concept	41
3.2.2.2	β -1,4-Glucan Cellobiohydrolase	43

3.2.2.3	C _x Components	45
3.2.2.4	β -Glucosidase	47
3.2.2.5	Synergism Among Components	48
3.2.3	Physical Properties of Cellulase	51
3.2.3.1	Molecular Weights of Cellulase Components	51
3.2.3.2	Diffusion Coefficient and Sedimentation Constant of Cellulase	52
3.2.3.3	Size and Shape of Cellulase Molecules	52
3.3	Pretreatment Methods	52
3.3.1	Physical Pretreatments	53
3.3.1.1	Milling and Grinding	54
3.3.1.2	Pyrolysis	57
3.3.1.3	High Energy Radiation	58
3.3.1.4	High Pressure Steaming	58
3.3.1.5	Extrusion and Expansion	59
3.3.1.6	Microwave Treatment	60
3.3.2	Chemical Pretreatments	60
3.3.2.1	Alkalis	60
3.3.2.2	Acids	61
3.3.2.3	Gases	63
3.3.2.4	Oxidizing Agents	64
3.3.2.5	Cellulose Solvents	64
3.3.2.6	Solvent Extraction	65
3.3.2.7	Swelling Agents	66
3.3.3	Biological Pretreatments	67
3.3.4	Economic Analysis of Pretreatments	68
3.4	Kinetics of Enzymatic Hydrolysis of Cellulose	69
3.4.1	Kinetic Characteristics of the Heterogeneous Cellulose-Cellulase System	71
3.4.1.1	Mass Transfer Limitation – Diffusion of Enzyme	71
3.4.1.2	Adsorption and Desorption of Enzyme	71
3.4.1.3	Surface Reaction, Fragmentation, and Changes of Surface Area During Hydrolysis	74
3.4.1.4	Product Inhibition and its Mechanism	76
3.4.2	Kinetic Models of Insoluble Cellulose Hydrolysis by Cellulase	78
3.4.2.1	Empirical Representations of the Kinetics of Enzymatic Hydrolysis	78
3.4.2.2	Michaelis-Menten Mechanism Applied to an Insoluble Cellulose-Cellulase System	79
3.4.2.3	McLaren's Approach to Enzyme Reactions in a Structurally Restricted System	85
3.4.2.4	Kinetic Models Based on the Combination of the Enzyme Adsorption Equation and the Michaelis-Menten Type Equation	87
3.4.2.5	Kinetic Model Based on the Depolymerization Mechanism	92
3.4.2.6	Distributed Parameter Kinetic Models	94
3.4.2.7	Mechanistic Kinetic Model	97
3.4.2.8	Miscellaneous Models	102

3.4.3	Kinetics of Cellulases on β -1,4-Oligoglucosides	104
3.4.4	Kinetics of β -Glucosidase	108
	Nomenclature	109
	References	112
4	Acid Hydrolysis of Cellulose	121
4.1	Mechanism of Acid Hydrolysis	121
4.1.1	Course of Hydrolysis Reaction	121
4.1.2	Identification of Mechanism	127
4.1.3	Degree of Polymerization	128
4.1.4	Recrystallization	131
4.2	Kinetics of Acid Hydrolysis of Cellulose	133
4.2.1	Homogeneous Kinetics	133
4.2.2	Heterogeneous Kinetics	138
	Nomenclature	144
	References	145
5	Design and Economic Evaluation of Cellulose Hydrolysis Processes	149
5.1	Enzymatic Hydrolysis	149
5.1.1	Pure Cellulose Substrate	149
5.1.2	Lignocellulosic Substrate	157
5.2	Acid Hydrolysis	164
5.2.1	Dilute Sulfuric Acid Processes	164
5.2.2	Concentrated Sulfuric Acid Processes	170
5.2.3	Hydrochloric Acid Processes	172
5.2.4	Hydrofluoric Acid Process	174
	Nomenclature	185
	References	186
6	Epilogue	189
	Author Index	191
	Subject Index	197