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DEGRADATION OF CELLULOSE - MECHANISMS AND APPLICATIONS

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Abstract - After a general survey of modes and mechanisms of cellulose degradation by input of energy or by chemical agents, experimental results on thermal, thermohydrolytic and hydrolytic degradation are presented, centering on the influence of cellulose physical structure on rate and yield in these processes. In this connection, homogeneous and heterogeneous thermal chain degradation is compared, and the influence of different structural parameters on acid and on enzymatic hydrolysis is considered. Finally, some current and future applications of cellulose degradation processes are discussed, especially with respect to cellulosic waste utilization.

INTRODUCTION

From the beginning of large-scale application of organic polymers as fibres, films and construction materials degradation processes of the macromolecules found attention in connection with material properties and with failure of end-use products. In recent years, investigations on kinetics and mechanism of polymer degradation received a further impetus by problems of polymer waste disposal and the necessity of manufacturing useful low-molecular products therefrom. In connection with polymers delivered by nature, chain degradation plays a role in isolation and purification of the polymer in question. All these degradation processes mainly proceed in an heterogeneous system and thus depend on physical structure of the substrate also. This additionally impedes a full understanding of these degradation processes and the transfer of laboratory results to technical systems, besides the well-known fact that - from a chemical point of view - chain degradation in general is more complicated than chain synthesis due to pre- and side reactions.

In this paper, experimental results and reaction models on cellulose degradation will be surveyed, stressing the rols of physical structure. A more detailed consideration will be given to results of our own on thermal and hydrolytic degradation in various systems of reaction. Finally, some conclusions will be drawn with regard to the interaction of chemical and physical factors in these degradation processes, and with regard to some current and future trends of their applications.

SOME GENERAL REMARKS ON CELLULOSE DEGRADATION

Like with all the other polymers, interactions with thermal and/or radiation energy are important for chain cleavage also with cellulose, degradation being accelerated in both cases by the presence of oxygen. Besides this, cellulose as a ß-1-4 linked glucan is sensitive to hydrolytic cleavage of the glycosidic linkage, and

also to bond-cleaving reactions in an alkaline medium.
Depending on the condition of reaction, thermal destruction of the macromolecules leads to varying amounts and different species of volatile low-molecular compounds and of char. Investigations on this type of chain destruction are relevant in connection with flame-proofing of cellulose fibres (Ref. 1). By a fast high-temperature pyrolysis with exclusion of oxygen at 420 °C levoglucosan may be obtained with a yield of 36 % (Ref. 2). In the lower range of temperature between 100 and 200 °C the macromolecular character of cellulose is persisting in spite of rather severe changes in chemical and physical structure, which will be considered later-on in connection with some results of our own.
Comparing the thermal stability of various polysaccharides by thermal analysis, cellulose proved to be more resistent than hemicelluloses like xylan (Ref. 3). Due to transformation of the macromolecule, chain splitting and crosslinking proceeding simultaneously, the mechanism of thermal degradation of cellulose is rather complex, and no clear-cut reaction model, but only several possible reaction path-ways can be concluded from the experimental evidence available Fig. 1.

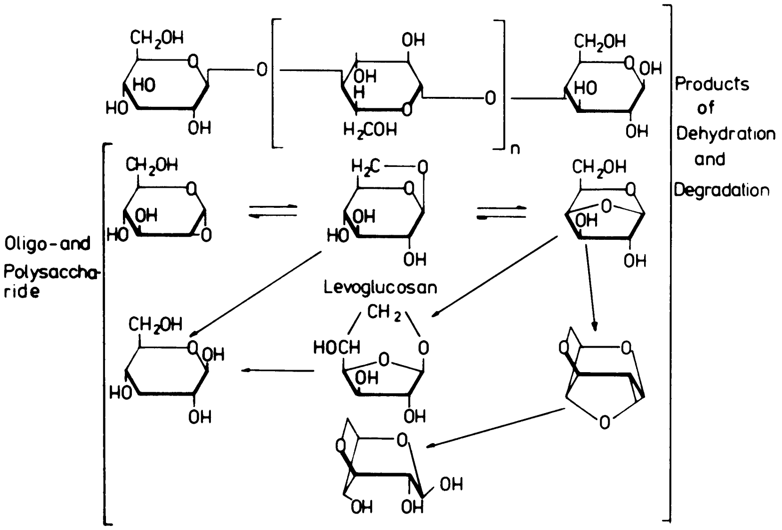

Fig. 1 Scheme of thermal degradation of cellulose.

Cellulose degradation by electromagnetic radiation, especially by UV and visible light is well-known since centuries on an empirical basis as "tendering" of cotton or linen due to sun-bleaching. The radical reactions in this type of chain degradation depend largely on the amount of O_2 and/or water present, as formation, reactions and decay of peroxy-radicals can play a major part (Ref. 4). Besides the chain cleavage usually associated with photodecomposition in the UV- and visible range, also some cross-linking reactions have been reported (Ref. 5). Photodegradation of cellulose can be enhanced largely by sensibilisation via formation of singlett oxygen (Ref. 6), and by cations of transition metals acting as redox-pairs in photooxidation or as a direct photocatalyst (Ref. 7).
In recent years, effects of high energy radiation on cellulose materials found an increasing attention (Ref. 8-13). Some of our results obtained by exposition of cotton linters to an electron beam radiation (Ref. 14) are summarized in Table 1.
Water retention value (WRV) is barely altered even after applying a high radiation dose and in spite of a large drop in DP and level-off DP. Effects on fibre-morphology are rather small as compared, for example, to a thermohydrolytic treatment (Ref. 15). Chain cleavage obviously occurs by bond scission in the lowordered and the crystalline regions as well, and is accompanied by some cross-linking already at low and medium radiation dose, as indicated by the low water retention and a significant inhibition of enzymatic hydrolysis after exposing the specimen to 0,5...5 Mrad of electron beam radiation (Ref. 14).

TABLE 1. Properties of linters after radiation treatment

Sample	Water Content (%)	Water Retention Value (%)	DP	LODP after 2 hr
Linters, untreated	4,2	41	1670	156
Linters, treated by electron beam radiation 10 kGy	6	47	520	116
Linters, treated by electron beam radiation 40 kGy	5,6	50	290	68

Cellulose degradation by hydrolytic cleavage of the glycosidic bond is catalysed by H_3O^+ (acid hydrolysis) or by cellulolytic enzyme systems (cellulases). In both cases, glucose may be obtained in a yield >95 % under suitable condition of reaction. The mechanism of acid hydrolysis is well-known and clear-ent. Cationic intermediates are playing an important role in determining overall rate of reaction and the rate differences observed between different glycosidic bonds Fig. 2.

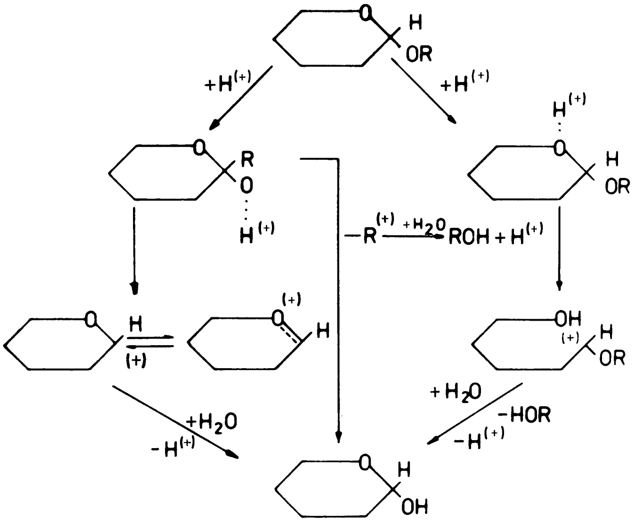

Fig. 2. Mechanism of acid hydrolysis of glycosidic bonds

Bond cleavage by interaction with H_3O^+ proceeds in a random way in a homogeneous reaction system, but is selective with respect to state of crystalline order in a heterophase reaction system. The course of enzymatic hydrolysis is somewhat more complicated, as different components of the multienzyme system have different and selective sites of action Fig. 3 (Ref. 16). Rate and sugar yield of heterophase acid and enzymatic hydrolysis are affected to a large extend by the physical structure of the substrate, a point to be treated in detail in the following part of this context. Due to differences in chemical and physical structure, the hemicellulose of wood generally are more susceptible to hydrolytic chain scission than cellulose itself.

Though cellulose is more resistent to alkali than to acid, OH^--ion-induced degradation by a stepwise "peeling reaction" at higher temperature proceeds rather quickly and is relevant in determining the yield in alkaline pulping processes (Ref. 17). Chain degradation in an alkaline medium proceeds very fast even at room temperature, if the cellulose moiety contains carbonyl groups. This multistep cleaving of the anhydroglucose ring by ß-alkoxy elimination causes the well-known "alkali-lability" of partially oxidized cellulose samples.

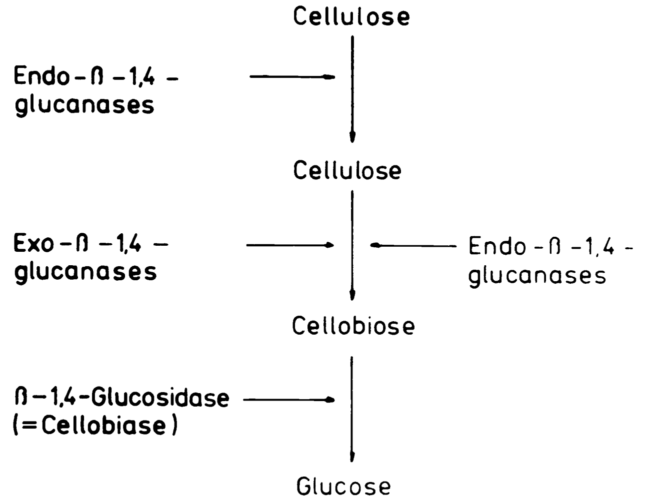

Fig. 3. Scheme of the enzymatic degradation of cellulose

EXPERIMENTAL RESULTS ON THERMAL AND HYDROLYTIC DEGRADATION

This experimental part of the context will be centered onto just one point, i. e. the influence of supermolecular and morphological structure of the substrate on its thermal, thermohydrolytic and hydrolytic chain cleavage, these two modes of degradation being selected mainly on account of their technical relevance. For the sake of briefness and clarity, this presentation of results will be limited to those obtained with cotton linters as a model substrate of rather pure cellulose.

Thermal degradation

As shown in detail in our previous publication (Ref. 15), the initial stage of heterophase thermal, thermooxidative or thermohydrolytic chain cleavage can be assessed by a zero order rate law $1/DP = A + k_0 \cdot t$, based on the "Spaltungsgrad-concept" of Matthes (Ref. 18). In a later stage of reaction the increase in 1/DP flattenes down and eventually levels off. The rate constant k_0 increases, of course, with temperature of degradation and also by adding O_2 or H_2O to the ambient N_2-atmosphere, and is further enhanced largely by small amounts of HCl, promoting thermohydrolysis Table 2. But

TABLE 2. Rate of thermal degradation of linters in different media

Medium	Zero-order rate constant ($DP^{-1} \cdot hr^{-1} \cdot 10^5$)			
	105 °C	140 °C	170 °C	200 °C
N_2	0,34	0,9	1,4	7,2
$N_2 + O_2$	0,62	2,0	11,0	37
$N_2 + H_2O$	0,62	3,1	14,6	31

k_0 also increases significantly after giving the linters a "decrystallizing" pretreatment with liquid NH_3. This clearly demonstrates "thermostabilizing" effects of the H-bond system of native, highly ordered cellulose. If we turn from the heterophase to a homogeneous course of reaction in thiocyanate-melts (Ref. 19), k_0 is enhanced by one to two orders of magnitude Table 3, and the linear, initial stage in the 1/DP-t-plot is extended to much lower DP-values, while the difference in rate between thermal (KSCN/NaSCN/DMSO) and thermohydrolytic ($Ca(SCN)_2 \cdot 3 H_2O$) process still persists. The Arrhenius energy of activation amounts to 15 ± 1 kcal/mol in both homogeneous and heterophase thermal degradation, while in thermohydrolysis a much higher E_A of 27 kcal/mol was found in the $Ca(SCN)_2 \cdot 3 H_2O$-system as compared to $N_2 + H_2O$ (14,3 kcal/mol), possibly due to an "hydration orientation" of the water molecules in the salt-hydrate melt.

TABLE 3. Rate of homogeneous degradation of spruce sulphite dissolving pulp in a melt solution of $Ca(SCN)_2 \cdot 3 H_2O$

Temperature (°C)	Zero-order rate constant ($DP^{-1} \cdot s^{-1} \cdot 10^5$)
120	0,40
130	0,60
140	1,76
150	4,25
160	8,10

Especially in thermohydrolytic heterophase degradation in the $N_2/H_2O/HCl$-system a minimal DP with a subsequent increase has been observed after prolonged time. This is in some general agreement with the "thermal LODP" reported earlier by Golova (Ref. 20) after prolonged thermal treatment of cotton under N_2, and may be caused by a competition between bond cleavage and bond formation, with the formation reaction showing the higher energy of activation. As a possible mechanism of this re-formation of chain links, a transglycosylation according to that proposed by Back (Ref. 21) can be considered here. In the course of homogeneous thermohydrolysis in $Ca(SCN)_2 \cdot 3 H_2O$, the approaching of a limiting DP is observed as a tendency only at a DP of about 100. It may be associated with the numerous microgels still persisting in this macroscopically homogeneous melt solution. An approach to a limiting DP is not observed in heating a melt solution of cellulose in N-methylmorpholine N-oxid. Finally, it may be accentuated that the various "high-temperature solvent systems" for cellulose described recently (Ref. 22 & 23) are relevant not only for cellulose structure formation via the dissolved state, but also for gaining a better understanding of thermal degradation processes realizable now in an homogeneous reaction system.

Heterogeneous acid hydrolysis

As being known from Battista's work, a levelling off DP (LODP) is reached after about 1 h of hydrolysis with dilute mineral acid at 100 °C due to a selective attack of the H_3O^+ - ions on glycosidic bonds in the less-ordered regions. This LODP remains rather constant during prolonged hydrolysis and depends only to a small extend on acid concentration, but very much on the state of supermolecular order of the substrate as demonstrated by our experiments with linters after different pretreatments Table 4.

Besides supermolecular order, also the state of swelling resp. drying of the substrats significantly affects the LODP and the percentage of residue. Higher swelling caused by changing the medium or by employing a never-dried sample increases the LODP Table 5. On the other hand, this DP-value is decreased by giving the sample a thermal pretreatment resulting in some

TABLE 4. Acid hydrolysis with HCl at 100 °C

Sample	(LODP (5 % HCl)	% Residue after 2 hr (5 % HCl)
No treatment, DP = 1800	155	93
NH_3 treated, DP = 1620	71	85
Mercerized, DP = 1580	68	89
Dry disintegrated, DP = 1425	110	89
Dry disintegrated, NH_3 treated, DP = 1120	50	66
Dry disintegrated, mercerized, DP = 1000	51	70

TABLE 5. Rate of acid hydrolysis of linters in 1 N H_2SO_4 at 80 °C in different media

Medium	DP of residue after 1 hr of hydrolysis	Zero-order rate constant $(DP^{-1} \cdot hr^{-1} \cdot 10^3)$
DMSO	227	1,8
Water	166	2,8
n-Propanol-water 90 : 10 by volume	143	15,5

cross-linking on the molecular level and in structural stress leading to corrosion and distortion of the fibrillar units on the level of morphological structure (Ref. 24). Although according to Krässig (Ref. 25) the LODP shows some correlation to the dimensions of the elementary fibrils resp. the "crystallites" especially within a series of cellulose II samples, the state of the surface of the morphological units also seems to play some part.

Heterogeneous acid hydrolysis in an aqueous medium leads to an increased supermolecular order as compared to the original sample (Ref. 26) due to preferential digestion of low-ordered material and recrystallization, but also to a decay of the fibrillar structure of the cellulose fibre into smaller fragments as shown for linters by the particle size distribution curves in Fig. 4. This decay of the fibre morphology by hydrolysis, which can be assisted by a subsequent mechanical treatment, is the decisive effect in manufacturing hydrolycally degraded cellulose powders "microcrystalline cellulose". Particle size and particle morphology of the products may be varied via the condition of hydrolysis, desintegration and drying, and may thus be adapted to each of the various fields of application (Ref. 27).

Enzymatic degradation and physical structure of cellulose

Due to the highly specific and cooperative action of the various components of the cellulase system, enzymatic chain cleavage proceeds very fast in an

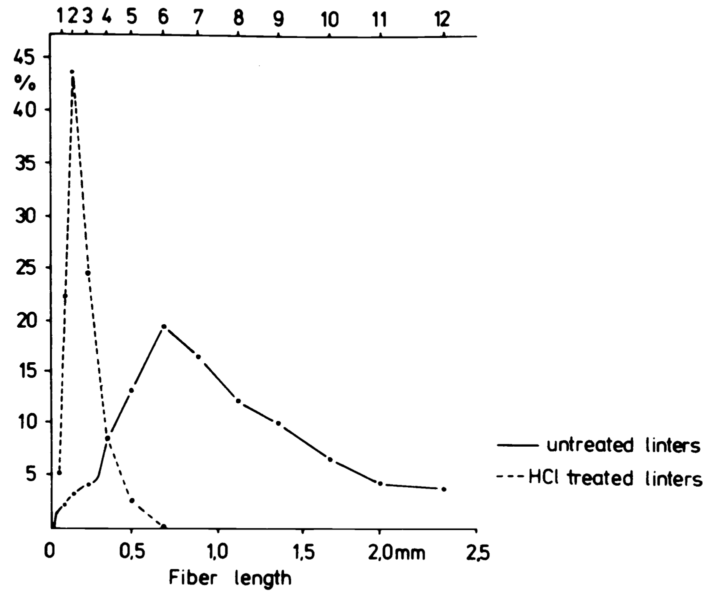

Fig. 4. Particle size distribution of linters

homogeneous system, as shown by our model experiments with water-soluble cellulose derivatives of low DS (Ref. 28). But this rate of formation of reducing sugars is retarded by several orders of magnitude by turning to the heterogeneous system of buffered aqueous enzyme solution and fibrous cellulose. Obviously, the limitation of accessibility for the large-sized protein macromelecules by the physical structure of cellulose plays a decisive role, and, thus, rate and yield in enzymatic hydrolysis are more sensitive to changes in supermolecular and morphological structure of the substrate than other processes of degradation.
The general course of amount and DP of residue in enzymatic hydrolysis is demonstrated in Fig. 5. Decrease in percentage of residue (% R), or - equivalent at the reaction condition applied - of conversion to glucose VS time

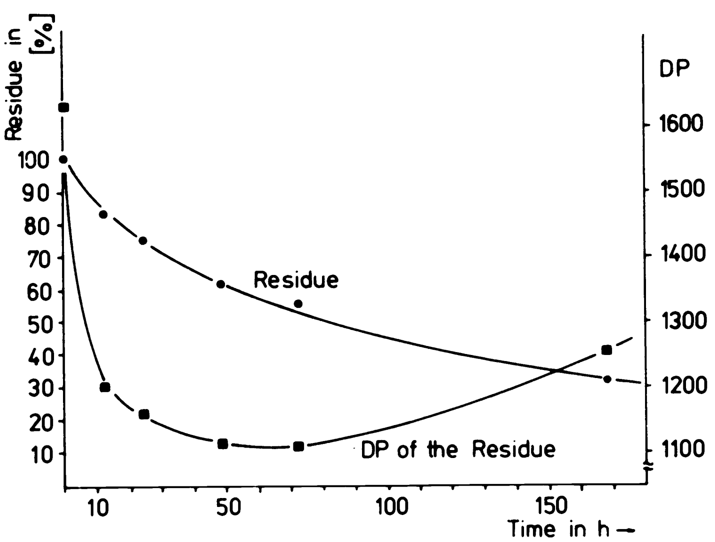

Fig. 5. General course of amount and DP of residue during enzymatic hydrolysis of linters

can be linearized by a two-parameter first order rate law - $\frac{dR}{dt} = k_1(A-(100-R))$ with A denoting an inaccessible part of the substrate structure remaining as residue after prolonged action of the enzyme. The course of residue-DP passing a minimum may be caused by a delay of exoglucanase action digesting insoluble fragments to soluble sugars as compared to the random cleaving of long chains by endoglucanase (Ref. 29).
Already small changes in state of swelling resp. drying of the substrate are reflected in k_1, A and the "minimal-DP" Table 6.

TABLE 6. Enzymatic degradation of linters in different states of swelling (Gliocladium spec., pH 5, 40 °C, 1 % substrate)

Sample	H_2O (%)	k_1 $10^2 \cdot h^{-1}$	A (%)	DP minimal
Original, dry	8	0,45	63	1320
Original, wet	80	0,57	63	1130
Wet-milled	82	0,97	95	790
Re-precipitated (cuam)	92	4,7	99	64

A thermal pretreatment definitely impedes enzymatic hydrolysis in contrast to chain cleavage by acid. Intense wet desintegration "colloidal milling" as well as reduction in supermolecular order via transient formation of addition compounds with NaOH, NH_3, ethylene diamine or guanidine, or by some chemical cross-linking from a highly swollen state, increase the rate of glucose formation, Table 7.

TABLE 7. Enzymatic degradation of linters after chemical pretreatment (Gliocladium spec., pH 5, 40 °C, 1 % substrate

Pretreatment	k_1 $10^2 \cdot h^{-1}$	A (%)	DP minimal
None	0,45	63	1320
24 % NaOH	1,05	98	870
NH_3	0,50	70	1020
Ethylene diamine	2,45	100	460
Guanidine	4,4	100	865

This relative order of substrate susceptibility remains about the same with enzyme preparations from different cellulolytic microorganisms (Ref. 30). This influence of physical structure is also clearly reflected in data obtained with isolated endoglucanases, while with a highly purified exoglucanase glucose yield is nearly nil with highly crystalline as well as with amorphous cellulose. But even here a significant drop in DP depending on state of order has been observed (Ref. 40).
The relevance of different parameters of physical structure on enzymatic chain cleavage can be concluded from Fig. 6. Lattice type of cellulose is of minor importance only. Of about equal relevance are supermolecular order "crystallinity" just as in acid hydrolysis, and - in contrast to acid hydrolysis - "fibrillar accessibility" reflected by the water retention

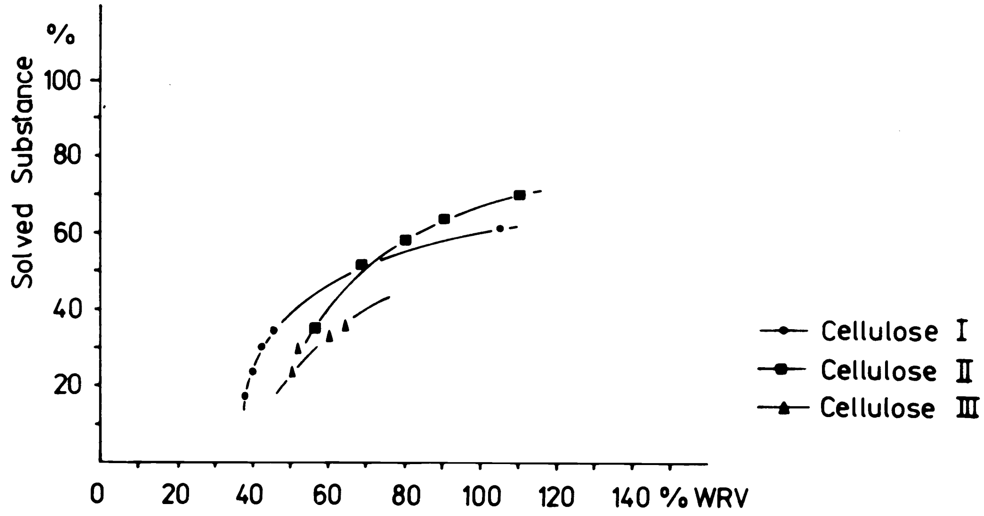

Fig. 6. Dependence of amount of substrats dissolved in enzymatic hydrolysis on water retention value for various lattice types of celluloses.

value. Fibrillar surface accessibility obviously plays a major part already in the first reaction step, i. e. enzyme sorption to the substrate, and thus influences the overall rate of sugar formation via the total concentration of the enzyme-substrate-complex. This is shown by our recent sorption experiments of Penicillium citrioviride cellulase to native and mercerized linters in the water-swollen and air-dry state Table 8 (Ref. 31).

TABLE 8. Enzyme sorption onto linters after different pretreatments (sorption at 20 °C for, 10 min)

Substrat	Sorbed protein (%)	Sorbed cellobiase activity (%)	Sorbed CMCL-activity (%)
Original	63	21	8
Mercerized [a]	65	22	14
Water swollen	22	19	9
Wet-milled linters [b]	73	6	28

a. culture filtrate I
b. culture filtrate II

DISCUSSION AND CONCLUSIONS

Before turning to some aspects of current and future large-scale application of cellulose degradation, some general ideas on the interaction of chemical reaction and physical structure may be considered although generalizations of this kind are severely limited by the broad variety of inducing agents and reaction paths in cellulose chain cleavage.

On the molecular level, some kind of reversal of in-vitro-chain-formation by polycondensation is observed only in the random splitting of glycosidic links during homogeneous acid hydrolysis. A kind of depolymerization reaction may occur at special condition of thermolysis by formation of levoglucosan and by "alkaline peeling". In all the other modes of degradation considered here, the mechanism is rather complex and cannot be simulated by a clear-cut reaction model due to a variety of primary chemical transformations at the cellulose chain giving rise to several subsequent pathways of chain cleavage at the glycosidic bond as well as within the anhydroglucose ring. In degradation processes induced by input of thermal or radiation energy, chain splitting always has to be considered in competition with cross-linking.

A high state of supermolecular order (high crystallinity) generally exerts a stabilizing effect against several ways of degradation induced by energy input as well as by chemical agents, while no significant influence of the type of lattice on these processes has been found up to now. Changes in fibrillar morphology may enhance or impede subsequent chain cleaving, depending on wether a change in accessibility of fibrils via the changes in pore structure or a formation resp. relaxation of structural stress play the dominant role in the subsequent degradation.

Resuming finally now recent and future large-scale applications of cellulose degradation, 3 main path-ways of utilization may be considered here. i.e.
- a better processability of cellulose in subsequent production stages by a controlled decrease in chain-length
- the manufacturing of carbon materials
- the transformation of cellulose and lignocellulose to well-defined low molecular products "wood chemicals".

Controlled degradation in processing is a classical field of application already, practised on a large scale, for example, in pulp bleaching or oxidative degradation of alkali cellulose in the viscose process (alkali cellulose pre-ripening). Recent developments in this area are new ideas to promote or impede alkali cellulose ripening, new bleaching sequences in the manufacture of dissolving pulps, controlled chain-length degradation by high energy radiation (Ref. 32), leading to a more even chain length distribution, and the large-scale manufacture of hydrolytically degraded cellulose powders .

Cellulose threads can be carbonized and graphitized by a thermal process and thus converted to graphite fibres (Ref. 33). Due to the rather low carbon content of cellulose of 44,4 %, however, yield is rather poor, and thus other polymers like polyacrylonitrile (Ref. 34) are preferred today. Economically more attractive is the manufacture of carbon products for sorption purposes (Ref. 35), as lignocellulosic waste can be utilized here without a previous isolation of the cellulose.

The most promising field of application of cellulose degradation processes is the production of defined, low-molecular"silvo-chemicals" by thermal or hydrolytic destruction of the macromolecules of cellulose, hemicellulose, or lignocellulose, while a destruction by alkali at elevated temperature leading to aliphatic carbonic acids (Ref. 36) seems not so favorable for large-scale realization due to unsolved seperation problems of the multicomponent system. By pyrolysis of waste wood a variety of compounds can be obtained, as demonstrated by the work of Fischer (Ref. 37). Phenols at one hand, laevoglucosan as a potential monomer at the other, are of special importance here.

Production of glucose and/or of compounds obtainable there-from like ethanol or single cell protein has been practised since many decades, but poor glucose yield and severe effluent problems inhibited further development of the "classical" acid wood hydrolysis. New ideas, like application of special hydrolizing agents (superconcentrated hydrochlorid acid, or hydrofluoric acid) or a high-temperature hydrolysis (Ref. 38) are available now, but their realization is still an open question, mainly due to corrosion problems.

Enzymatic hydrolysis of cellulosic materials yielding glucose, ethanol, or single cell protein was considered with much enthusiasm as the process of the future in the early 70th. This way of cellulose destruction still seems to be promising, but several decisive problems like increase of rate of sugar formation via enhancement of substrate accessibility or separation and isolation of the reaction products including enzyme recycling are not yet solved in an economically and technologically satisfactory manner. A so-called "direct conversion" of cellulose to protein by an interpenetrating growth of microorganisms into the cellulose or lignocellulose matrix with a simultaneous formation and utilization of sugars from the polysaccharides is considered today as an interesting alternative to the application of isolated cellulases, in spite of unsolved microbiological and toxicological problems. In connection with the biotechnological conversion of cellulose the rotting processes accurring aboundantly in nature should be mentioned briefly, which are becoming more and more "industrialized" now for compost preparation and soil-upgrading (Ref. 39).

It may be concluded from the survey given here that many ideas do exist today for utilization of degradation processes of cellulose, but further research is necessary to test their technological relevance and to select for realization those most favorable for the national economy of the appropriate country. Combination of chemical and biotechnological process steps are considered promising here. Thus, by a deliberate, controlled degradation of its macromolecules, cellulose may be used to solve problems of ressources in a new and promising way.

REFERENCES

1. H.A. Shuyten, J.W. Weaver and J.D. Reid, Fire Retardant Paints, Advences in Chemistry, Academic Press, New York (1954).
2. G.A. Byrne, D. Gardiner and F. Holmes, J. Appl. Chem. 16, 81-88 (1966).
3. D. Fengel, Holz als Roh- und Werkstoff 25, 102-111 (1967).
4. P. Baugh, Dev. Polym. Photochem. 2, 165-214 (1981).
5. R.L. Desai and J.A. Shields, Polym. Letters 8, 839-842 (1970).
6. J. Griffiths and C. Hawkins, Polymer (London) 17, 1113-1114 (1976).
7. T. Kawai and T. Sakata, Nature (London) 286, 474-476 (1980) 5772.
8. I. Sakurada, K. Kaji, T. Okada and A. Tsuchija, Cellulose Chem. Technol. 9, 503-511 (1975).
9. A. Blonin and J.C. Arthur, Text. Res. J. 28, 198-202 (1958).
10. Ch.U. Usmanov and N. Vachidov, Vysokomol. Soed. Serija A 22, 77-82 (1980).
11. D.C. Dan, V. Jacopian, U. Kasulke and B. Philipp, Acta Polymerica 31, 388-393 (1980).
12. D.C. Dan, H.-P. Fink, U. Kasulke and B. Philipp, Acta Polymerica 32, 164-171 (1981).
13. D.C. Dan, C. Fanter and B. Philipp, Acta Polymerica 31, 463-464 (1980).
14. B. Philipp, D.C. Dan, V. Jacopian and A. Heger, Acta Polymerica 33, 542-545 (1982).
15. B. Philipp and W. Stöhr, Faserforsch. und Textiltechn. 28, 355-361 (1977).
16. B. Philipp, V. Jacopian, F. Loth, W. and G. Schulz, Hydrolysis of Cellulose: Mechanisms of Enzymatic and Acid Catalysis Advences in Chemistry Series 181 American Society, Washington, D.C. (1979).
17. O. Franzon and O. Samuelson, Svensk Papperstidn. 60, 872-877 (1957).
18. A. Matthes, Kolloid-Z. 98, 319-329 (1942).
19. B. Lukanoff, B. Philipp and H. Schleicher, Acta Polymerica (in press).
20. O.P. Golova, R.G. Krylova and N.V. Nikolaeva, Vysokomol Soed. 1, 1295-1304 (1950).
21. F.L. Back, Pulp Paper Mag. (Canada), 1-7 (1967).
22. B. Lukanoff, H. Schleicher and B. Philipp, Cellulose Chem. Technol. (in press).
23. S.M. Hudson and J.A. Cuculo, J. Macromol. Sci. Rev. Macromol. Chem. C 18, 1-82 (1980).
24. B. Philipp, V. Jacopian, F. Loth, W. Hirte and G. Schulz, Das Papier 32, 538-544 (1978).
25. H. Krässig, Lenzinger Ber. 43, 141-151 (1977).
26. J. Baudisch, J. Dechant, D. Nighi, B. Philipp and Ch. Ruscher, Faserforsch. u. Textiltechn. 19, 62-68 (1968).
27. B. Philipp and H. Frommelt, Cellulose Chem. Technol. 14, 831-843 (1980).
28. B. Philipp, U. Kasulke, B. Lukanoff and V. Jacopian, Acta Polymerica 33, 714-718 (1982).
29. D.C. Dan, V. Jacopian, U. Kasulke and B. Philipp, Acta Polymerica 31, 388-393 (1980).
30. B. Philipp, D.C. Dan, H.-P. Fink, K.-E. Eriksson and B. Pettersson, Acta Polymerica (submitted)
31. B. Shawky, U. Kasulke, B. Philipp, G. Schulz and W. Hirte, Acta Polymerica (submitted).

32. K. Fischer, M. Wilke, W. Goldberg and N. Sendner, DD WP 747.
33. A. Shindo, Y. Nakanishi and I. Soma, Appl. Polym. Symp. 9, 271-284 (1969).
34. W. Watt and W. Johnson, Appl. Polym. Symp., 9, 215-227 (1969).
35. O. Wienhaus and F. Fischer, Holztechnol. (Leipzig) 24, 102-110 (1983); DD WP 128824.
36. W. Voss, Sitzungsbericht der ADW Berlin Klasse Chemie, Geologie und Biologie 1, (1962).
37. F. Fischer, Plaste und Kautschuk 28, 501-505 (1981).
38. S.M. Selke and M.C. Hawley, Ind. Eng. Chem. Prod. Res. Dev. 21, 11-16. (1982).
39. C.I. Simionescu, The VIIth Symp. on Cellulose Chemistry and Technology (Iasi) "Opening Lecture".
40. B. Philipp, D.C. Dan, H.-P. Fink, K.-E. Eriksson and B. Pettersson, Acta Biotechnologica (in press).