MECHANISM OF DEPOLYMERIZATION OF CELLULOSE IN LOW SULFURIC ACID MEDIUM:

Kinetic Investigation and Stochastic Simulation

By: Zin Eddine Dadach

PhD Thesis

Chemical Engineering Department
Laval University, Sainte-Foy
Quebec, Canada
March, 21st 1994.

PREFACE

This is an English rewritten version of the PhD thesis written originally in French. This version is based on the following publications:

1. Acid hydrolysis of glucosidic bonds in polysaccharides: Modelling and Stochastic simulation: Advances in thermochemical biomass conversion, edited by A.V. Bridgewater, vol. 2, pp1583-1597, 1992

2. Acid hydrolysis of cellulose. Part I: Experimental kinetic Analysis: The Canadian Journal of Chemical Engineering, vol. 71, December 1993

3. Effects of cotton pre-treatments on wax layers and cellulose acid hydrolysis: Cellulose Chemistry and Technology, vol. 27, pp 597-625, 1993

4. Acid hydrolysis of cellulose, Part II: stochastic simulation using a Monte Carlo technique: The Canadian Journal of Chemical Engineering, vol. 71, February 1994

Abstract for the thesis:

The final objective of this investigation is to model the kinetic behaviour of cellulose during hydrolysis by means of stochastic simulation. Part I of this study will thus report the experimental determination of kinetic parameters to be used in the simulation. These were established from kinetic experiments on cellobiose hydrolysis and glucose degradation. Furthermore, both cotton morphology and outer layer are analysed and the effects of cotton wax on cellulose depolymerization are studied. Finally, the effects of cotton milling on both cellulose depolymerization and glucose yield are investigated and presented in this first part. Part II will deal more specifically with the stochastic modelling of these data. This simulation should be realistic enough to allow a representation of the effect of milling on the cellulose structure and its influence on acid hydrolysis kinetics.

Abstract for the kinetic investigation:

The main objective of this first part is to investigate the effects of milling on the rate of cellulose depolymerization during cotton acid hydrolysis. The data indicate that some glycosidic bonds of cellulose have very high accessibility to catalytic ions. It was also shown that a mechanical pretreatment increases the accessibility of some glycosidic bonds of cellulose and decreases the volume of the crystalline regions of cotton. From the glucose yield versus time data, it was found that the effects of milling on the rate of cellulose depolymerization depends on the reactivity and accessibility of the glycon rings of cellulose. Furthermore, conditions that eliminate the influence of cotton wax on the rate of cellulose depolymerization were found by investigations on the effects of cotton wax extraction and cotton boiling on the rate of cellulose

depolymerization. It was shown that the shift in the controlling mechanism of cellulose depolymerization, from a mass transfer control to a kinetic control, is located in the melting temperature range of the fatty acids of cotton. It was concluded that, at temperatures higher than the wax melting point, the effects of cotton extraction on the rate of cellulose depolymerization become negligible. The reason for this result is that the wax rolling up process happens in original sample and solvent extracted sample in which wax is still present. This effect was confirmed by showing that cotton boiling affects significantly the rate of hydrolysis at temperatures below the wax melting point, due to the increased rate of cotton wetting associated with the observed process of cotton wax rolling up during boiling.

Abstract for the stochastic simulation:

A Monte Carlo procedure was developed to simulate cellulose acid hydrolysis at high temperatures. Both the kinetic information related to the model compound cellobiose and the morphological aspect of cellulose including crystalline, semi-amorphous and amorphous zones were estimated from experimental data and introduced in a FORTRAN program. In our model of cellulose acid hydrolysis, the cleavage of a glycosidic bond and the degradation of glucose are considered as two irreversible reactions in series. For all the temperatures, the overall glucose disappearance rate constant used in our model, was higher than the experimental constant obtained from the degradation of pure glucose. The changes related to the effects of milling on the cellulose acid hydrolysis were successfully considered in the procedure. Finally, the observed good agreement between the simulated and the experimental data of glucose yield versus time proved that Monte Carlo simulation associated with a Markov chain is a flexible connection between cellobiose (model compound) and cellulose conversion reactions.

TABLE OF CONTENTS

ZIN-EDDINE DADACH

SIMULATION STOCHASTIQUE DU PROCESSUS DE DÉPOLYMÉRISATION DE LA CELLULOSE DURANT L'HYDROLYSE DES FIBRES DE LINTERS DE COTON EN MILIEU ACIDE DILUÉ

Thèse
présentée
à la Faculté des études supérieures
de l'Université Laval
pour l'obtention
du grade de Philosophiæ Doctor (Ph.D.)

Département de Génie Chimique
FACULTÉ DES SCIENCES ET DU GÉNIE
UNIVERSITÉ LAVAL
QUÉBEC

MARS 1994

UNIVERSITÉ LAVAL
École des gradués

Zin-Eddine Dadach

ATTESTATION

Ce 21ème jour du mois de mars 1994.
les personnes soussignées , en leur qualité de membres du jury, ont assisté à la soutenance de cette thèse.

NOMS	UNIVERSITÉ	SIGNATURE
GILLES DORRIS	PAPRICAN	Gilles Dorris
Serge KALIAGUINE	LAVAL	
Bernard Grandjean	LAVAL	
Jacques Doucet	LAVAL	
Abdellatif Aït-Kadi	Laval	

SIGNATURE DU PRÉSIDENT DE LA SOUTENANCE

Abderahmane Bencheikh
Arabic - English - French & Vice Versa
Legal Translation

RÉSUMÉ 1

Une procédure mathématique a été proposée dans cette étude pour simuler le processus de dépolymérisation des fibres de linters de coton en milieu acide dilué. Le travail expérimental a été réalisé dans un réacteur discontinu agité fonctionnant à température constante. La première étape a consisté à estimer l'énergie d'activation et le facteur préexponentiel de la constante cinétique de la vitesse d'hydrolyse acide de la liaison β(1,4) de la cellulose à partir des essais expérimentaux d'un composé modèle, le cellobiose. Le stade suivant a consisté à développer un modèle de chaîne β(1,4) glucane hypothétique à partir des principales propriétés des fibres de linters de coton, à savoir leurs degrés de polymérisation viscosimétrique moyen initial et limite ainsi que leur cristallinité. Les paramètres cinétiques et morphologiques obtenus dans ces deux étapes ont été introduits dans une procédure statistique utilisant des probabilités de transition des processus de morts pures. La simulation stochastique de l'évolution temporelle de la concentration du glucose a fait intervenir une technique de Monte Carlo associée à une chaîne de Markov. Les valeurs simulées de la concentration du glucose ont été comparées à celles obtenues lors des essais d'hydrolyse des fibres de linters de coton en milieu acide dilué et à différentes températures.

Une étude préliminaire de nature cinétique a montré que la présence du film de la cuticule n'a pas d'effets significatifs sur la vitesse d'hydrolyse des fibres cellulosiques aux températures supérieures aux points de fusion des acides gras des fibres de linters de coton.

Zin-Eddine Dadach

ZIN-E-DADACH

Serge Kaliaguine

EXPERIMENTAL STUDY I: CELLULOSE PRETREATMENTS

INTRODUCTION TO CELLULOSE

Cellulose is synthetized by all higher plants as well as by a wide variety of other organisms. The amount of synthesis is enormous, making cellulose the most abundant biopolymer on earth.[1] Cellulosic materials could then be used as a potential source of organic materials and fuels currently derived from petroleum fractions.[2–3] The objective of many research projects is to obtain the highest yield of glucose during acid hydrolysis of wood and cotton fibers.[4–6] The glucose formed could for example be fermented to ethanol or hydrogenated into sorbitol. This last compound may be transformed into low molecular weight polyalcohol or used for the production [7] of vitamin C. In botanical science, cotton is defined as seed hair, but in common usage one refers to cotton as a fiber where the microscopy, each fiber appears as an irregularly twisted, collapsed, flattened cell. [8] It is also well known that the cotton fiber is covered with a thin layer of tightly moulded materials and, according to Peters, [9] waxes, resins and nitrogen-containing compounds are the main impurities detected in this outer layer of cotton cell. Cotton wax is described as a mixture of aliphatic monoalcohols in C_{28} - C_{34}, fatty acids in C_{24} - C_{34}, saturated and unsaturated hydrocarbons, resins and resin acids, sterol and sterol glucosides.[10]

Because of their low surface energy, the wax materials could represent a resistance to cotton wettability and therefore decrease considerably the rate of cellulose hydrolysis.[11] From the fact that wax is not an integral part of the cotton cell, many extraction techniques are used for the purification of fibers.[11] For example, for the hydrolysis of Egyptian cotton at 50° in 0.1N sulfuric acid solution, fibers were first purified by extraction with boiling alcohol and ether.[12] However, the ESCA analysis, reported by Ahmed el al.,[13] indicate that cotton wax was not completely removed even after drastic treatments. On the other hand, Peters[11] reported that if cotton is immersed in hot water (97-99°) for 15 minutes and air-dried at 20°, it becomes wettable. This suggests that wax material melts when immersed in hot water, rolls up into droplets in the cotton surface and remains as such if the fiber is then dried at 20°. Moreover, the high temperature coefficient of detergency is partly associated with the melting of some wax materials.[14] Finally, grinding was found to detach some wax from the cellulosic materials.[15]

Cellulose is a linear polysaccharide having the anhydro-cellobiose moiety as the repeating unit. This unit itself is formed by two anhydro-glucose linked by a β(1,4) glycosidic bond, [16] but the process by which the β (1,4) linked glucan chains are synthetized and assembled into the cellulose microfibrils of cotton remains one of the major mysteries of plant biology.[17] Glucose and intermediate oligomers are produced when the catalytic agents disrupt these

links. However, the highly ordered structure and, particularly, the crystallinity of cellulose constitutes a major obstacle for the hydrolysis of cellulosic materials.[6] As a result, during cellulose hydrolysis in dilute acid solution, the production rate of glucose decreases drastically when the rupture of the β(1,4) bonds with very low accessibility is achieved. On the other hand, in concentrated acid solutions, the quantitative saccharification of cellulose is followed by a fast degradation of the glucose formed into furfural and levoglucosan.

Experimental investigations of cellulose hydrolysis demonstrate clearly that the decrease of the average degree of polymerization occurs in at least three major stages.[9] According to the data presented by Sharples,[12] the first rapid stage of cellulose depolymerization represents the rupture of the bonds with high accessibility. Indeed, the postulated weak bonds, which were thought to be created by inductive effects, caused by the presence of some oxidized groups, were not found during the study of kinetics of cellulose depolymerization. [12, 20] The following stages of the process have a smaller rate and are related to the breaking of the glycosidic bonds with lower accessibility, located in the noncrystalline regions.[19] The third stage of the process starts very close to the so-called levelling-off degree of polymerization (LOPD) and its extremely low rate is due to the rupture of the β(1,4) bonds located in the crystallities.[21]

According to Harris,[22] the accessibility of the glycosidic bonds is directly related to the rotational energy barrier encountered in their glycon rings flexure. Therefore, when the rate of cellulose depolymerization is controlled by the rupture of the glycosidic bonds with low accessibility, the low rotational energy of the glycon rings imposes a higher energy of activation. Indeed, the very slow degradation rate of the crystalline parts of cellulose is a consequence of the hydrogen bonds holding tightly the glycon rings.

To make efficient use of the glucose potential of cellulosic materials, during acid hydrolysis, many physical and chemical pretreatments are reported in the literature. [5, 23] It was found that milling enhances the degradation of cellulose by loosening its structure and disrupting the durable hydrogen bonds between cellulose molecules of the crystalline areas within the microfibril or between microfibrils. [5, 24] The investigation by Millet et al.[25] of the effects of ball milling on dilute acid hydrolysis of cotton, shows that both the rate of hydrolysis of cotton and the maximum yield of glucose are increased by the mechanical pretreatment. Furthermore, the work of Saeman[4] showed that the increase of the rate of hydrolysis of milled cellulosic material is partly related to the smaller particle size of the sample.

The main objective of the present work is to study the effects of cotton milling on the rate of cellulose depolymerization. Therefore, the effects of milling on the morphology of cotton, on the rate of cellulose depolymerization and on the net rate of glucose production are

investigated. Furthermore, in order to study the influence of the cotton wax film on the rate of cellulose depolymerization, the effects of cotton extraction and cotton boiling on cotton wax and on the rate of cellulose depolymerization are also investigated.

EXPERIMENTAL APPARATUS

The apparatus used in our experiments was a 725 ml. steel autoclave (AMINCO), where the agitation was kept at 650 rpm by a magnetic stirrer. The heat input from an internal source (500-W cartridge) was regulated by a three mode temperature controller (Lindberg M 211). An external source (1200-W) was added during the warm-up period. During the reaction time, the temperature deviation was less than 0.6°. To avoid any cotton conversion during the warm-up period, a concentrated acid solution was placed in a vertical closed conical reservoir upstream the autoclave. When the desired temperature eas reached, the acid solution was pushed into the reactor by a gas supply. Liquid samples were collected from a micro-valve connected to a capillary tube immersed in the reacting solution. A quantity equivalent to the dead volume of the sampling system was discarded before collecting samples.

COTTON PRETREATMENTS

Milling

The milling pretreatment of the cotton fibers was done in a Thomas-Wiley intermediate mill where cotton samples were introduced through the hopper and swept around by the rotor until cut to sufficient fineness to pass through the sieve top of a delivery 20 mesh (0.85 mm) tube. The shearing action was produced by four cutting edges and two stationary blades.

Boiling

Cotton samples were boiled in de-ionized water (pH=6.7) at 100° for 20 minutes, then dried at room temperature for two days.

Extraction

Cotton samples were purified in a Soxhlet extractor using ethanol, for 8 hours. A second extraction by ethyl-ether was carried out in the same conditions. After this, the samples were washed with distilled water, and air-dried at room temperature.

COTTON CHARACTERIZATION

IR spectra

Each cotton sample (3 mg) was ground with 100 mg of IR grade KBr powder, and pressed into a 13 mm diameter disk. The infrared spectra were recorded using the Harrick diffuse reflectance Fourier transform (DRIFT) cell, in a Digilab FTS 60 spectrometer. The band at 1372 cm^{-1} (C-H bending) was chosen by Nelson and coworkers[26] to monitor the crystallinity

of the sample and the absorbance ratio of this band to the one at 2900 cm^{-1} (C-H stretching) was used to measure the crystallinity index (CI).

Transmission Electron Microscopy (TEM)

Pieces of $1mm^3$, cut from cotton samples, were fixed with 3% glutaraldehyde in 0.1 M sodium cacodylate buffer (pH 7.2) for 2 hours, at 4°, and post-fixed with 1% osmium tetroxide in the same buffer. Samples were repeatedly dehydrated in ethanol and embedded in Epon 812. Ultrathin sections collected on nickel grids were processed for ultrastructural investigation. These analyses were performed at the "Département de phytologic, Université Laval" with the assistance of Dr. N. Benhamou.

Scanning Electron Microscopy

A gold-Palladium coating was deposited on all cotton samples prior to examination in a JEOL-840A scanning electron microscope.

Degree of Polymerization by viscosity determination

Viscosities were measured in 0.5M cupriethyldiamine solution (CED) at 20° with a Cannon-Feske viscosimeter, size 100 (ASTM). From these measurements, the intrinsic viscosity was determined using the relation of Martin. Values for the average degree of polymerization were then obtained using the relation of Mark-Houwink (AFNOR NET 12-005). All samples were first washed with de-ionized water and dried at room temperature for two days. Cellulose solutions were prepared by dissolving dry cotton samples in the cupriethyldiamine solution at 20°, for two hours. These experiments were performed at the "Département des sciences du bois, Université Laval" with the assistance of Dr. J. Doucet.

ESCA spectra

C_{15}, O_{15} spectra and both O/C and N/O ratio at the interface of cotton fibers were measured using an ESCA spectrometer. The equipment utilized was a VG ESCALAB MK 11 spectrometer fitted on the microlab system from Vaccum Generators. It was equipped with a dual Mg-Al anode X-ray source, non-monochromatized. Kinetic energies were measured using a hemispherical electrostatic analyzer with 150 mm radius working in the constant pass energy 20 eV mode. Vacuum was maintained in the range of 10^{-8} to 10^{-6} Torr.

Glucose HPLC analysis

Solutions taken from the reactor were first neutralized with calcium carbonate ($CaCO_2$), centrifuged and filtered through a 0.45 micron nylon filter unit (Cole-Parmer). High-performance liquid chromatography (HPLC) was used to analyze all samples. The mobile phase (filtered, degassed HPLC grade water from Fisher Scientific) was delivered through a pump (Perkin-Elmer 3B) at a flow-rate of 0.6 mL min^{-1}. The Aminex HPX-87P Pb form column (Bio-Rad, 300 x 7.8 mm) was equipped with a Carbohydrate Analysis ion-exclusion Micro-Guard pre-column (Bio-Rad). The column temperature was maintained at 85.0 ± 0.2°, by means of an insulated heating system connected to a temperature controller (model D921K;

Omega). The injector (model 7125, Rheodyne) was equipped with a 20-µL sample loop. A differential refractometer (L.C25; Perkin-Elmer) was used as detector with a 3392A integrator (Hewlet-Packard) to record the signals. Calibration curves for glucose and cellobiose were constructed periodically using galactose as an internal standard in all samples.

Fatty acids identifications by GC/MS analysis

A HP 5890 gas chromatograph with splitless injector and helium carrier gas at about 1mL/min flow rate was used with HP fused silica column 12m x 0.2 mm coated with 0.25 µm film with crosslinked methyl silicone gum. The GC temperature was programmed from 50° to 290°, at a rate of 10°/min. The end of the column was directly introduced into the ion source of a HP 5970 series mass selective detector. Derivatization of the fatty acids was obtained using Diazald (N-methyl-N-nitroso-p-toluenesulfonamide).

EXPERIMENTAL RESULTS AND DISCUSSION

Cotton structure and morphology

Chinese white cotton fibers were obtained from the "Centre des technologies textiles, Conseil national de la recherché scientifique, Ste-Hyacinthe, Québec, CANADA". A typical scanning electron photomicrograph shows that cotton fibers grow as twisted single cells (Fig, 1). A cross section of one fiber, obtained using a transmission electron microscope (Fig. 2), shows that cotton cell is a tube, having a width of 20µm, with a central canal or lumen running throughout its length. When the plant matures, the dry protoplasm becomes the lumen and the dried resides (minor amounts of protein and salts), either as solid deposits or as a thin layer on the lumen wall, give the characteristic dark areas observed in the TEM micrograph. Furthermore, a more detailed examination, by transmission electron microscopy (Fig. 3), reveals that the fiber is covered with a dark thin layer (0.2 µm) of tightly molded material, called cuticle.

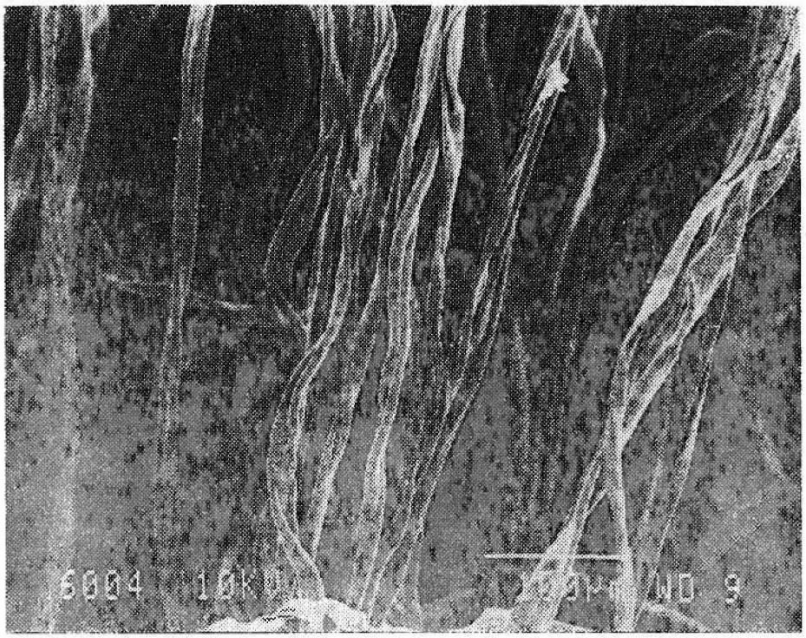


Fig. 1 — Scanning electron photomicrograph of typical cotton fibers.

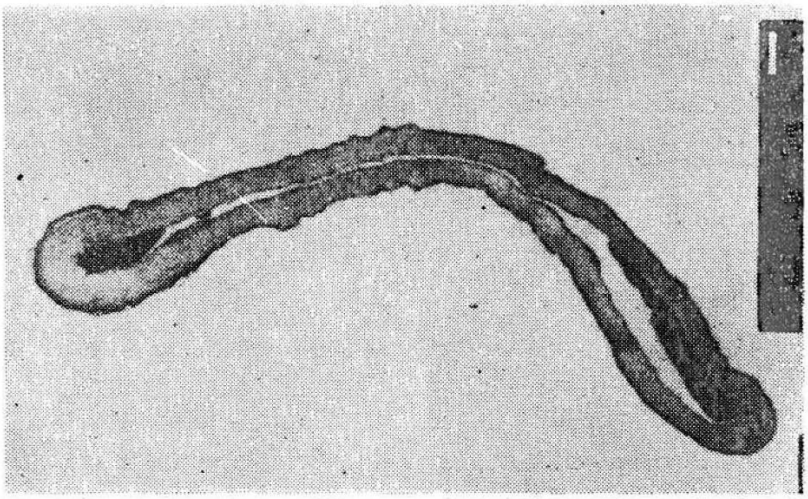


Fig. 2 — TEM micrograph of cotton sample : cross-section of a cotton cell.

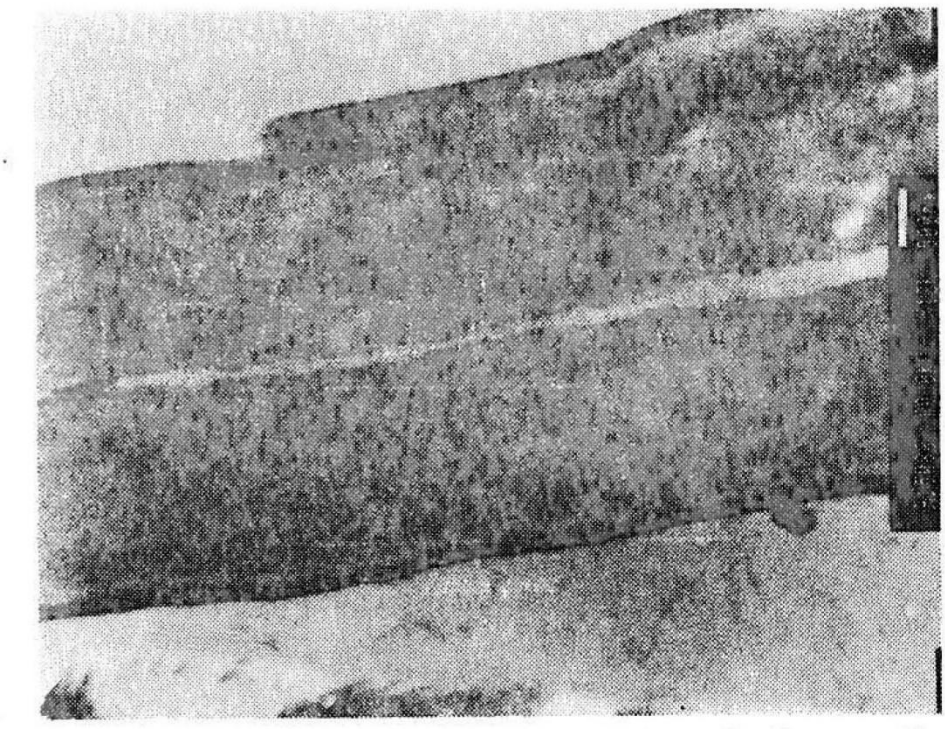
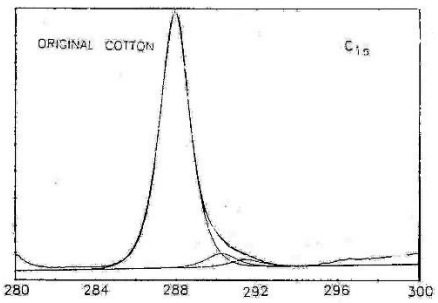
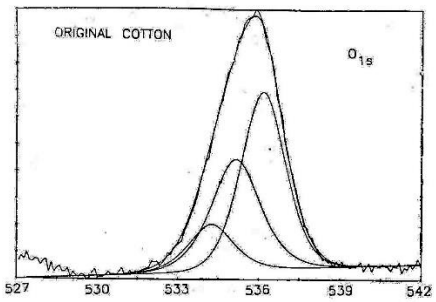


Fig. 3 – TEM micrograph of cotton sample: cross section of a portion of a cotton cell.

Moreover, Peters[9] reported that the major impurities are proteins (14%) and wax material (8%), located in the cuticle and primary wall. On the other hand, 99 wt% (on dry basis) of the secondary wall of cotton is pure cellulose. In agreement with this, the ESCA C_{15} spectra, shown in Figure 4 and the N/O and O/C ratios, presented in Tables 1 and 2, indicate clearly that the surface of cotton fibers is covered with some non-cellulosic compounds. The high C_1 fraction (93.1%) is consistent with the large number of carbons in long chains monoalcohols and monoacids. Therefore, the small percentages of C_2 (5.7%) and C_3 (1.2%) are entirely different from the composition C_2 (83%), C_3 (17%) of cellulose. This drastic difference is also apparent in the O/C ratio of cotton (0.08), compared to the value of pure cellulose (0.83). Moreover, the GC/MS analysis of the other solution used for the cotton extraction, shows that the cotton wax contains fatty acids from C_{15} to C_{33} (Fig. 5).

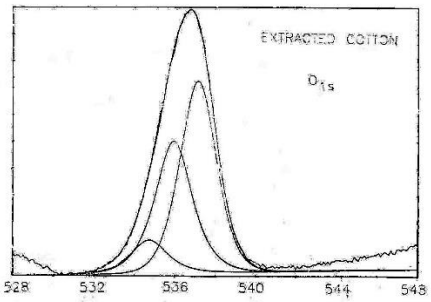


a

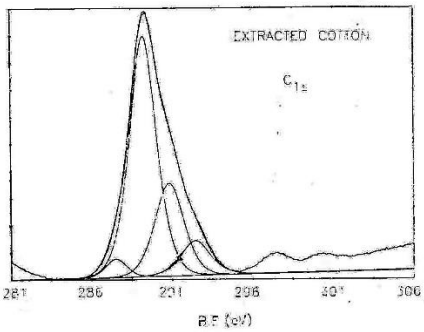


b

Fig. 4

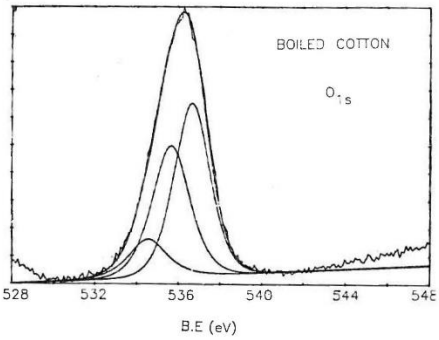


c

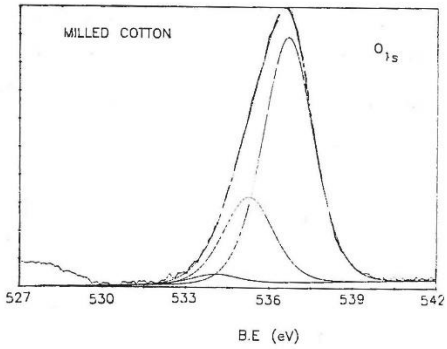


d

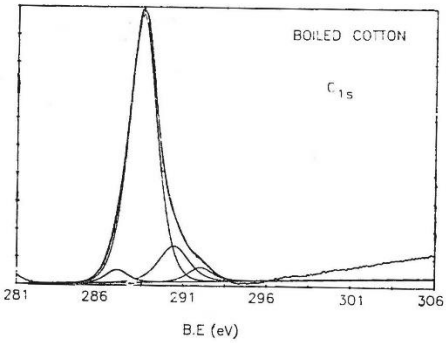
Fig. 4



e

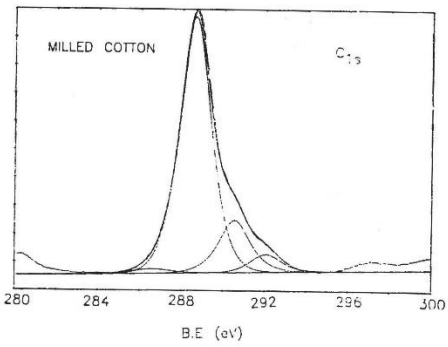


g



f

Fig. 4



h

Fig. 4 — ESCA C_{1s} and O_{1s} spectra of an original, extracted, boiled and milled cotton sample.

TABLE 1: Surface analysis of C_{15} spectra by ESCA technique of (1) original, (2) boiled, (3) extracted and (4) milled cotton samples

Sample	O/C	E_e (eV)	C_{15} binding energy,				C_{15} % Area			
			C_0	C_1	C_2	C_3	C_0	C_1	C_2	C_3
1	0.08	3	-	285	287.3	288.5	-	93.1	5.7	1.2
2	0.17	3.5	283.6	285.1	287	288.6	2.1	83.7	10.7	3.5
3	0.47	4	283.6	285.3	286.9	288.5	3.2	62.4	25.1	9.3
4	0.19	3.5	283.1	285.2	287.1	288.6	1.5	78.3	15.1	5.1

* O_{15} peak of cellulose (533.2 eV) was used as reference for the B. E. scale$_{15}$

TABLE 2: Surface analysis of O_{15} spectra by ESCA technique of (1) original, (2) boiled, (3) extracted and (4) milled cotton samples

Sample	N/O	E_e (eV)	O_{15} binding energy,			O_{15} % Area		
			O_0	O_1	O_2	O_0	O_1	O_2
1	0.09	3	531.1	532.2	533.2	13.8	35.80	50.40
2	0.11	3.5	531.1	532.2	533.2	11.52	39.43	49.05
3	0.10	4	530.8	532	533.2	8.80	38.13	53.07
4	0.08	3.5	530.6	531.8	533.2	2.40	25.20	72.4

Furthermore, inside the cuticle, there come respectively the primary and secondary walls where cellulose is concentrated.[27] The high crystallinity index of cotton sample (79%), obtained by infrared spectra (Fig. 6), indicates that cellulose microfibrils, located in the inner walls of the cotton fiber, are highly organized. We may conclude that the accessibility of the glycosidic bonds of cellulose may be affected by both the wax outer film of the cotton fiber and the organization of cellulose microfibrils detected by a high crystallinity index.

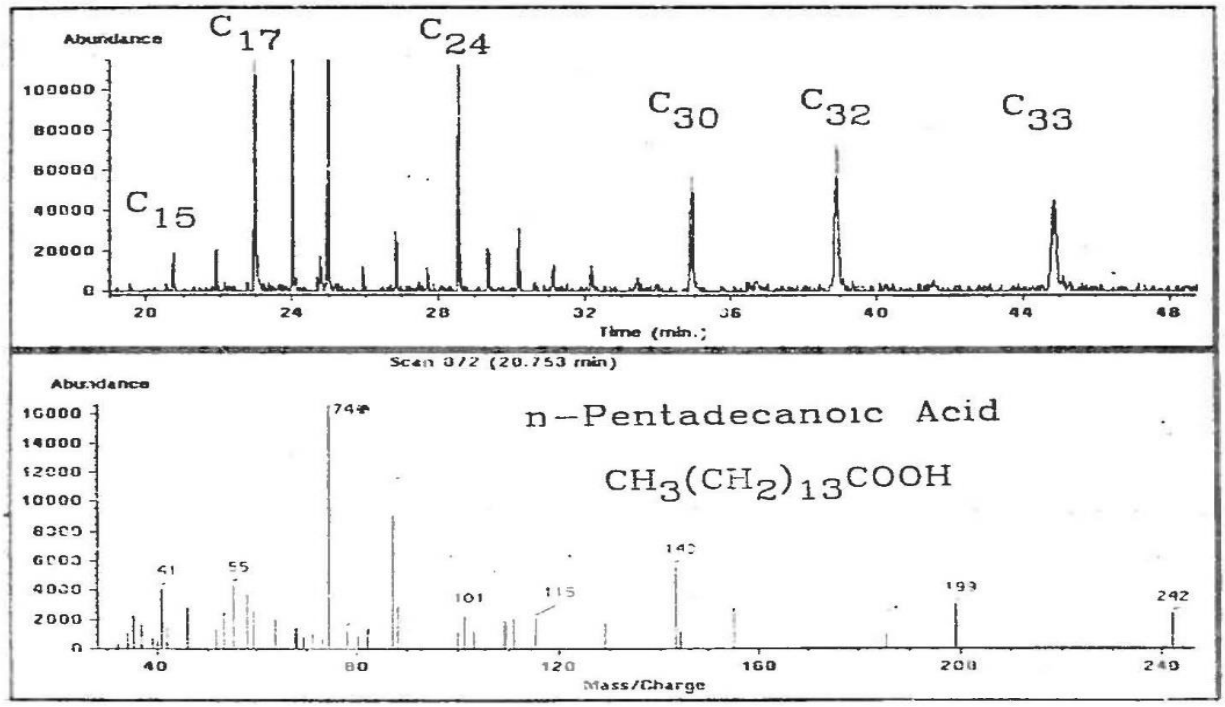


Fig. 5 — GC/MS identification of fatty acids extracted from cotton.

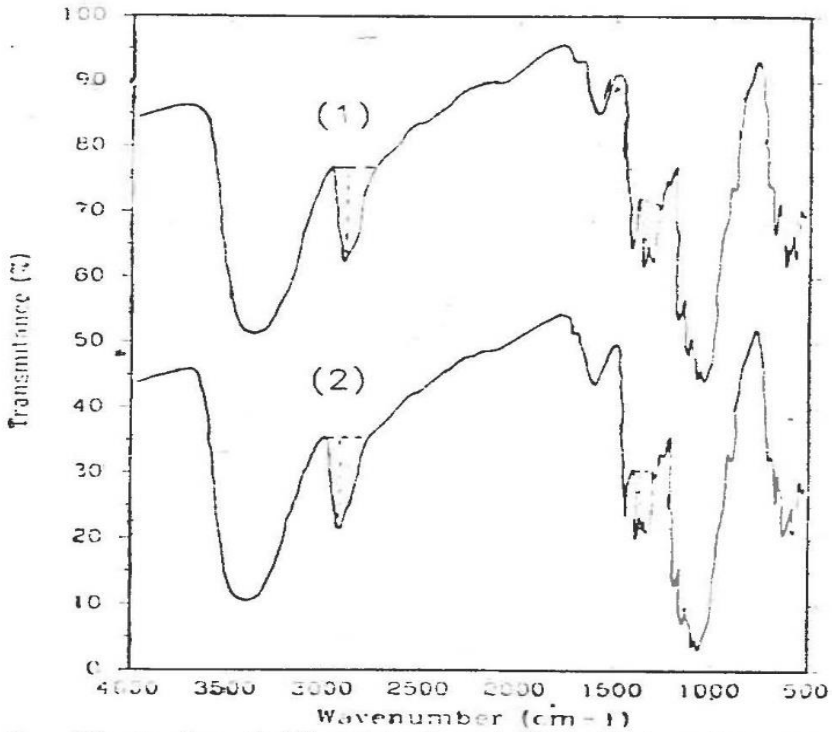


Fig. 6 — IR spectra of (1) original and (2) milled cotton samples.

Effects of cotton extraction on cellulose acid hydrolysis

It is well known that, during cotton hydrolysis, the accessibility of the β (1,4) glycosidic bonds by the reactive ions depends on the wettability of cellulose. The hydrophilic surface character of cotton is confirmed by many authors but, as they are covered with wax materials, cotton fibers behave like a "low-energy surface". [11, 28] Therefore, water forms droplets on the surface of fibers and the rate of cotton wetting is considerable lowered.[10, 28] In order to investigate the effects of cotton wax on cellulose depolymerization, the interface of the extracted cotton sample was first analyzed by ESCA technique (Fig. 4) and compared to the original cotton sample in Tables 1 and 2. The increase of the C/O ratio from 0.08 to 0.47 indicates that some of the cotton wax has been removed from the cotton outer layer. However, this value remains small compared to the theoretical value of pure cellulose (C/O=0.83). The relative small C_2 and C_3 values of the extracted cotton sample, compared to the values of pure cellulose (C_2 = 83% and C_3 = 17%) also indicate a poor extraction of the cotton wax. Moreover, in agreement with the ESCA analysis, Figure 3 shows clearly that the catalytic ions should first diffuse through the wax layer before reacting with the glycosidic bonds of cellulose located in the inner walls of cotton. Under these circumstances, the variation in time and space of the acid ions concentration in the cotton wax layer could be described by Fick's second law of molecular diffusion:

$$D\tau \ \frac{\partial^2[H^+]}{\partial x^2} = \frac{\partial[H^+]}{\partial^{\mathrm{t}}} \qquad (1)$$

Considering diffusion as an activated process, the temperature dependence of the molecular diffusivity could then be estimated by a relationship similar to Arrhenius equation:[29]

$$D\tau = D_0 e^{(-\ \frac{^{\mathrm{E}}D}{RT}\ )} \qquad (2)$$

Where the activated energy of diffusion ($^{\mathrm{E}}D$) is defined as a measure of the energy expanded against the cohesive forces of the polymer in forming the gaps through which diffusion will occur. Figure 7 shows that the effects of temperature on the volume of a condensed film of stearic acid [$CH_3(CH_2)_{16}COOH$] are very small.[30] Therefore, we assume that the of a temperature increase on the diffusivity ($D\tau$) of the catalytic ions remain small, below the melting point of the fatty acids. In agreement with this, the experimental data of cellulose depolymerization, during the hydrolysis of both original and extracted cotton samples in 0.16 N sulfuric acid for 15 minutes (Fig. 8), show that the decrease of the average DP of cellulose remains most constant when the temperature is raised from 20° to 60°. These results indicate that the rate of cellulose depolymerization is mass transfer controlled when the temperature is below the wax melting region. On the other hand, Figure 8 shows that, at temperatures higher than 70°, the decrease of the average DP of cellulose is significantly affected by an

increase in temperature. The experimental data suggest that a resistance to the mass transfer of the catalytic ions, caused by the fatty acids with higher melting points, is still present, but the rate of cellulose depolymerization seems to be controlled by the chemical process in the high temperature region. From the fact that the transition between these two controlling regimes is located in the melting temperature range (52.3° – 84.15°) of most fatty acids of the cotton sample (C_{15}, C_{24}) (Fig. 9), the shift in controlling regime is assumed to be mainly caused by the melting process of the cotton wax.

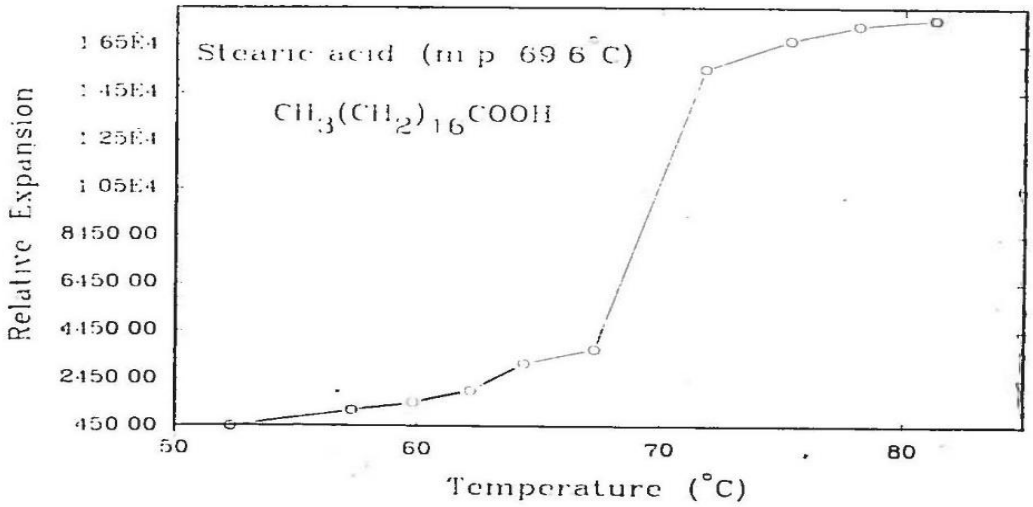


Fig. 7 — Melting dilatation of stearic acid.[30]

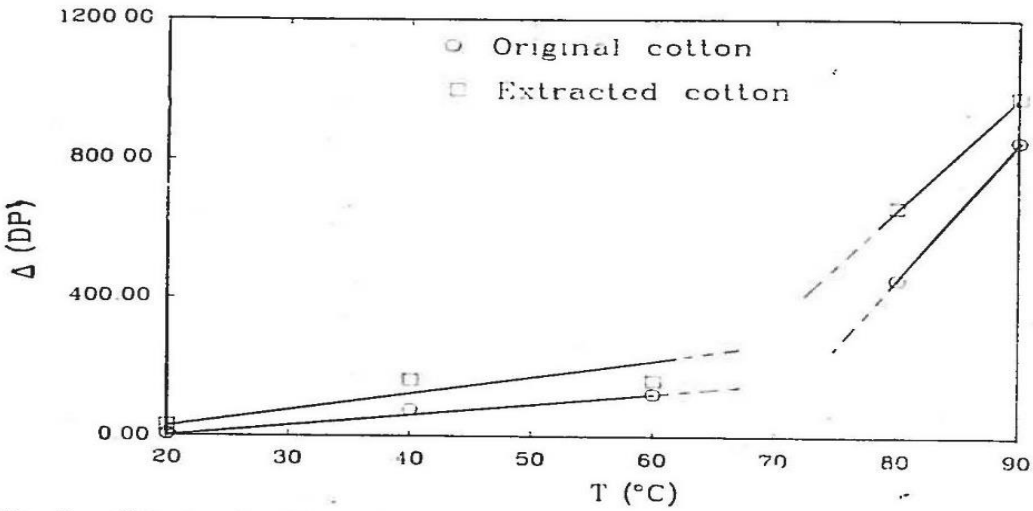


Fig. 8 — Effects of cotton extraction on cellulose depolymerization as a function of temperature in 0.16N sulfuric solution.

Rolling up process of cotton wax

The rolling up process of cotton wax consists in the formation of wax droplets upon wax melting. It is a thermodynamically driven process associated with the change in free energy of the cotton-wax-water system upon wax melting.

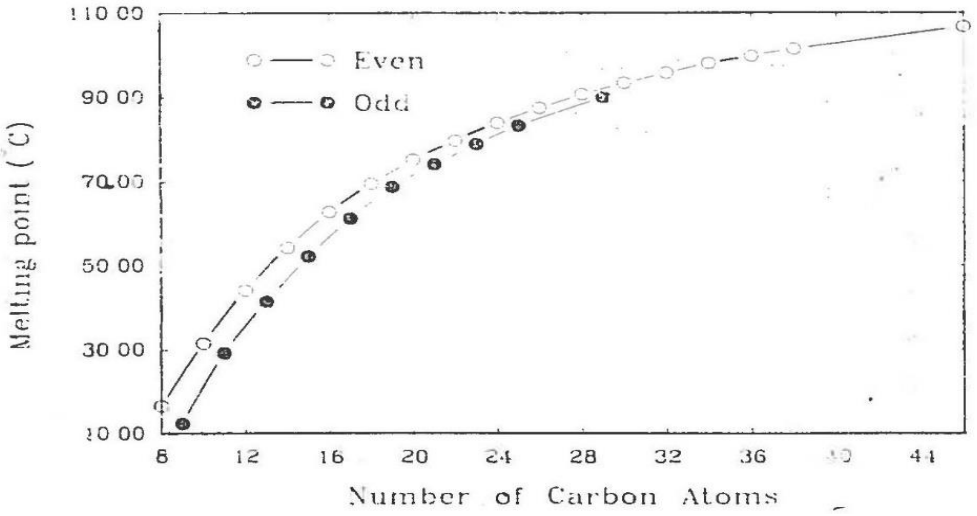


Fig. 9 – Melting point of some cotton fatty acids as a function of carbon number.[38]

ESCA analysis as performed on cotton samples boiled in water, as described above. From the data in Figure 4, the small value of O/C ratio (0.17) and the small percentages of O_2 (10.7%) and O_3 (3.5%) (Table 1) show that boiling does not remove wax material from the cotton outer layer. However, by comparison with the original cotton sample, the rolling up phenomenon of cotton wax is clearly observed in scanning electron photomicrographs of the boiled sample (Fig. 10). It must be underlines that, before the rolling up process of cotton wax takes place, water molecules should first reach the cotton surface. As shown in Figure 7, the large increase of the wax volume in the crystal melt transition is caused by a high thermal expansion (α_m) of the melted material, compared to the small thermal expansion α_c of the crystalline material. The resulting decrease of the wax surface tension could be described by the following equations: [3,1]

$$(d\gamma/dT)_m = (\alpha_m / \alpha_{cr}) (d\gamma/dT)_{cr} \qquad (3)$$

On the other hand, in the crystalline region, the effects of temperature on the wax surface tension are negligible and could be described by:

$$(d\gamma/dT)_{\alpha} = (11/9)\,(\gamma_0/T_0)\,(1-T/T_0)^{2/9} \qquad (4)$$

Where γ_0 and T_0 are the wax surface tension at T_0 (K) and the wax critical temperature (K), respectively. The data reported by Singleton [30] show that all the saturated fatty acids, when spread on the surface of distilled water at 20°, exhibit essentially similar behavior with respect to the compressibility of their films. This behavior, illustrated by the force-area curve shows that, when the area occupied per molecule is lower than 21 10^{-16} cm², the compressing force increases practically linearly with decreasing area up to the point at which the film collapses, due to piling up of the molecules of the film. From the fact that 21 10^{-16} cm² is the area of the cross section of the CH_2 group, determined by other methods, the author concluded that the molecules of fatty acids are oriented. It was concluded that the film attracts water molecules and could be subject to mechanical compression. In agreement with these results, Peters[11] reported that the spreading coefficient of water on an oily film increases by decreasing the surface tension of the wax materials. Moreover, during the cotton hydrolysis experiments, the negative charge, arising from the (COOH) groups of the fatty acids, could have caused an unequal distribution of the catalytic ions, between the film and the solution, [18, 32] which could cause the increase of pH in the bulk solution detected during our hydrolysis experiments (Fig. 11).

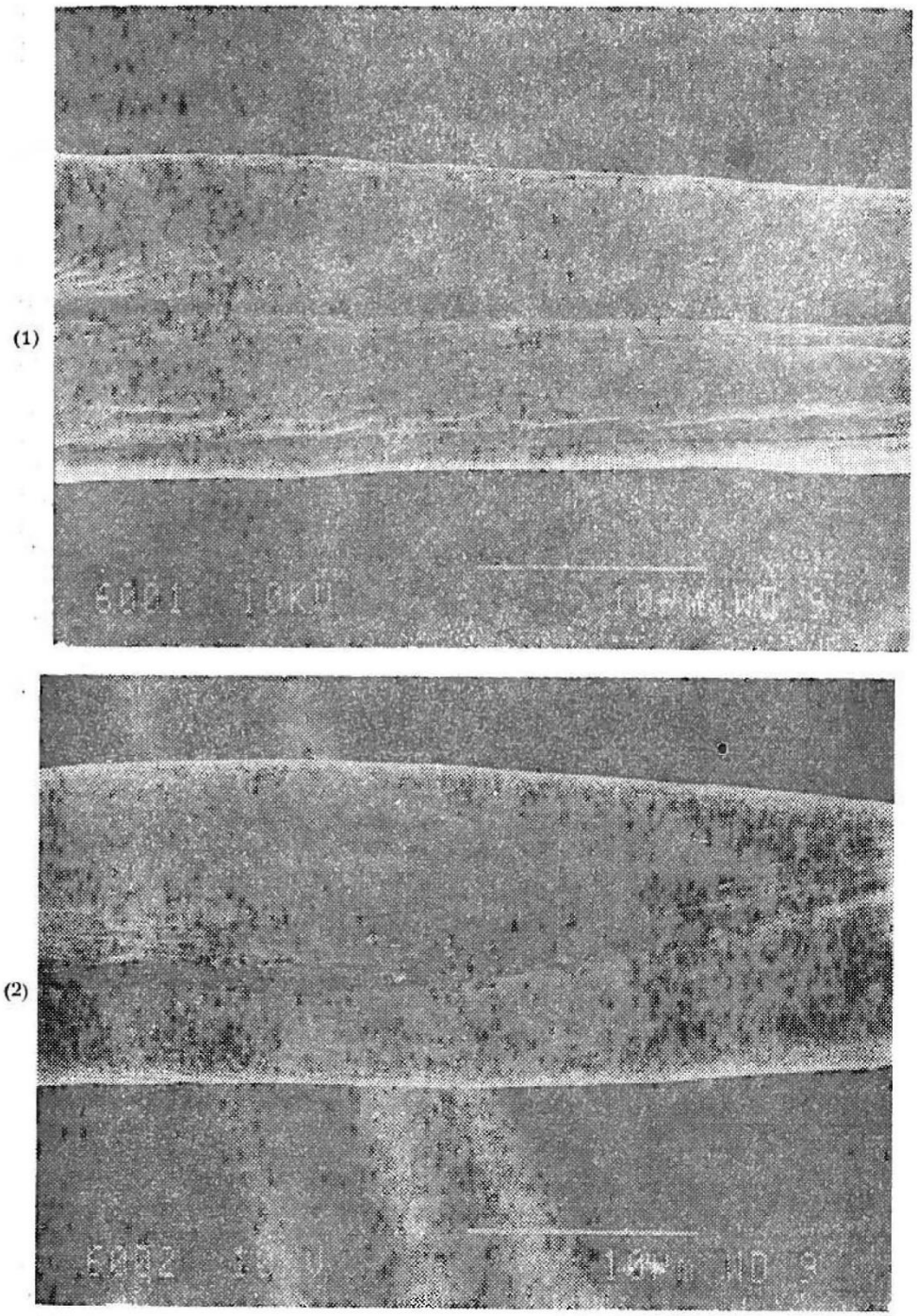


Fig. 10 – Scanning electron photomicrograph of (1) original and (2) boiled in cotton samples

Therefore, we may conclude that the decrease of the film-water interface free energy (ϒm), caused by wax melting, results in attracting both fatty acid chains and water molecules at this interface. Moreover, as shown in Figure 7, the volume occupied by

a fatty acid increases drastically in the crystal-melt region. As a result, the smaller remaining solid islands of the expanded film are separated by an increased number of water molecules.[33] The resulting film pressure (π), caused by the difference between the surface tensions of water and the film will tend to disrupt the film.[34] As a consequence, water molecules will reach the cotton surface. According to the cotton-wax interface free energy balance (appendix), water molecules could easily displace the wax materials from the cotton fiber surface because the large cotton-film interface free energy (Υf) is replaced by a smaller cotton-water interface free energy (Υm).[14]

$$\pi = \Upsilon_m - \Upsilon f \qquad (5)$$

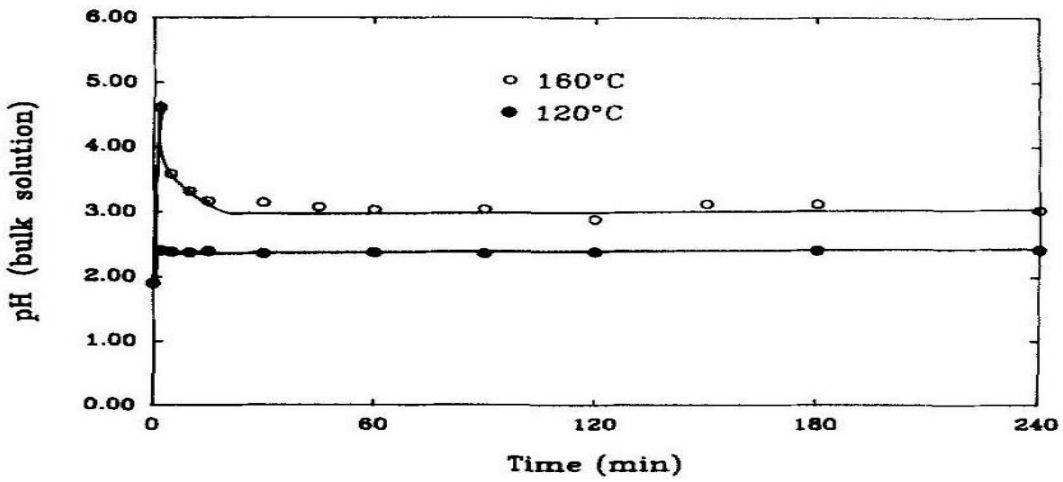


Fig. 11 – pH evolution during cotton hydrolysis in 0.03N sulfuric acid solution.

Effects of cotton boiling on cellulose depolymerization

In order to investigate the effects of cotton boiling on cellulose depolymerization, both boiled and original cotton samples were hydrolysed, during fifteen (15) minutes, in 0.16N sulfuric acid solution at temperatures ranging from 20° to 90°. The experimental data show that the decrease of the average DP of cellulose is lower after the hydrolysis of the boiled cotton sample (Fig. 12). These results indicate that the mass transfer resistance of the wax film was considerably decreased by boiling. On the other hand, the ESCA C_{15} spectra (Fig. 4) and the small value of the O/C ratio (0.17), shown in Table 1, indicate that, after boiling, almost no wax was detached from the cotton surface.

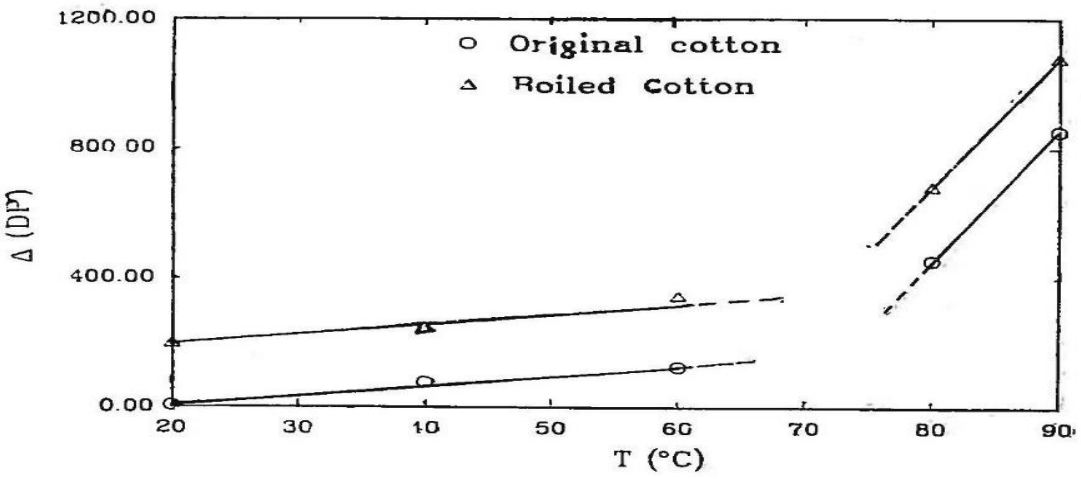


Fig. 12 – Effects of cotton boiling on cellulose depolymerization as a function of temperature in 0.16N sulfuric acid solution.

Moreover, the effects of boiling are still important at the high temperature region and the observed shift from the mass transfer control to chemical control, during the hydrolysis of the boiled sample, may be explained by the fact that not all the wax materials were affected by the rolling up process during the boiling pretreatment. Therefore, the rolling up process of the fatty acids continues during the hydrolysis of the boiled cotton sample, when the temperature becomes higher than the wax melting point.

Furthermore, the effects of wax extraction on the rate of cellulose deloymerization, during hydrolysis in 0.16N sulfuric acid solution at 100, were investigated (Fig. 13). One of the samples was originally extracted following the procedure described in the apparatus and methods section and the two samples were preliminary boiled at 100°, for one hour, before hydrolysis. The time evolution of the average DP of both samples shows clearly that the degradation process is characterized by an initial rapid stage related to the hydrolysis of the completely amorphous areas and a final stage of persistent DP corresponding to the hydrolysis of the crystalline zones.[35]

Moreover, Figure 13 shows also that the decrease of the average DP of cellulose was not affected by the extraction pretreatment. These results suggest that an increase of the rate of cotton wetting created by a rolling up process of the wax, during the one hour warm up period, eliminated the effects of the decrease of wax film thickness caused by cotton extraction. Finally, Figure 13 shows that, after 15 minutes, the depolymerization rate of cellulose is still controlled by the fast rupture of the glycosidic bonds located in the amorphous regions. As a consequence, the shift in the controlling mechanism of cellulose depolymerization could be

discernable in Figures 8 and 12. On the other hand, this shift will not be observed in the experiments of hydrolysis of the most crystalline regions of cotton.

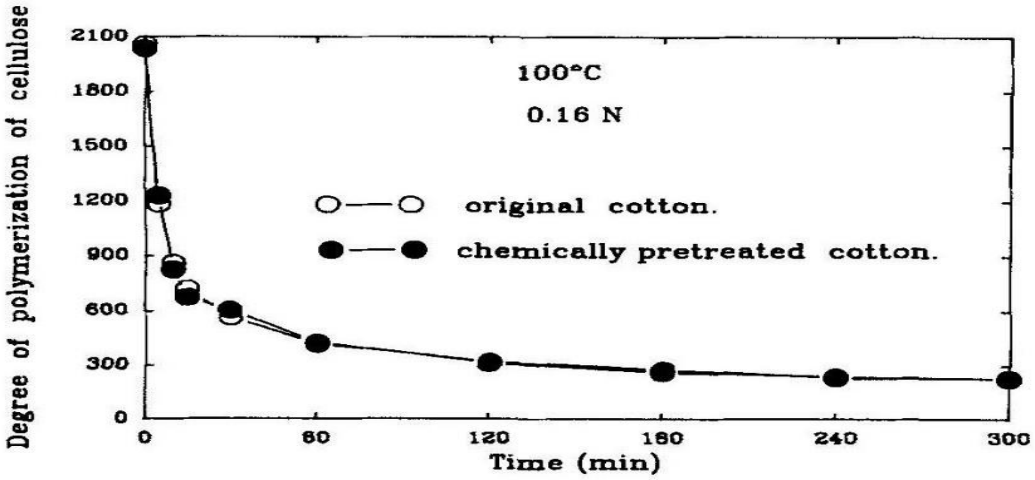


Fig. 13 – Effects of cotton extraction on cellulose depolymerization at 100° in 0.16N sulfuric acid solution (both samples were preliminarily boiled at 100° for one hour).

Effects of milling on cotton morphology

The direct effects of milling on cotton sample show that pretreatment reduced the sample particle size from large pieces (3 cm) to a powder (< 0.85 mm), but that the average degree of polymerization of the cotton sample (DP=1868) was not affected. Moreover, the TEM micrographs show that both the outer later and inside walls of the milled cotton microfibril are less dense and more disordered (Fig. 14). The changes in the ESCA C_{15} of the milled sample, presented in Figure 4 and Table 1, are related to the structural changes of the cotton outer layer caused by milling. Therefore, as shown in the TEM micrographs, the increase of the C_2 component is associated to the unravelling of the cellulose surface. [13] In agreement with Figure 14, the low value of the O/C ratio (0.19) of the milled sample, compared to the value of cellulose (0.83), indicates that the wax material is not very much broken off by milling. Furthermore, the ESCA O_{15} spectra of both original and milled cotton samples are also presented in Table 2 and Figure 4. The large changes observed in the O_0 and O_2 value suggest that these peaks are respectively related to wax material and cellulose. Moreover, the fact that the N/O ratio was not affected by milling, indicates that the nitrogen compounds are equally distributed in the primary wall of the cotton cell. Finally, as already shown in our TEM micrographs and according to the IP spectra (Fig. 6), milling had also decreased the crystallinity index (CI) of the cotton fibers from 70% to 64%.

We may conclude that, compared to cotton extraction, less wax materials are detached from the cotton fiber. However, the TEM micrographs and the IR spectra indicate that milling affects the wax layer morphology as well as cellulose crystallinity.

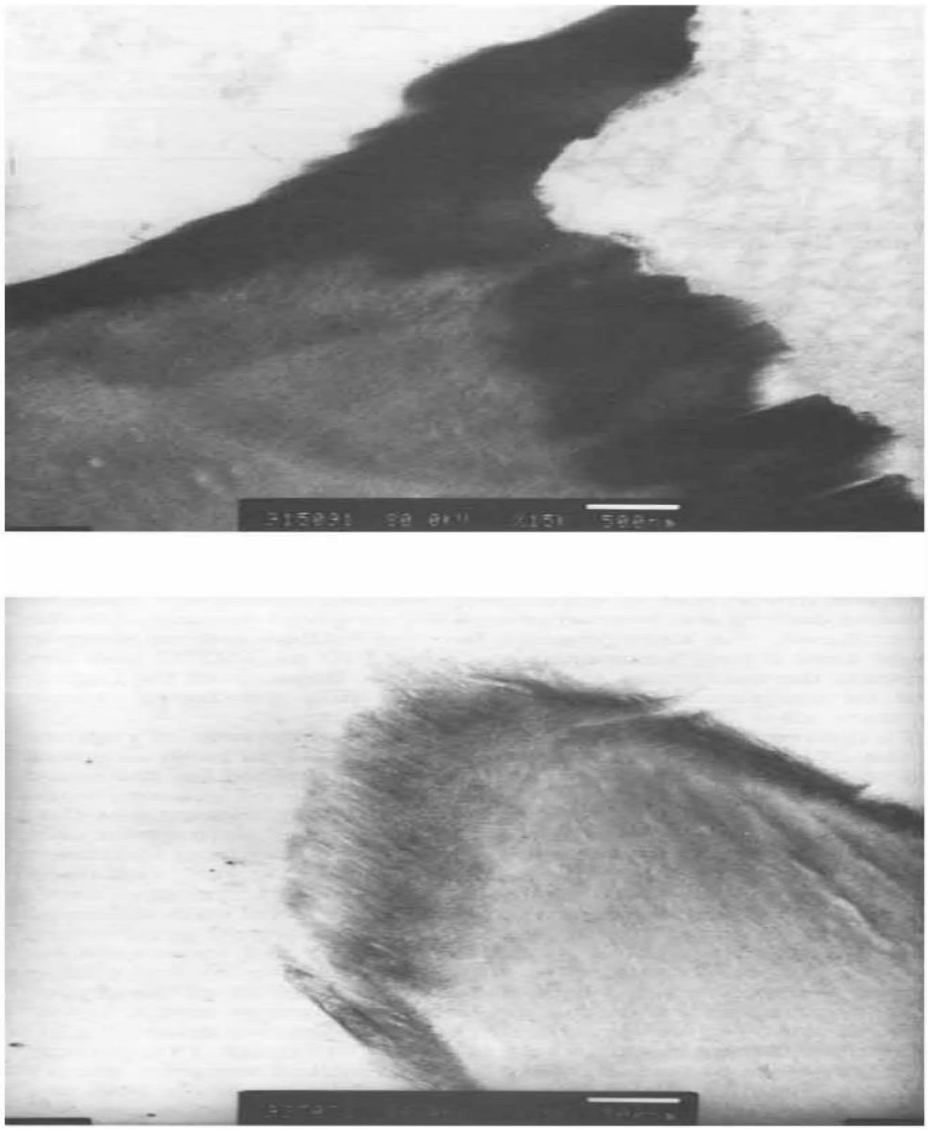


Fig. 11 – TEM micrographs of original (1) and milled (2) cotton samples

Effects of milling on cellulose depolymerization

Changes in the average degree of polymerization of cellulose, during the hydrolysis of both original and milled cotton samples, were used to investigate the influence of milling on the acid hydrolysis of cotton. The two samples were first boiled for one hour, and the experiments, conducted at 100° in 0.16N sulfuric acid solution, are reported in Figure 15

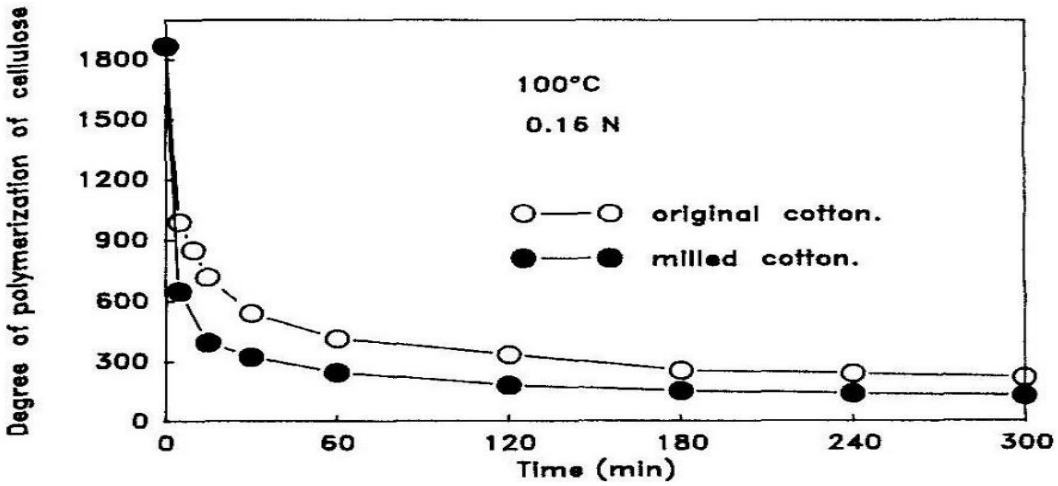


Fig. 15 – Effects of cotton milling on cellulose depolymerization during cotton hydrolysis at 100° in 0.16N sulfuric acid solution.

Unlike cotton extraction, these data show clearly that, for the same reaction conditions, cotton milling affects considerably the rate of cellulose depolymerization. Furthermore, from the fact that these experiments were conducted at temperatures higher that the cotton wax melting point, we assume that the influence of cotton wax is negligible and the effects of milling on cellulose depolymerization are principally caused by the changes in cotton morphology observed before.

TABLE 3 : Effects of milling on initial and final degradation rates of cotton fibers (from data in Fig. 15)

Stages (min)	Original Cotton			Milled Cotton			Ratio of slopes Milled/Original
	DP_0	DPf	slope (min^{-1})	DP_0	DPf	slope (min^{-1})	
0 - 5	2061	989	176	1868	648	244	1.39
180 - 420	255	200	0.16*	153	110	0.15*	1.07

*these slopes are obtained by averaging over four experimental points

These experimental data indicate clearly that the initial stages of cotton hydrolysis are enhanced by milling. Furthermore, in accordance with the IR spectra, the lower LODP value of the milled samples demonstrates that the volume of the crystalline regions of cotton is also decreased by milling. On the other hand, from the fact that the ratio of the two cellulose depolymerization rates is very close to ours (1.07) in the last degradation stages (Table 3), it may be concluded that the rate of degradation of the more resistant crystalline parts of the

cotton sample is not increased by the mechanical pretreatment. Therefore, as in these experimental conditions, the rate of rupture of the β(1,4) bonds located in the amorphous regions is increased by milling, some bonds, originally located in the crystalline regions must have been disrupted, which is in line with the decreased cotton crystallinity.

Effects of milling on the rate of glucose formation

To eliminate any resistance related to the transport of catalytic ions through the wax film, the experiments related to the effects of milling on the yield of glucose were conducted at temperatures higher than 100°. Moreover, in order to investigate the effects of milling on the rate of rupture of the glycosidic bonds with different accessibilities, these experiments were performed in a sulfuric acid solution with low acidity (0.03), compared to the experiments on cellulose depolymerization (0.16N). Furthermore, from the fact that the probability of rupture of the glycosidic bonds depends on both the reactivity and accessibility of the glycon rings. The effects of milling were investigated at different temperatures (120°C to 160°C). The yield of glucose, reported in Figures 16-18, shows that the rise in temperature increases both the initial rate of formation and the maximum yield of glucose during hydrolysis of the original sample. On the other hand, the experiments for the milled cotton sample show that rising temperature from 140° to 160° did not increase the maximum yield of glucose. Because of the higher rate of cellulose depolymerization, this maximum value appears after a shorted time at 160°C.

The slow increase of glucose concentration observed at 120° (Fig. 16) demonstrates that the rate of depolymerization of the cellulose chain molecules was low. The fact that the two curves are identical indicates that, during the reaction time, the rate of cellulose depolymerization was independent on the sample morphology. On the other hand, the experimental data obtained at 140° (Fig. 17) show that both the initial production rate and the maximum yield of glucose are increased by milling.

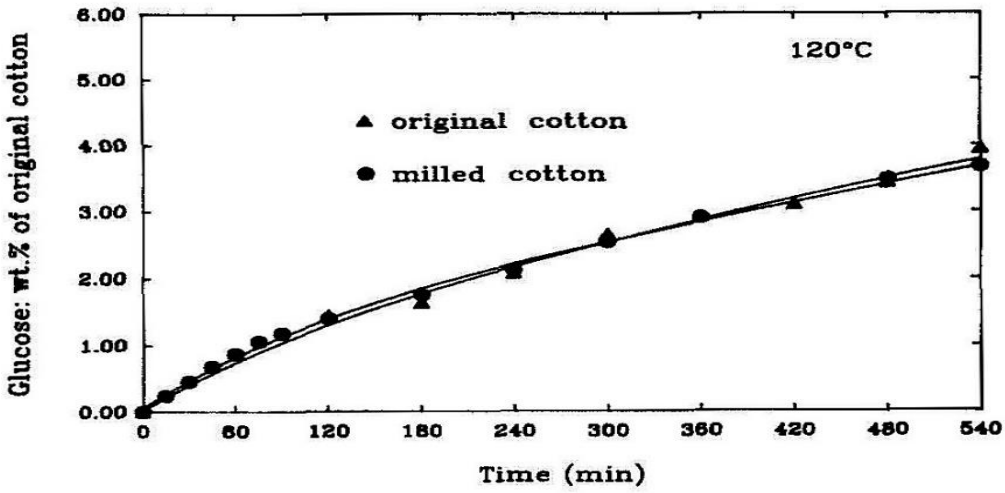


Fig. 16 - Glucose build up during cotton hydrolysis at 120° C in 0.03N sulfuric acid solution

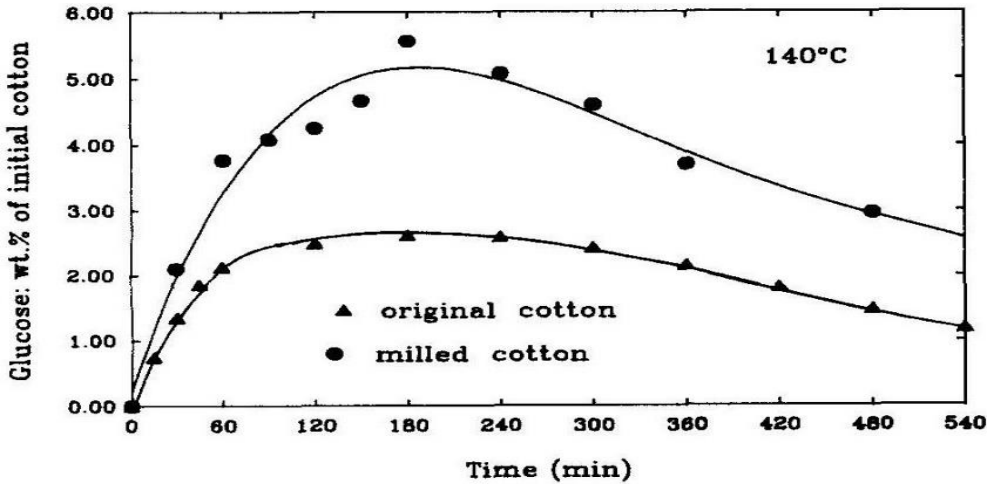


Fig. 17 – Glucose build up during cotton hydrolysis at 140° in 0.03N sulfuric acid solution

These results reflect the fact that the milled cotton sample is characterized by a higher accessibility of the glycosidic bonds located in the amorphous regions and a lower crystallinity. However, the same initial fast increase of glucose concentration observed at 160° (Fig. 18) during the hydrolysis of both the original and milled samples, shows that the initial rate of cellulose depolymerization was not affected by the changes in the morphology of cotton sample. The slightly higher maximum glucose yield could be related to the rupture of glycosidic bonds, originally located in the crystalline regions.

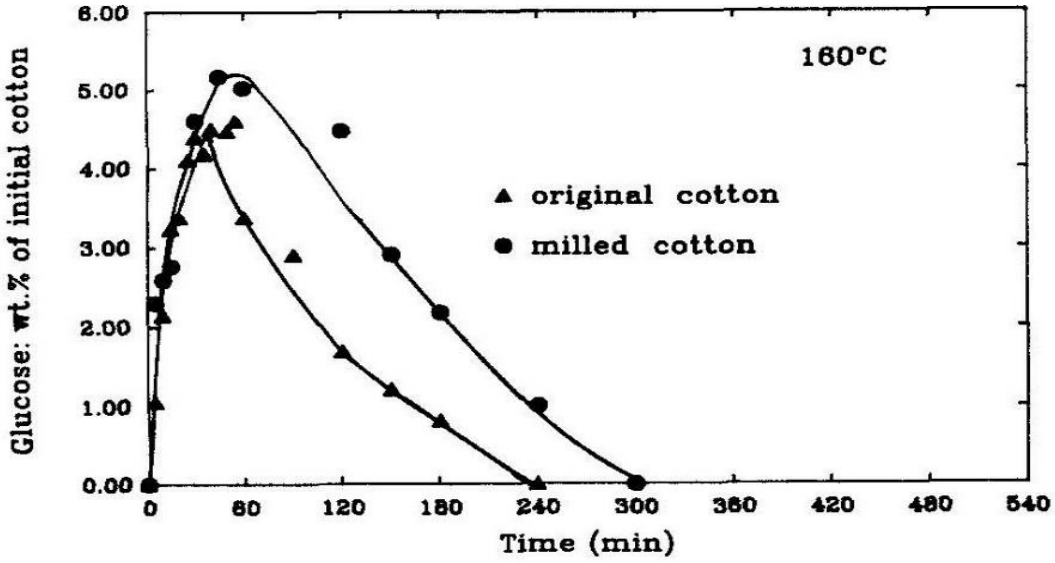


Fig. 18 – Glucose build up during cotton hydrolysis at 160° in 0.03N sulfuric acid solution

These experimental observations demonstrate that the effects of milling on the rupture of the glycosidic bonds depend on the temperature of reaction. At 120°, the reactivity of the glycosidic bonds might be low and the acid ions could then disrupt only the glycon rings in the amorphous regions which have no increased rotational energy barrier, due to interfibril hydrogen bonds and are therefore not affected by milling. As a result, the mechanical pretreatment did not affect the probability of rupture of the bonds with high accessibility. At 140°, we observe that the rise in temperature increased the probability of rupture of the glycosidic bonds of both original and milled samples. The relatively large difference in the maximum yield of glucose shows the effects of milling were significant. These results could be related to the fact that the depolymerization rate of cellulose was controlled by the accessibility of the β(1,4) bonds and the rupture of the links having some rotational energy barrier was an important step of the process. However, at 160°, we observe that milling did not affect the initial rate of glycosidic bonds rupture. This could be explained by the fact that the rupture of these bonds was increased not only by a higher reactivity of their glycon rings but also by the increase of their accessibility caused by a faster rupture of bonds with a lower rotational energy barrier. The former effect was certainly more important that the unravelling caused by milling. This behavior was also observed [25] during cotton hydrolysis in 0.1N sulfuric acid solution and 180°.

CONCLUSION

In order to eliminate the influence of the transport of the catalytic ions through the wax film on the rate of cellulose depolymerization, a study was undertaken to determine the effects of cotton extraction and boiling on the fatty acids located in the outer layer of the cotton fiber. The data show clearly that the rate of cellulose depolymerization is controlled by two different mechanisms steps, depending on the temperature of the reaction. From the fact that the shift between these two controlling regimes is located in the melting temperature range of the fatty acids of cotton, this phenomena was related to a rolling up process of the fatty acid. Therefore, wettability of the cellulosic materials plays an important role in acid hydrolysis.

It was shown that cotton extraction has no observable effects on the rate of cellulose depolymerization at temperatures higher than the melting point of the fatty acids located in the cotton outer layer. On the other hand, diffusion of the acid ions through the cotton wax layer seemed to control the cellulose depolymerization rate when the temperature is lower than the melting point of all fatty acids. Our investigation demonstrated that cotton boiling is more effective than cotton extraction in the low temperature region. Furthermore, the use of strong chemicals (ethanol, ether,...) is expensive and could also give rise to problems associated with toxic waste when the cotton materials are washed after extraction.

The experimental results showing a decrease in the average degree of polymerization of cellulose allows us to conclude that milling increases the accessibility of the glycosidic bonds located in the amorphous regions and decreases the crystalline of the cotton sample. On the other hand, data on the yield of glucose, during the hydrolysis of cellulose, show that the effects of milling on cellulose saccharification will depend on both the accessibility and the reactivity of the glycosidic bonds. At high temperatures, only the maximum yield is affected by the pretreatment, which could be more related to the decrease of the sample crystallinity. Therefore, a more severe milling is needed to increase the maximum glucose concentration.[25] On the other hand, at lower temperatures, the production of glucose is mostly affected by the loosening of the cotton sample structure. The maximum effect, observed at 140°, could be related to both the loosening of the structure of the same and to a smaller volume of the crystalline regions. Moreover, the data observed at 120° are in agreement with the fact that cellulose contains glycosidic bonds with very high accessibility.[12]

Finally, the fact that nitrogen was detected at the cotton surface and the N/O ration remains constant for all cotton samples (Table 2) suggest that nitrogen was an integral part of cellulose biosynthesis at least in the first stages of cotton growth.

APPENDIX

The degree of wetting of a solid is described as a contact angle phenomenon between a liquid and a solid. Therefore, when the contact angle is close to zero, the liquid spreads over the solid easily. On the other hand, nonwetting means that the angle is greater than 90°, so that the liquid tends to ball up and run off the surface easily.[36] With clean cotton fibers, the contact angle 0 between water and fibers surface is always small, but if they are covered with fatty acids,[14] 0 may be of the order of 150°. However, when the temperature of the system is higher than the melting point of the cotton fatty acids, the wax film is considered as a liquid expanded film and, as a consequence, the wetting of cotton fibers could be considered as a contact angle phenomenon. Therefore, when water molecules reach the cotton surface, the tendency of the liquid wax to roll up from the cotton surface could then be expressed by the surface free energy balance:

$$\Upsilon f\omega \cos\theta = \Upsilon c\omega - \Upsilon cf - \Upsilon\omega \quad (6)$$

Where θ is the contact angle, $\Upsilon f\omega$, $\Upsilon c\omega$ and Υcf are the film-water, cotton-water and cotton-film interfacial tensions, [37] respectively. For fatty acid films on water, Young'equation does not hold true and the term $\Upsilon\omega$ is added because of the entropic effect taking place in the immediate neighborhood of the hydrophobic interface.[38] Therefore, the removal of the wax material could be possible only if the different surface forces tend to reduce the free energy of the system ($\Delta G \leq 0$) or:

$$\Upsilon cf \geq \Upsilon c\omega - \Upsilon f\omega \cos\theta + \Upsilon\omega \quad (7)$$

The wax could then be removed because the cotton-wax surface tension Υcf is replaced by the smaller cotton-water surface tension $\Upsilon c\omega$.[14] Therefore, to regain the free energy balance, cos θ should decrease and, as a result, the wax will tend to roll up on the cotton surface. Alternatively, according to the definition of the work of adhesion:[36]

$$Wcf = \Upsilon f\omega (1 + \cos\theta) \quad (8)$$

We may conclude that the removal of the wax material from the cotton surface is related to the decrease of the adhesion forces caused by wax melting

NOMENCLATURE

Latin alphabet symbols
B.E = binding energy, eV
D = diffusivity, m^2s^{-1}
Δ (DP) = decrease of the average degree of polymerization, from the initial value
E = activation energy, kJ mol^{-1}
[G] = glucose concentration, $g.L^{-1}$
[H] = sulfuric acid concentration, $mol.L^{-1}$
k = mass transfer coefficient, $m.s^{-1}$
t = time, min
T = temperature, K
Wcf = work of adhesion of wax on cotton, $m^2N.m^{-2}$
x = distance in the diffusion direction, m

Greek alphabet letters
α = thermal expansion, K^{-1}
ϒ = surface and interfacial tension, $mN.m^{-1}$
θ = contact angle
δ = wax film thickness, in
π = film pressure, $mN.m^{-1}$

Subscripts
0 = initial state
c = critical conditions
cr = crystalline phase
D = diffusion
m = melted phase
w = water surface
F = final state
f = wax film surface
fw = film-water interface
cw = cotton-water interface
cf = cotton-film interface
T = selected temperature
w = water

REFERENCES

1. P. A. Richmond, Occurrence and Functions of Native Cellulose, in Haigher, C. H. AND P. J. Weimer ed. Biosynthesis and Biodegradation of Cellulose, Marcel Decker, New York, 1991, pp. 5-23.
2. M. Chang and G. T. Tsao, *Cellulose Chem. Technol*., 15, 383, (1981)
3. A. E. Humphrey, The Hydrolysis of Cellulosic Materials to Useful Products. Advances in Chemistry. ACS series, 181: 25-53. Brown, R., D. and L., Jurasek eds., Washington D. C., 1979.
4. J. F. Saeman, *Industrial and Engineering Chemistry*, 37, 43 (1945).
5. M. A. Millet, A. J. Baker and L. D. Satter, 1976. Physical and Chemical Pretreatments for Enhancing Cellulose Saccharification, Biotechnol. & Bioeng. Symp. 6: 125-153, John Wiley & Sons Publication, New York.
6. D. K. Sidiras and E. G. Koukios, *Biomass*, 19, 289, (1989).
7. L.W. Wright, *Chemtech*, 42, 40 (1974).
8. L. Segal and P. J. Wakelyn, 1985. Cotton fibers. in Lewin, M. and E. M. Pearce eds., Handbook of Fiber Science and Technology, Marcel Dekker, New York pp. 800-908.
9. P. H. Peters, Textile Chemistry: The Chemistry of Fibers. Elsevier Publishing Company Amsterdam, (1963).
10. E. I. Valko, Chemistry and Chemical Technology of Cotton, Interscience Publishers, New York, (1955).
11. R. H. Peters, Textile Chemistry: Impurities in Fibers: Purification of Fibers. Elsevier Publishing Company, New York, (1967).
12. A. Sharples, J. Polym Sci., 13, 393 (1954).
13. A. A. Ahmed. A. Adnot, J. L. Grandmaison, S. Kaliaguine and J. Doucet, *Cellulose Chem. Technol*., 21, 483 (1987).
14. J. T. Davies and E. K. Rideal, Interfacial Phenomenon, Academic Press, New York, (1961).
15. A. Ahmed, 1988, Characterization of the Liquid and Solid Products of Wood Liquefaction, *PhD. Thesis*, Département de genie chimique, Université Laval, Québec, Canada.
16. E. Sjöström, Wood Chemistry: Fundamentals and Applications, Academic Press, New York, (1981).
17. S. M. Read and D. P. Delmer, 1991, Biochemistry and Regulation of Cellulose Synthesis in Higher Plants, pp. 117-200, in Haigler C. H. and P. J. Weimer eds., Biosynthesis and Biodegradation of Cellulose, Marcel Dekker, New York.

18. A. H. Conner, B. F. Wood, C. G. Hill and J. F. Harris, 1986. Kinetic Modeling of the Saccharification of Prehydrolyzed Southern Red Oak. pp. 281-296 in R. A. Young and R. M. Rowell ed. Cellulose Structure, Modification and Hydrolysis, Wiley-Interscience Publication, New York.
19. R. L. Feller, S. B. Lee and J. Bogaard, 1986. The Kinetics of Cellulose Deterioration, Advances in Chemistry, ACS series 212:329-297, Washington D. C.
20. B. G. Ranby, *J. Polym. Sci*., 53, 131 (1975).
21. M. M. Y. Chang, Crystallite Structure of Cellulose. *J. Polym. Sci*., 12, 1349 (1974).
22. J. F. Harris, *Appl. Polym, Symp*., 28, 131 (1975).
23. M. M. Chang, T. Y. C. Chou and G. T. Tsao, *Advanced Biochem*, Eng., 20, 15 (1981).
24. E. S. Lipinsky, 1979. Perspectives on Preparation of Cellulose for Hydrolysis. Advances in Chemistry, ACS series, 181: 1 – 21 in R. D. Brown, and L., Jurasek eds., Washington D. C.
25. M. A. Millet, M. J. Effland and D. F. Caulfield, 1979. Influence of Fine Grinding on the Hydrolysis of Cellulosic Materials-Acid Vs Enzymatic. pp. 71-89 in R. D. Brown Jr. and L. Jurasek, eds., Hydrolysis of Cellulose: Mechanisms of Enzymatic and Acid Catalysis, Advances in Chemistry series 181, Washington D. C.
26. L. N. Nelson and R. T. O'Conner, 1964. *J. Appl. Polymer. Sci*., 8, 1325 (1964).
27. N. Hollen and J. Saddler, 1968, Textiles, Macmillan Company, New York.
28. P. Weiss, 1962. Adhesion and Cohesion, Elsevier Publishing Company, New York.
29. W. R. Vieth, Diffusion in and Through Polymers; Principles and applications. Hanser Publishers, New York (1991).
30. W. S. Singleton, 1983, Solutions Properties, pp. 609-678, in K. S. Markley, ed. Fatty Acids, Robert E. Krieger Publishing Company, Malabat (Florida).
31. J. Brandrup and E. 11. Immergut, 1989. Polymer Handbook, John Wiley & Sons, New York.
32. A. M. Scallan, S. Katz and D. S. Argypoulos, 1989, Conductometric Titration of Cellulose Fibers, pp. 1457-1471, in John Wiley ed. Proceedings of the 10th Cellulose Conference, Syracuse (USA).
33. M. F. Fowkes, 1967, Surface Chemistry, pp. 325-449, in R. L. Patrick, ed. Treatise on Adhesion and Adhesives: Theory, Marcel Decker, New York.
34. L. I. Osipow, 1962, Surface Chemistry: Theory and Industrial Applications, Reinhold Publishing Corporation, New York.
35. M. R. Ladish, 1989, Hydrolysis. pp. 434-453, in O. Kitani and C. W. Hall eds., Biomass Handbook. Gordon and Breach, New York.

36. A. W. Adamson, 1990, Physical Chemistry of Surfaces, Wiley Interscience, New York.
37. D. K. Chattoraj and K. S. Birdi, 1984, Absorption and the Gibbs Surface Excess, Plenum Press, New York.
38. A. L. Bailey, 1950, Melting and Solidification of Fats, Interscience Publishers, New York.

EXPERIMENTAL STUDY II: KINETIC INVESTIGATION

INTRODUCTION TO CELLULOSE ACID HYDROLYSIS

Cellulose, the major component of plant cell walls, exists as long fibers composed of smaller structural units called microfibrils. These, in turn, consist of aggregates of elementary fibrils. The models proposed to represent the structure of cellulose assume the existence of two distinctly different regions in the microfibril: one of highly-ordered cellulose molecules called the crystalline area, and the other of less ordered cellulose molecules called the amorphous area. These two zones are probably separated by regions of intermediate crystallinity (Bertran and Dale, 1986; Segal, 1971).

Since the oil crisis of the early 1970's, cellulosic material has been considered as a potential source of organic materials and fuels currently derived from petroleum fractions (Chang and Tsao, 1981; Humphrey, 1979). The objective of many research projects is to obtain the highest yield of glucose during acid hydrolysis of wood and cotton fibres (Saeman, 1945; Millet et al., 1976; Sidiras and Koukios, 1989). The glucose formed could for example be fermented to ethanol or hydrogenated into sorbitol. This last compound may be transformed into low molecular weight polyalcohols or used for the production of vitamin C (Wright, 1974).

Cellulose is a linear polysaccharide having the anhydro- cellobiose moiety as the repeating unit. This unit itself is formed by two anhydro-glucose linked by a β(1, 4) glyco-sidic bond (SjGstrom, 1981).Therefore glucose and inter- mediate oligomers are produced when catalytic agents disrupt these links. However, because of the morphology of the cel- lulosic materials, the rate of rupture of the β(1, 4) bonds is affected not only by the reactivity of the glycon rings but also by the relative ease by which they can be reached by the reactive agents (Segal, 1971; Feller et al., 1986).

Experimental results from cellulose hydrolysis demonstrate clearly that the decrease of the average degree of polymerization occurs in at least three major stages (Feller et al., 1986). According to the data presented by Sharples (1954), the first rapid stage of cellulose depolymerization represents the rupture of the bonds with high accessibility. Indeed the postulated weak bonds, which were thought to be created by inductive effects, caused by the presence of some oxi- dized groups, were not found during the study of kinetics of cellulose depolymerization (Ranby, 1961; Sharples, 1954). The following stages of the process have a smaller rate and are related to the breaking of the glycosidic bonds with lower accessibility located in the noncrystalline regions (Feller et al., 1986). The final stage of the process starts

very close to the so called levelling-off degree of polymerization (LODP) and its extremely low rate is caused by the rupture of the β(1, 4) bonds located in the crystallites (Chang, 1974).

According to Harris (1975), the accessibility of the glyco- sidic bonds is directly related to the rotational energy barrier encountered in their glycon rings flexure. Therefore, when the rate of cellulose depolymerization is controlled by the rupture of the glycosidic bonds with low accessibility, the rotational energy of the glycon rings is the limiting factor.

Indeed, the very slow degradation rate of the crystalline parts of cellulose is caused by hydrogen bonds which hold the glycon rings tightly. Therefore, during cellulose hydrolysis in dilute acid solution, the production rate of glucose decreases drastically when the rupture of the β(1, 4) bonds with very low accessibility is involved. On the other hand, in concentrated acid solutions, the quantitative saccharifica- tion of cellulose is followed by a fast degradation of the glu- cose formed into furfural and levoglucosan (Conner et al., 1986).

To overcome this rotational energy barrier, many chemical and physical pretreatments of cellulosic materials have been proposed (Chang and Tsao, 1981; Millet et al., 1976; Sidiras and Koukios, 1989). It was found that milling enhances the degradation of cellulose by loosening its structure and disrupting the durable hydrogen bonds between cellulose molecules of the crystalline areas within the microfibril or between microfibrils (Lipinsky, 1979; Millet et al., 1976). Furthermore, the work of Saeman (1945) showed that the increase of the rate of hydrolysis of milled cellulosic material is partly related to the smaller particule size of the sample.

Cotton is described as a seed hair which could contain about 96 wt% cellulose (Peters, 1967). Microfibrils of cellulose are a fundamental component of the cell walls of cotton but the process by which the 1,4-β-glucan chains are synthesized and assembled into the cellulose microfibrils of the wall remains one of the major mysteries of plant biology (Read and Delmer, 1991). It is also well known that the outer layer of cotton, covered by some organic compounds, protects the fibers from atmospheric oxydation (Peters, 1961). Waxes, resins and nitrogen-containing compounds are the principal impurities detected in this layer (Segal and Wakelyn, 1985). Cotton wax is described as a mixture of aliphatic monoalcohols in C_{28}-C_{34}, fatty acids in C_{24}-C_{34}, saturated and unsaturated hydrocarbons, resins and resin acids, sterol and sterol glucosides (Valko, 1955). Because of its low surface energy, the wax material could represent a resistance to cotton wettability and decrease considerably the rate of cellulose hydrolysis. However, from the fact that wax is not an integral part of the cotton cell, many extraction techniques are used for the purifi- cation of the fibres (Peters, 1967). For example, for the hydrol- ysis of egyptian cotton at 50°C in 0.1N sulfuric acid solution, fibres were first purified by extraction with boiling alcohol and ether (Sharples, 1954). The ESCA

analysis, presented by Ahmed et al., (1987), indicate that cotton wax is not completely removed even after drastic treatments. On the other hand, Peters (1967) reported that if cotton is immersed in hot water (97-99°C) for 15 minutes and air dried at 20°C, it becomes wettable. This suggests that wax material melts when immersed in hot water and rolls up into droplets on the cotton surface which remains as such if the fiber is then dried at 20°C. Moreover, the high temperature coefficient of detergency is partly associated with the melting of some wax materials (Davies and Rideal, 1961). Finally, grinding was found to detach some wax from cellulosic materials (Ahmed, 1988).

The overall objective of the present work is to model the kinetic behaviour of cellulose during hydrolysis by means of stochastic simulation. Part I of this communication will thus report the experimental determination of kinetic parameters to be used in the simulation. These were established from kinetic experiments on cellobiose hydrolysis and glucose degradation. Furthermore, both cotton morphology and outer layer are analysed and the effects of cotton wax on cellulose depolymerization are studied. Finally, the effects of cotton milling on both cellulose depolymerization and glucose yield are investigated and presented in this first part. Part II will deal more specifically with the stochastic modelling of these data. This simulation should be realistic enough to allow a representation of the effect of milling on the cellulose structure and its influence on acid hydrolysis kinetics.

EXPERIMENTAL RESULTS AND DISCUSSION

Glucose Degradation

The experiments of glucose degradation and hydrolysis of cellobiose in dilute sulfuric acid solution are performed at different temperatures in order to provide the respective pseudofirst-order rate constants and activation energies. A mathematical simulation of glucose build up during cellobiose hydrolysis is presented and the activation energy of the simulated glucose degradation is compared to its experimental value.

The second objective of this part of the work is to study both the effects of wax material on the depolymerization of cellulose and the influence of milling on cellulose depolymerization and glucose build up during dilute sulfuric acid hydrolysis of cotton. The presence of wax in the cotton outer layer is first investigated using TEM micrographs and ESCA analysis. Therefore the decrease of the average degree of polymerization (DP) during hydrolysis of both original and extracted cotton samples is measured in order to study the effects of cotton wax on cellulose depolymerization.

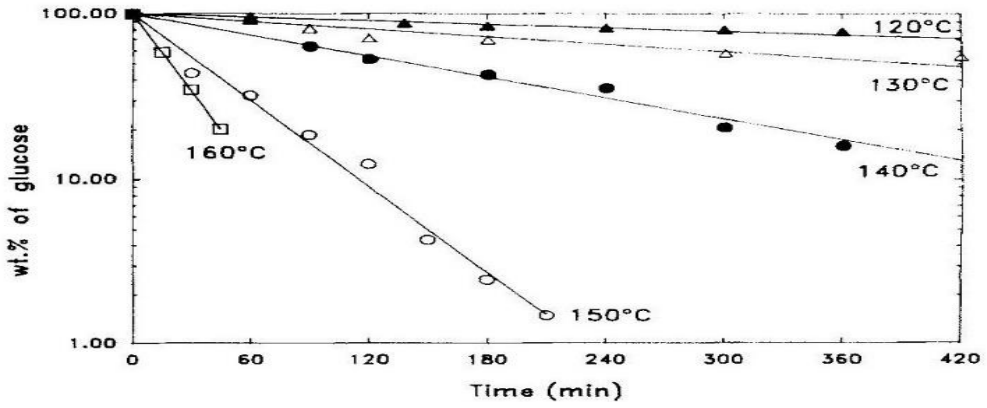


Figure 1 –Pseudo first-order kinetics for glucose degradation in sulfuric acid solution (0.03 N).

To illustrate the direct effect of milling on the morphology of the cotton sample, the crystallinity index (CI) and TEM micrographs analysis of both original and milled samples are presented. The interface of both samples is also investigated by ESCA C_{15} spectra, C/O and N/O ratios. Therefore the effects of milling on the cellulose hydrolysis process is investigated using the decrease of the average degree of polymerization (DP) as a function of time for both samples. Finally, the influence of milling on the net production of glucose, as a function of time, is studied at different temperatures.

This reaction was carried out in the temperature range from 120 to 160°C. The initial glucose concentration was varied from 5.0 to 6.0 g/L and the sulfuric acid Concentration was kept constant (0.03 N) during all the experiments. The kinetic data shown in Figure 1 indicate that the concentration of glucose follows a pseudo first-order time dependence:

$[G] = [G]_0 \exp(-k'_3 t)$ …… (1)

The rate constants k'_3 were determined by linear least square regression analysis and the corresponding values of second order rate constant k_D were calculated as follows:

$k_D = k'_3 / [H^+]$ ……(2)

The experimental values of the dissociation constant for the bisulfate ion at temperatures in the range 120 o 160°C, necessary to estimate actual proton concentration are those given by Lietzke (Lietzke et al., 1961). Figure 2 shows that the rate constant k_D follows Arrhenius law from which the experimental activation energy k_D = 140.7 kJ/mol and the preexponential factor $2.62 \cdot 10^{17}$ $(min \cdot mol/L)^{-1}$ are obtained.

The values of the activation energy reported in the literature are in the range 136 - 144 kJ/mol (Bienkowski et al., 1987). High pressure liquid chromatography (HPLC) results did show the presence of a minor peak of an unidentified saccharide when the temperature exceeded

140°C. As it appeared for a short period of time, this peak could be a reverse reaction product. Enolization of glucose to fructose and mannose and its polymerization to di- and oligosaccharides were observed elsewhere at temperatures higher than 180°C (Smith et al., 1982).

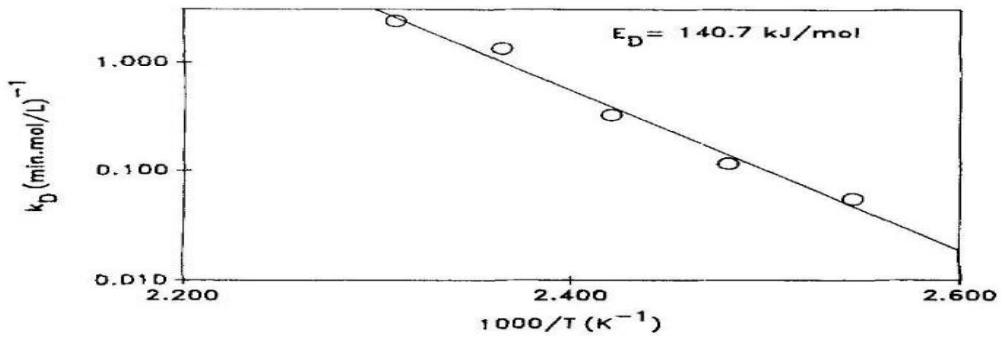


Figure 2 — Arrhenius plot for glucose degradation in sulfuric acid solution.

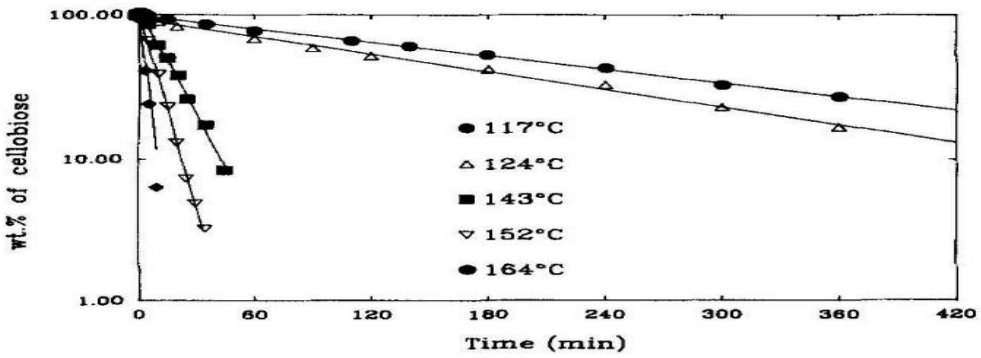


Figure 3 — Pseudofirst-order kinetics for cellobiose hydrolysis in sulfuric acid solution (0.03 N).

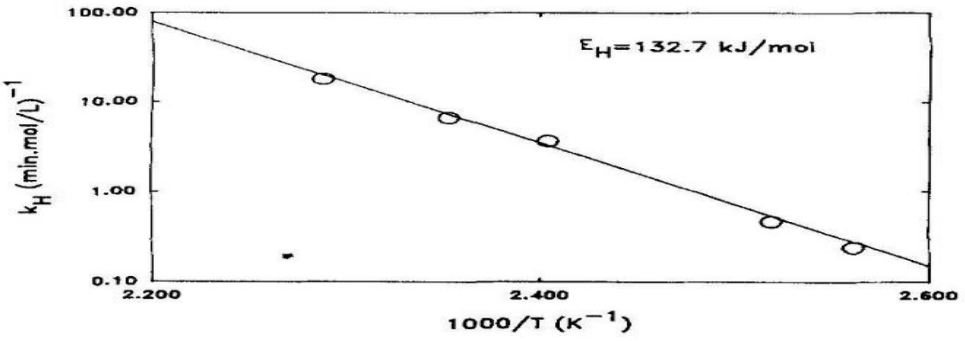


Figure 4 - Arrhenius plot for cellobiose hydrolysis in sulfuric acid solution.

Cellobiose Hydrolysis

Experiments of cellobiose hydrolysis were conducted in a 0.03 N sulfuric acid solution at temperatures ranging from 117 to 165°C and the initial concentration of cellobiose between 5.0 and 6.0 g/L was used. The disappearance of cellobiose obeys pseudofirst-order kinetics (Figure 3):

$$[C] = [C]_0 \exp(-k'_2 t) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

A deviation from these kinetics would have indicated the occurrence of direct cellobiose hydrothermal degradation (Bobleter and Bonn, 1983). The corresponding second order rate constants k are related to the acid proton concentration by the relation:

$$k_H = k'_2 / [H^+] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

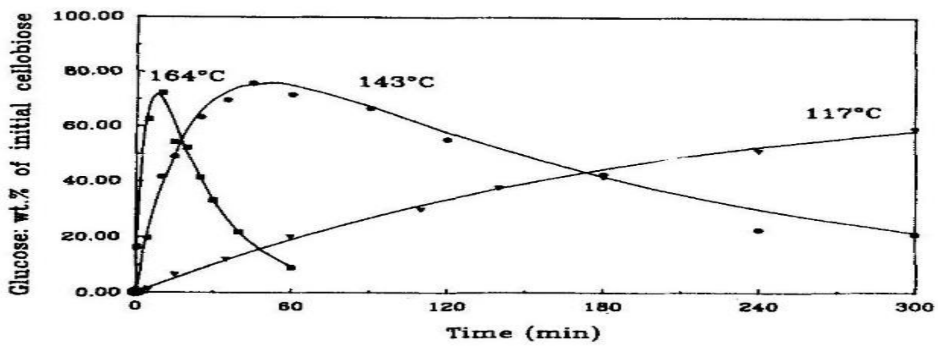


Figure 5 — Experimental glucose build up in cellobiose hydrolysis (0.03 N sulfuric acid).

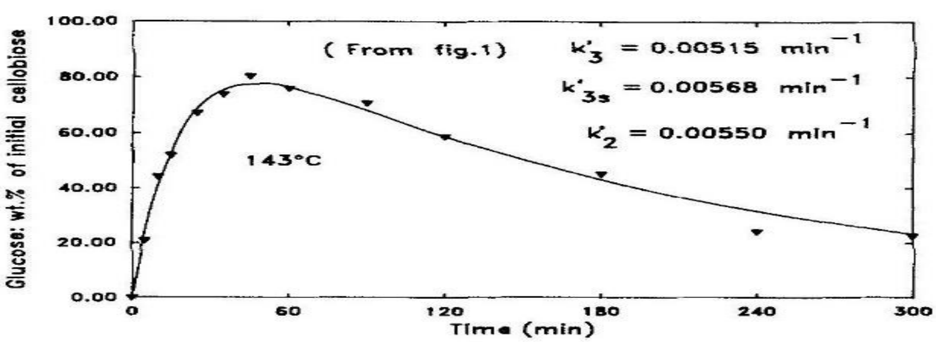


Figure 6 - Mathematical modeling of glucose build up in cellobiose hydrolysis (0.01 N sulfuric acid).

From the Arrhenius plot shown in Figure 4, both the preexponential factor $7.7 \cdot 10^{16}$ (min - mol/L)$^{-1}$ and the observed activation energy E_H = 132.7 kJ/mol are obtained. The value of the activation energy is in the range (124-138 kJ/mol) obtained in other works (Pinto and Kaliaguine, 1991).

Glucose build up during cellobiose hydrolysis

The glucose concentration in the reactor was also measured and our results show that the maximum yield of glucose is obtained at 143°C where 78% of cellobiose was converted to glucose, (Figure 5). Furthermore, for each temperature, the simulated rate constant of glucose degradation k'_3s, was estimated by mathematical fitting of the experimental data of glucose build up, using the following equation, (Figure 6):

$$[G] = [\,[G]_0\, k'_2 / (k'_2 - k'_3)]\, [\exp(-k'_3\, t) - \exp(-k'_2\, t)] \quad \ldots\ldots (5)$$

where k'_2 is the experimental rate constant for the hydrolysis of cellobiose. The SAS software employing a weighted non linear least-squares method was used for this curve fitting. At temperatures higher than **143°C,** a **small and broad peak** of some unidentified saccharides of **higher** molar **mass** than cellobiose was detected in the hplc analysis. These products could be related to glucose reverse reactions (Smith et al., 1982). However, since this peak was more important than the one observed during glucose degradation experiments, it might suggest a formation of **glycosidic links** that could also be formed by a dehydration process between the glucose produced and the reducing ends of cellobiose molecules.

As shown in Figure 6**,** the later reaction could explain the necessary increase of the rate constant of glucose degradation used for the simulation k'_3s = 0.00568 min^{-1}), compared to the one obtained from glucose degradation experiments (k'_3 = 0.00515 min^{-1}). However, Figure 7 shows that this increase did not affect sensitively the Arrhenius plots related to the rate constants of glucose degradation derived either from the fitting of Equation (5) or from experiments conducted with pure glucose (Figure 2).

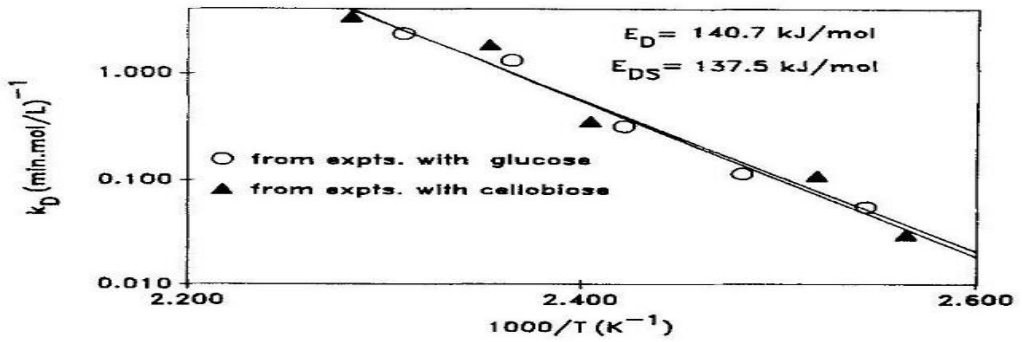


Figure 7 - Arrhenius plot for experimental and simulated values of the pseudofirst-order constant k_D **.**

Cellulose saccharification

Chinese white cotton fibers were obtained from the “Centre des technologies textiles, Conseil national de larecherche scientifique, Ste-Hyacinthe, Qukbec, Canada”. As shown in the TEM micrographs (Figure 8) cotton microfiber is a single cell with a central canal (lumen) running throughout its length. The hair is covered with a dark thin layer of tightly molded material (cuticle). Inside this come respectively the primary and secondary walls (Hollen and Saddler, 1968). First, the fiber grows to almost full length as a hollow tube through which nourishment travels. When the plant matures, the dry protoplasm becomes an empty canal (lumen) and the dried residues (minor amounts of protein and salts) either as solid deposits or as a thin layer on the lumen wall give the characteristic dark areas observed in the TEM micrographs (Segal and Wakelyn, 1985). Peters (1967) reported that the major impurities are proteins (14%) and wax material (8%) which are located in the cuticle and primary wall. On the other hand 99 wt% (on dry basis) of the secondary wall of cotton is pure cellulose. In agreement with this, the ESCA C_{1s} spectra, shown in Figure 9 and the N/O and O/C ratios, presented in Tables 1 and 2, indicate clearly that the surface of cotton fibre is covered with some noncellulosic compounds.

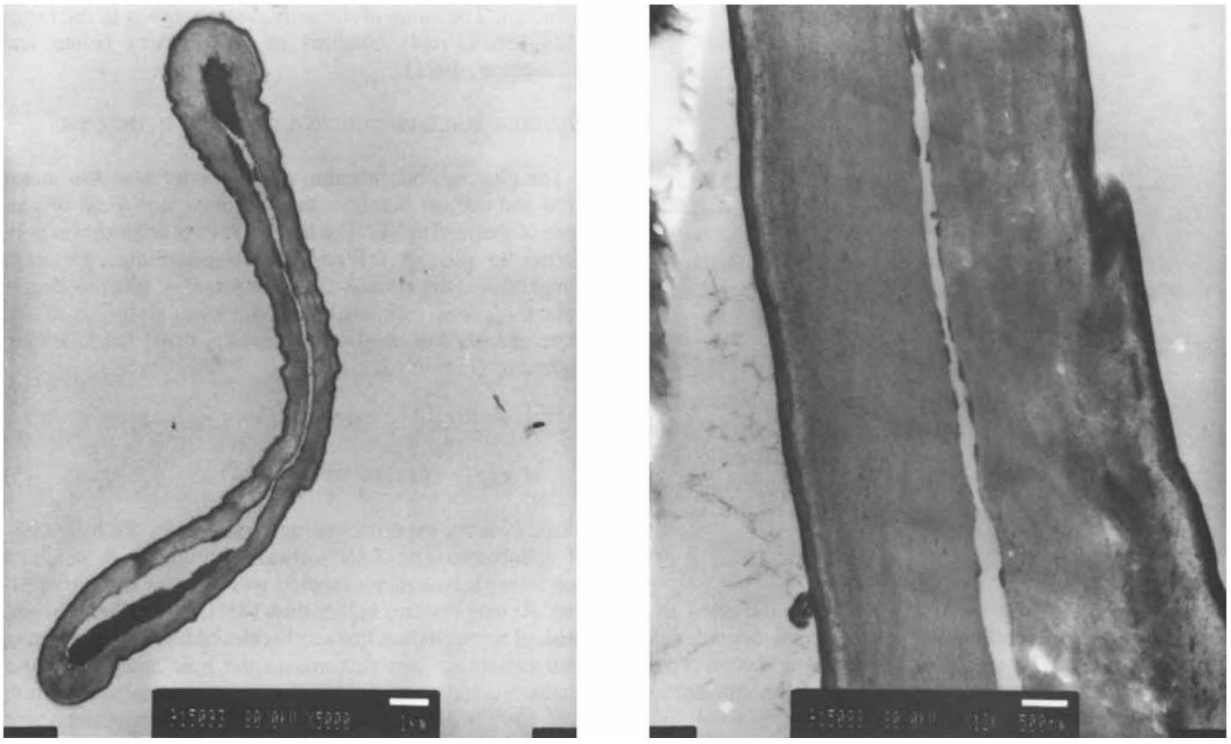


Figure 8 — TEM micrographs of cotton cell. Left: cross-section of cotton cell. Right: cross section of a portion of a cotton cell.

The high C_1 fraction (93.1 %) is consistent with the large number of carbons in long chain

monoalcohols and monoacids. Therefore the small percentage of C_2 (5.7%) and C_3 (1.2%) are entirely different from the composition C_2 (83%), C_3 (17%) of cellulose. This drastic difference is also apparent in the O/C ratio of cotton (0.08) compared to the value of pure cellulose (0.83). Finally a small percentage of protein, as nitrogen-compound, was also detected at the cotton surface (N/O = 0.09). Effects of wax on cellulose depolymerization During cotton hydrolysis, the accessibility of the β(1, 4) glycosidic bonds by the reactive ions depends on the wettability of cellulose fibres. The hydrophilic surface character of cotton is confirmed by many authors but, as they are covered with wax materials, cotton fibres behave like a "low-energy surface" (Weiss, 1962; Peters, 1967). Consequently, water forms droplets on the surface of fibres and the rate of cotton wetting is considerably lowered (Valko, 1955; Weiss, 1962). On the other hand, the experimental data of cotton hydrolysis in 0.16 N sulfuric acid solution show that the decrease of the average degree of polymerization of cellulose was not affected by the pretreatment (Figure 10). These experimental results indicate that the wax material, located at the outer layer, did not have observable effects on the process. From the fact that the temperature used in our experiments (100°C) was higher than the melting point of the fatty acids (80°C) (Peters, 1961), these results could be explained by a melting process of the cotton wax.

In the crystal-melt transition, the increase of the wax volume, caused by a large thermal expansion, is important (Singleton, 1983) and the resulting decrease of the wax surface tension could be described by the following equations (Brandrup and Immergut, 1989):

$$(d\gamma/dT)_m = (\alpha_m / \alpha_{cr})\,(d\gamma/dT)_{cr} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where α_m and α_c are, respectively, the thermal expansion for the melted and crystalline wax material. The effects of temperature in the crystalline region are described by:

$$(d\gamma/dT)_{cr} = (11/9)\,(\gamma_0/T_0)\,(1 - T/T_c)^{2/9} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Where γ_0 and T_c are, respectively, the wax surface tension at 0 K and the wax critical temperature (K). Furthermore the data presented by Singleton (1983) show that all the saturated fatty acids, when spread on the surface of distillated water at 20°C, exhibit essentially similar behaviour with respect to the compressibility of their films.

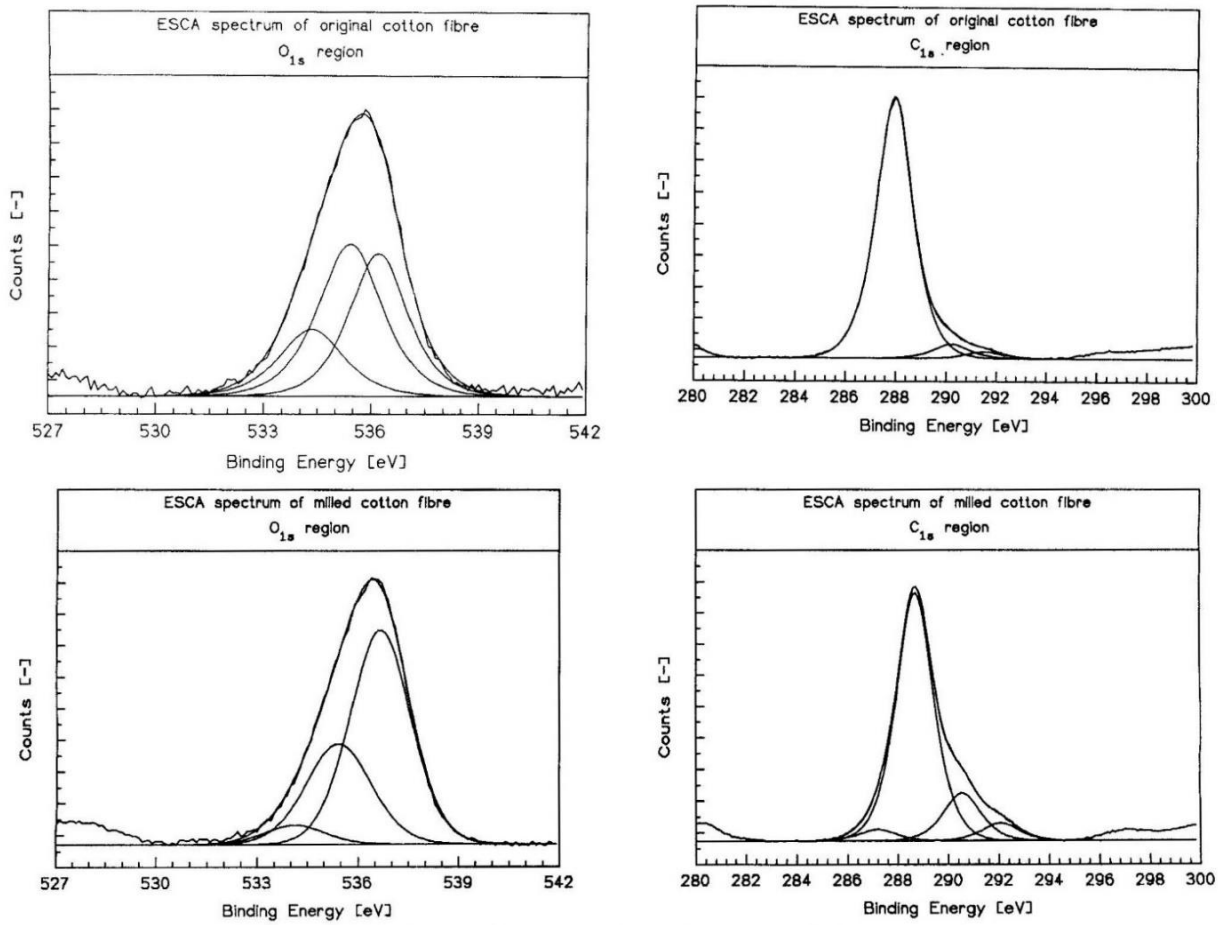


Figure 9 — ESCA spectra for: top - original and bottom - milled cotton samples.

TABLE 1
Surface Analysis of C_{1s} Spectra by ESCA Technique of (1) Original and (2) Milled Samples

Sample	O/C	E_c (eV)	C_{1s} binding energy (eV)				C_{1s} (% Area)			
			C_0	C_1	C_2	C_3	C_0	C_1	C_2	C_3
(1)	0.08	3.0	—	285.0	287.3	288.5	—	93.1	5.7	1.2
(2)	0.19	3.5	283.1	285.2	287.1	288.6	1.5	78.3	15.1	5.1

*O_{1s} peak of cellulose (533.2 eV) was used as reference point for the determination of the C_{1s} peaks (Ahmed, 1988).

TABLE 2
Surface Analysis of O_{1s} Spectra by ESCA Technique of (1) Original and (2) Milled Samples

Sample	N/O	E_c (eV)	O_{1s} binding energy (eV)			O_{1s} (% Area)		
			O_0	O_1	O_2	O_0	O_1	O_2
(1)	0.09	3.0	531.1	532.2	533.2	13.8	35.8	50.4
(2)	0.08	3.5	530.6	531.8	533.2	2.4	25.2	72.4

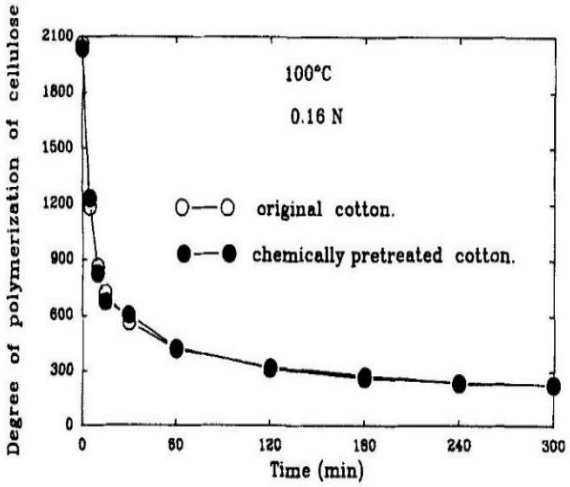


Figure 10 — Effect of wax extraction on cellulose depolymerization during cotton hydrolysis at 100°C in 0.16 N sulfuric acid solution.

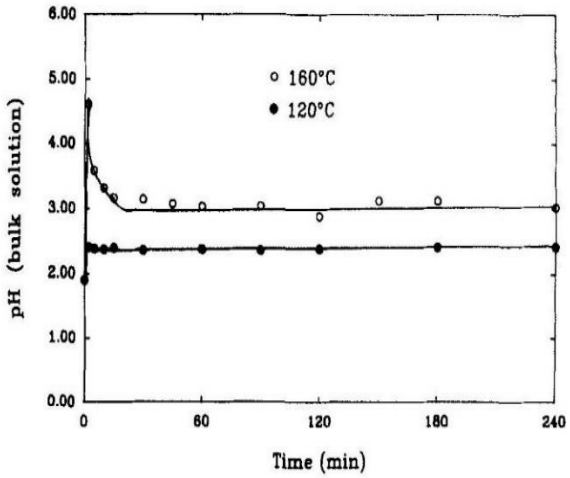


Figure 11 — pH of bulk solution during cotton acid hydrolysis.

This behavior illustrated by the force-area curve shows that, when the area occupied per molecule is lower than $21 \cdot 10^{-16}$ cm², the compressing force increases practically linearly with decreasing area up to the point at which the film collapse due to piling u of the molecules of the film. From the fact that $21 \cdot 10^{-16}$ cm² is the area of the cross section of the CH_2 group determined by other methods, the author concluded that the molecules of fatty acids are oriented and could be subject to mechanical compression. Moreover, the immersed polar groups (COOH) are also found to attract water molecules. In agreement with these results, Peters (1967) reported that the spreading coefficient of water on an oily film increases by decreasing the surface tension of the wax materials. Therefore, we may conclude that the decrease of the film-water interface free energy Υ_{fw}, caused by lowering of the wax surface tension results in attracting both the fatty acid chains and water molecules at this interface. Moreover, during wax melting, the smaller remaining solid islands of the expanded film are separated by an increased number of water molecules (Fowkes, 1967). The resulting film pressure (π), caused by the difference between the surface tensions of pure water and the film will tend to disrupt the film (Osipow, 1962):

$$\pi = \Upsilon_w - \Upsilon_f \quad \text{.....(8)}$$

As a consequence, water molecules will reach the cotton surface and, according to Young's equation (Appendix), water could easily displace the wax material from the cotton fibres because the large cotton-film interface free energy (Υ_{cf}) is replaced by a smaller cotton-water interface free energy (Υ_{cw}) (Davies and Rideal, 1961). The experimental data of Figure 10 could then be explained by the fact that, during the warm up period and the reaction time, the wax material was removed from the cotton surface by a rolling up process (Dadach and

Kaliaguine, 1993) and, as a result, the rate of cotton wetting was considerably increased. Finally, during cellulose depolymerization, the negative charge, arising from the (COOH) groups of the fatty acids, could have caused an unequal distribution of the catalytic ions between the film and the solution (Conner et al., 1986; Scallan et al., 1989).This could cause the increase of pH in the bulk solution detected during the experiments (Figure 11).

Effects of milling on cotton morphology

The direct effects of milling on a cotton sample show that the pretreatment reduced the sample particle size from large pieces (3 cm) to a powder (< 0.85 mm) but the average degree of polymerization of the cotton sample (DP = 2200) was not affected. Moreover, the TEM micrographs show that both the outer layer and the inside walls of the milled cotton microfibril are less dense and more disordered (Figure 12). The changes in the ESCA C_{1s} of the milled sample, presented in Figure 9 and Table 1, are related to the structural changes of the cotton outer layer caused by milling. Therefore, as shown in the TEM micrographs, the increase of the C_2, component is associated to the unravelling of the cellulose surface (Ahmed et al., 1987). In agreement with the TEM pictures of Figure 12, the low value of the O/C ratio (0.19) of the milled sample, compared to the value of cellulose (0.83), indicates that the wax material is not very much disrupted by milling. However, as indicated before, the presence of the wax will not cause major effects on cellulose depolymerization process when the temperature is higher than the wax melting point. Furthermore, the ESCA O_{1s}, spectra of both original and milled cotton samples are presented in Table 2 and Figure 9. The large change observed in the O_0 and O_2 values suggest that these peaks are respectively related to wax material and cellulose. Moreover, the fact that the N/O ratio was not affected by milling, indicates that the nitrogen compounds are equally distributed in the primary wall of the cotton cell. Finally, as already shown in our TEM micrographs and according to the IR spectra, milling had also decreased the crystallinity index (CI) of the cotton fibres from 79% to 64% (Figure 13).

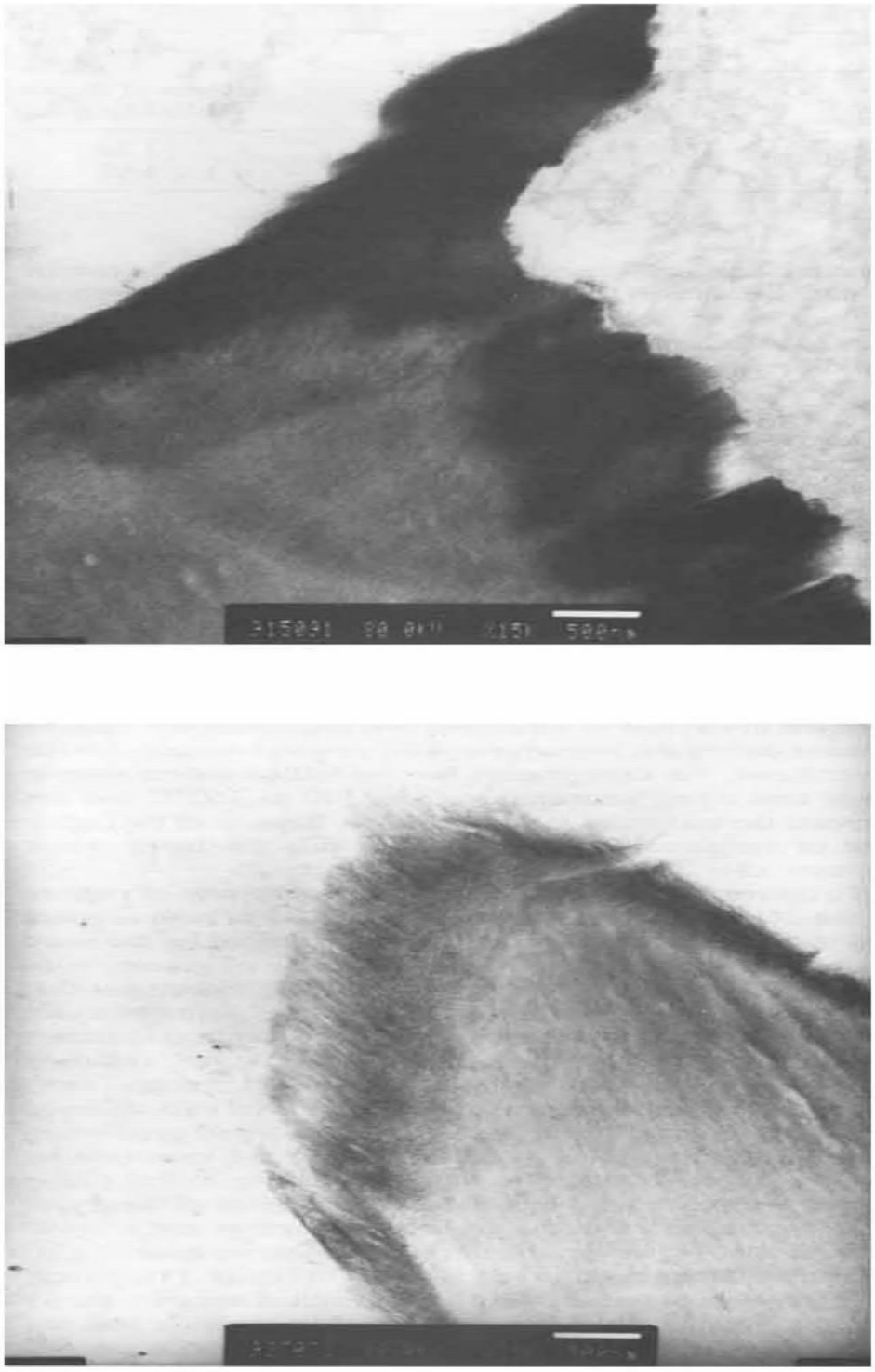


Figure 12 – TEM micrographs of: original (top) and milled (bottom) cotton samples.

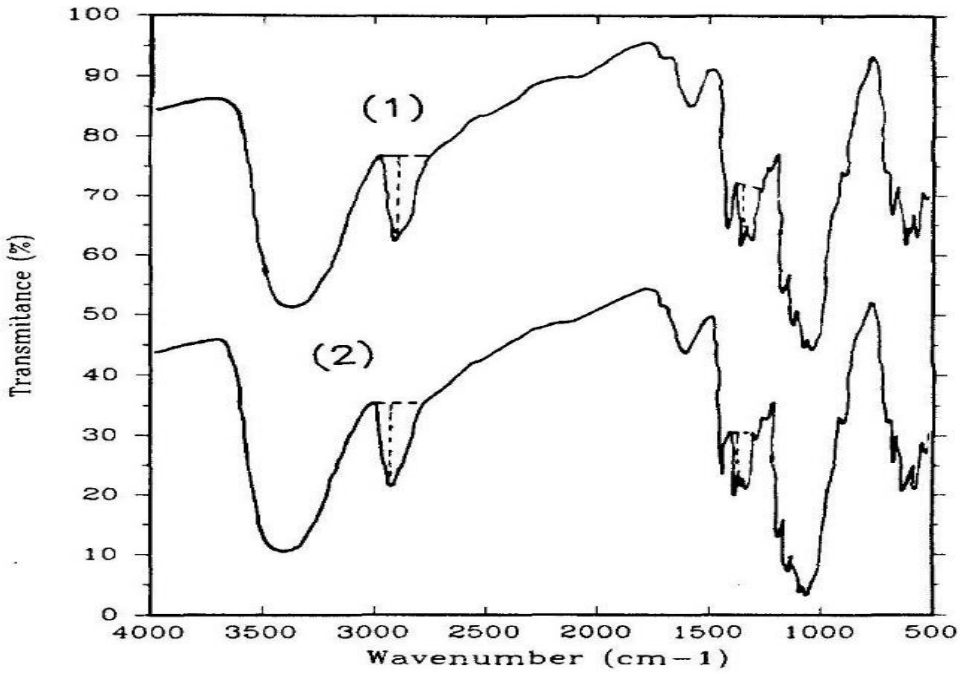


Figure 13 — IR spectra of (1) original and (2) milled cotton samples.

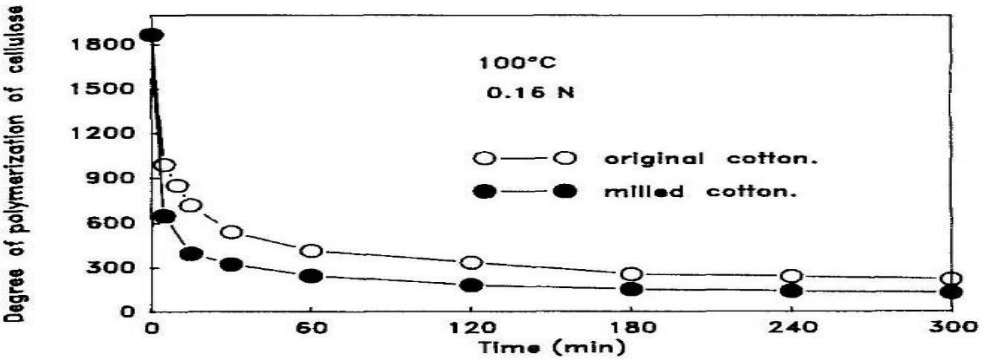


Figure 14 — Effects of milling on cellulose depolymerization during cotton hydrolysis at 100°C in 0.16 N sulfuric acid solution.

Effects of milling on cellulose depolymerization

Changes in the average degree of polymerization of cellulose, during the hydrolysis of both original and milled cotton samples, were used to investigate the influence of milling on the acid hydrolysis kinetics (Figure 14). The results of experiments conducted at 100°C in 0.16 N sulfuric acid solution, show that the degradation process is characterized by an initial rapid stage related to the hydrolysis of the completely amorphous areas and a final stage of persistent DP corresponding to the hydrolysis of the crystalline zones (Ladish, 1989). As shown in Table 3, the ratio between the two initial rates of DP decrease (1.39) indicates that the initial depolymerization rate of cellulose is enhanced by the treatment. On the other hand,

the decrease of the same ratio (1.07) suggests that milling does not affect significantly the last stages of the process. Therefore the rate of degradation of the more resistant crystalline parts of the cotton sample does not seem to be increased by the mechanical pretreatment. However, in accordance with the IR spectra, the lower LODP value of the milled sample demonstrates clearly that the volume of the crystalline regions is decreased by milling. Therefore from Figure 14, we may conclude that, in these experimental conditions, the rate of rupture of the β(1,4) bonds, located in the amorphous regions, is increased by milling and some bonds, originally located in the crystalline regions, were disrupted, in line with the decreased cotton crystallinity.

Effects of milling on the yield of glucose

In order to investigate the effects of milling on the rate of rupture of glycosidic bonds with different accessibilities, experiments of cotton saccharification were performed in a sulfuric acid solution with a lower acidity (0.03 N), compared to the experiments of cellulose depolymerization. Furthermore, from the fact that the probability of rupture of the glycosidic bonds depends on the relative competition between the reactivity and the accessibility of the glycon rings, the effects of milling were investigated at different temperatures (120°C to 160°C). The yield of glucose, presented in Figures 15-17, shows that the rise in temperature increases both the initial rate of formation and the maximum yield of glucose during the hydrolysis of the original sample. On the other hand, the experiments for the milled cotton sample show that rising temperature from 140 to 160°C did not increase the maximum yield of glucose. Because of the higher rate of cellulose depolymerization, this maximum value appears after a shorter time.

TABLE 3
Effects of Milling on Initial and Final Degradation Rates of Cotton Fibres

	Original cotton			Milled cotton			
Stages (min)	DPi	DPf	Slope (min^{-1})	DPi	DPf	Slope (min^{-1})	Ratio of slopes Milled/Original
0–5	1868	989	176	1868	648	244	1.39
180–420	255	200	0.16*	153	110	0.15*	1.07

*These slopes are obtained by averaging over four experimental points.

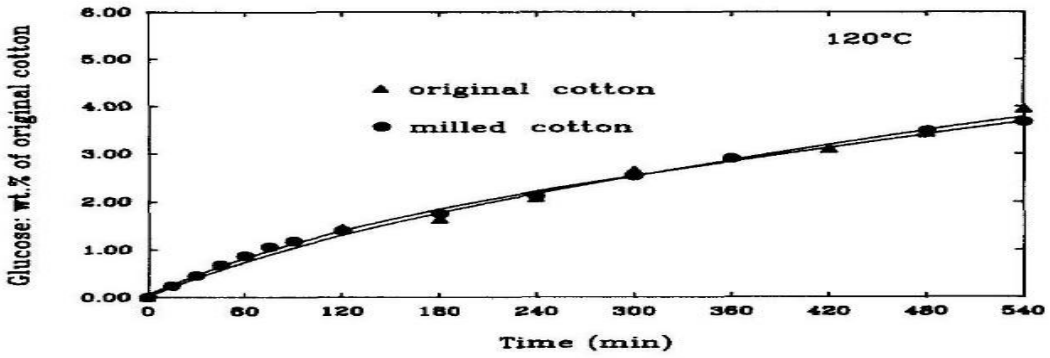


Figure 15 — Glucose build up during cotton hydrolysis at 120°C in 0.03 N sulfuric acid solution.

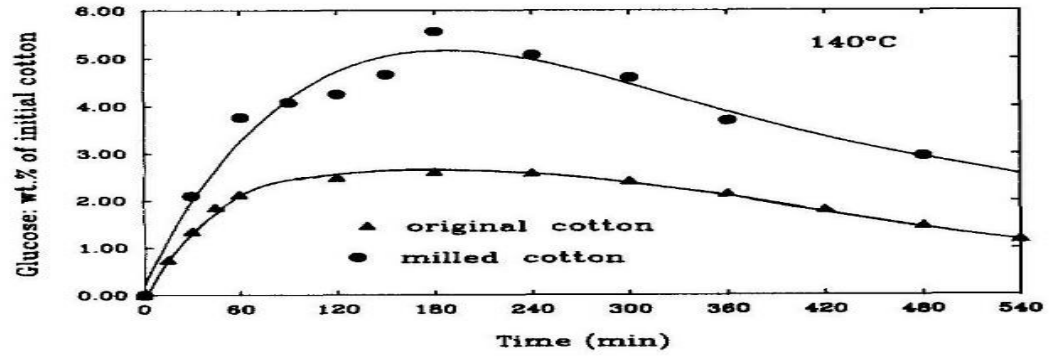


Figure 16 — Glucose build up during cotton hydrolysis at 140°C in 0.3 N sulfuric acid solution.

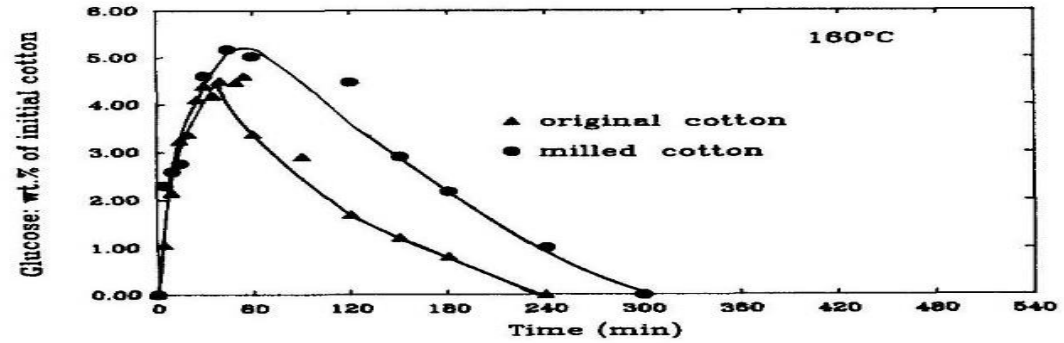


Figure 17 — Glucose build up during cotton hydrolysis at 160°C in 0.03 N sulfuric acid solution.

To determine the effects of milling on the rate of rupture of the β(1, 4) bonds, the experimental data of both original and milled samples are presented and compared for the same temperature. Therefore, the slow increase of glucose concentration observed at 120°C (Figure 15) demonstrates that the rate of depolymerization of the cellulose chain molecules was low. The fact that the two curves are identical indicates that, during the reaction time, the rate of cellulose depolymerization was independent of the sample morphology. On the other hand, the experimental data obtained at 140°C (Figure 16) show that both the initial production rate and the maximum yield of glucose are increased by milling. These results

reflect the fact that the milled cotton sample is characterized by a higher accessibility of the glycosidic bonds located in the amorphous regions and a lower crystallinity. However, the same initial fast increase of glucose concentration observed at 160°C (Figure 17), during the hydrolysis of both the original and milled samples, shows that the initial rate of cellulose depolymerization was not affected by the changes in the morphology of cotton sample. The slightly higher maximum glucose yield could be related to the rupture of glycosidic bonds, originally located in the crystalline regions.

These experimental observations demonstrate that the effects of milling on the rupture of the glycosidic bonds depend on the temperature of the reaction. At 120°C, the reactivity of the glycosidic bonds might be low and the acid ions could then disrupt only the glycon rings in the amorphous regions which have no increased rotational energy barrier due to interfibril hydrogen bonds and are therefore not affected by milling. As a result the mechanical pretreatment did not affect the probability of rupture of the bonds with high accessibility. At 140°C, we observe that the rise in the temperature increased the probability of rupture of the glycosidic bonds of both original and milled samples. The relatively large difference in the maximum yield of glucose shows that the effects of milling were important. These results could be related to the fact that the depolymerization rate of cellulose was controlled by the accessibility of the β(1, 4) bonds and the rupture of the links having some rotational energy barrier was an important step of the process. However at 160°C, we observe that milling did not affect the initial rate of glycosidic bonds rupture. This could be explained by the fact that the rupture of these bonds was increased not only by a higher reactivity of their glycon rings but also by the increase of their accessibility caused by a faster rupture of bonds with a lower rotational energy barrier. The former effect was certainly more important than the unravelling caused by milling. This behaviour was also observed during cotton hydrolysis in 0.1 N sulfuric acid solution and 180°C. The data presented by Millet et al. (1976) show that the maximum yield of glucose is increased and appears after a longer reaction time when the time of ball milling is increased but the initial rate of glucose production does not seem to be affected by the pretreatment. As a consequence, the probability of rupture of the β(1, 4) bonds was not controlled by their rotational energy barrier and the small increase of the maximum yield of glucose could be caused by the rupture of some bonds originally located in the crystalline areas of the sample.

CONCLUSION

Because of their fundamental importance in cellulose saccharification, the acid hydrolysis of cellobiose and the degradation of glucose were both investigated. Their respective pseudofirst-order rate constants were successfully used to simulate the glucose build up during cellobiose hydrolysis.

A study was undertaken to determine the effects of the wax material, located in the outer layer of the cotton microfibril, on the depolymerization of cellulose. The data show that the presence of the wax had no observable effects on the process. Our analysis demonstrates that, during the warm-up period, a removal of the wax material was caused by a rolling-up process.

The experimental results of the decrease in average degree of polymerization of cellulose allows us to conclude that milling increases the accessibility of the glycosidic bonds located in the amorphous regions and decreases the crystallinity of the cotton sample. On the other hand, the data of the yield of glucose, during the hydrolysis of cellulose, show that the effects of milling on cellulose saccharification will depend on both the accessibility and the reactivity of the glycosidic bonds. At high temperatures, only the maximum yield is affected by the pretreatment which could be more related to the decrease of the sample crystallinity. Therefore a more severe milling is needed to increase the maximum glucose concentration (Millet et al., 1976). On the other hand, at lower temperatures, the production of glucose is mostly affected by the loosening of the cotton sample structure. The maximum effect, observed at 140°C**,** could be related to both the loosening of the structure of the sample and a smaller volume of the crystalline regions. Moreover, the data observed at 120°C are in agreement with the fact that cellulose contains glycosidic bonds with very high accessibility (Sharples, 1954). Because of cellulose fibre complexity, many kinetic constants should be introduced in any cellulose depolymerization model. The rupture of the glycosidic bonds with high accessibility would appear in the first stages kinetic constants. The effects of morphology on the accessibility of the bonds should be introduced as the limiting factor in the following stages. The necessary changes for the modeling of the acid hydrolysis of the milled cotton sample will appear first in the initial conditions by a lower volume of crystalline regions and, during the depolymerization process, by a higher accessibility of the bonds in the intermediate steps of the reaction.

NOMENCLATURE

Latin alphabet symbols

B.E = binding energy, eV
[*C*] = cellobiose concentration, kg/m³
[*G*] = glucose concentration, kg/m³
k_D = second order kinetic constant for glucose hydrolysis, m³/mol · min
k_H = second order kinetic constant for cellobiose degradation, m³/mol · min
k^1_2 = pseudofirst-order constant for cellobiose hydrolysis, min^{-1}
k^1_3 = pseudofirst-order constant for glucose degradation, min^{-1}
t = time, min
T = temperature, K
W_{cf} = work of adhesion of wax on cotton, $m^2N.m^{-2}$

Greek alphabet letters

α = thermal expansion, K^{-1}
ϒ = surface and interfacial tension, m · N/m
θ = contact angle
π = film pressure, m · N/m

Subscripts

0 = initial state
c = critical conditions
m = melted phase
f = wax film surface
fw = film-water interface
cw = cotton-water interface
cf = cotton-film interface
s = simulated value
w = water surface
cr = crystalline phase

REFERENCES

1. Adamson, A. W., "Physical Chemistry of Surfaces", 5th edition, Wiley Interscience, New York (1990).
2. Ahmed, A., "Characterization of the Liquid and Solid Products of Wood Liquefaction", PhD. thesis, Dtpartement de genie chimique,
Universitt Laval, Qutbec, Canada (1988).
3. Ahmed, A., A. Adnot, J. L. Grandmaison, **S.** Kaliaguine and J. Doucet, "ESCA Analysis of Cellulosic Materials", Cellulose Chem. Technol. 21, 483-492 (1987).
4. Brandrup, J. and E. H. Immergut, "Polymer Handbook", John Wiley & Sons, New York (1989).
5. Bertran, M. S. and B. E. Dale, "Determination of Cellulose Accessibility by Differential Scanning Calorimetry", **J.** Appl. Polym. Sci. 32, 4241-4253 (1986).
6. Bienkowski, P. R., M. R. Ladisch, R. Narayan, G. T. Tsao and R. Eckert, "Correlation of Glucose (Dextrose) Degradation at 90 to 190°C in 0.4 to 20% Acid", Chem. Eng. Commun. 51, 179-192 (1987).
7. Chang, M. M. Y., "Crystallite Structure of Cellulose", J. Polym. Sci. **12,** 1349-1374 (1974).
8. Chang, M. and G. T. Tsao, "The Effects of Structure on Hydrolysis of Cellulose", Cellulose Chem. Technol. 15, 383-395 (1981).
9. Chattoraj, D. K. and K. **S.** Birdi, "Adsorption and the Gibbs Surface Excess", Plenum Press, New York (1984).
10. Conner, A. H., B. F. Wood, C. G. Hill and J. F. Harris, "Kinetic Modeling of the Saccharification of Prehydrolyzed Southern Red Oak", in "Cellulose Structure, Modification and Hydrolysis", R. A. Young and R. M. Rowell, Eds.,
Wiley-Interscience, New York (1986), pp. 281-296.
11. Dadach, Z. and **S.** Kaliaguine, "Effects of Cotton Pretreatments on Wax Layers and Cellulose Acid Hydrolysis", Cellulose Chemistry and Technology, 1993, (accepted for publication).
12. Davies, J. T. and E. K. Rideal, "Interfacial Phenomena", Academic Press, New York (1961).
13. Feller, R. L. **S.** B., Lee and J. Bogaard, "The Kinetic of Cellulose Deterioration", Advances in Chemistry, ACS series 212, 329-347 (1986).
14. Fowkes, M. F., "Surface Chemistry" in "Treatise on Adhesion and Adhesives: Theory",
15. R. L. Patrick, Ed., Marcel Dekker, New York (1967), pp. 325-449.
16. Harris, **J.** F., "Acid Hydrolysis and Dehydration Reactions for Using Plant Carbohydrates", Appl. Polym. Symp. 28, 131-144 (1975).
17. Hollen, N. and J. Saddler, "Textiles", Macmillan, New York (1968).

18. Humphrey, A. E., “The Hydrolysis of Cellulosic Materials to Useful Products”, Advances in chemistry, ACS series 181, 25-33 (1979).
19. Ladisch, M. R., “Hydrolysis”, in “Biomass Handbook”, 0. Kitani and C. W. Hall, Eds., Gordon and Breach, New York (1989), pp. 434-451.
20. Lietzke, M. H., R. W. Stoughton and **T.** F. Young, “The Bisulfate Acid Constant from 25 to 225 “C as Computed from Solubility Data”, J. Phys. Chem. *65,* 2247-2249 (1961).
21. Lipinsky, E. S., “Perspectives on Preparation of Cellulose for Hydrolysis”, Advances in Chemistry, ACS series 181, 1-21 (1979).
22. Millet, M. A., A. **J.** Baker and L. D. Satter, “Physical and Chemical Pretreatments for Enhancing Cellulose Saccharification”, Biotechnol. Bioeng. Symp. 6, 125-153 (1976).
23. Nelson, L. N. and R. T. O’Connor, “Relation of Certain Infrared Bands to Cellulose Crystallinity and Crystal Lattice Type. Part **II.** A New Infrared Ratio for Estimation of Crystallinity in Cellulose I and **II”, J.** Appl. Polym. Sci. 8, 1325-1341 (1964).
23. Osipow, L. I., “Surface Chemistry: Theory and Industrial Applications”, Reinhold, New York (1962).
24. Peters, P. H., “Textile Chemistry: The Chemistry of Fibers”, Elsevier, Amsterdam (1961).
25. Peters, R. H., “Textile Chemistry: Impurities in Fibres, Purification of Fibres”, Elsevier, New York (1967).
26. Pinto, J. H. *Q.* and S. Kaliaguine, “A Monte Carlo Analysis of Acid Hydrolysis of Glycosidic Bonds in Polysaccharides”, AIChE 37, 905-914 (1991).
27. Ranby, B. G., “ “Weak Links”, in Polysaccharide Chains as Related to Modified Groups”, J. Polym. Sci. 53, 131-140 (1961).
28. Read, S. M. and D. P. Delmer, “Biochemistry and Regulation of Cellulose Synthesis in Higher Plants”, in “Biosynthesis and Biodegradationof Cellulose”, C. H. Haigler and P. J. Weimer, Eds., Marcel Dekker, New York (1991), pp. 117-200.
29. Saeman, J. F., “Kinetics of Wood Saccharification:Hydrolysis of Cellulose and Decomposition of Sugars in Dilute Acid at High Temperature”, Ind. Eng. Chem. 37, 43-52 (1945).
30. Scallan, A. M., S. Katz and D. S. Argypoulos, “Conductometric Titration of Cellulose Fibres” in Proceedings of the 10th Cellulose Conference, Syracuse (USA), 1988, John Wiley, New York (1989), pp. 1457-1471.
31. Segal, L., “Cellulose and Cellulose Derivatives”, Wiley, New York (1971).
32. Segal, L. and P. J. Wakelyn, “Cotton Fibers” in “Handbookof Fiber Science and Technology: Fiber Chemistry”, M. Lewin and E. M. Pearce, Eds., Marcel Dekker, New York (1985), pp. 809-908.
33. Sharples, A., “The Hydrolysis of Cellulose. I: The Fine Structure of Egyptian Cotton”, J. Polym. Sci. 13, 393-401 (1954).

34. Sidiras, D. K. and E. G. Koukios, “Acid Saccharification of Ball-Milled Straw”, Biomass 19, 289-306 (1989).
35. Singleton, W. S., “Solutions Properties” in “Fatty Acids”, K. S. Markley, Ed., Robert E. Krieger, Malabar, FL (1983).
36. Smith, P. C., H. E. Grethlein and A. 0. Converse, “Glucose Decomposition at High Temperature, Mild Acid and Short Residence Times”, Solar Energy 28, 41-48 (1982).
37. Sjostrom, E., “Wood Chemistry: Fundamentals and Applications”, Academic Press, new York (1981).
38. Valko, E. I., “Chemistry and Chemical Technology of Cotton”, Interscience Publishers, New York (1955).
39. Weiss, P., “Adhesion and Cohesion”, Elsevier, New York (1962).
40. Wright, L. W., “Sorbitol and Manitol”, Chemtech 42, 40-44 (1974).

STOCHASTIC SIMULATION OF THE YIELD OF GLUCOSE

INTRODUCTION TO STOCHASTIC SIMULATION

Experimental investigations of cotton fibres saccharification by acid hydrolysis have been achieved in the first part of this study. The values of the pseudofirst-order rate constant for the rupture of β(1,4) glycosidic bonds were estimated from the acid hydrolysis of cellobiose. Since glucose is thermally degraded during experiments of cellulose acid hydrolysis performed at high temperatures, the experimental rate constants of pure glucose acid degradation were also obtained. The main objective of the present work is to investigate whether the kinetic data observed for cellobiose acid hydrolysis and glucose degradation as well as the experimental information related to the morphology of cotton fiber could be successfully used in a computer-oriented simulation procedure in order to simulate the experimental glucose concentrations as a function of time during cellulose acid hydrolysis.
Such a stochastic approach has already been used by many authors for reaction kinetics modeling (Gillespie, 1977; Turner, 1977; McDermott and Klein, 1986; Train and Klein,

1988). Recently McDermott et al. (1990) and Pinto and Kaliaguine (1991) have used a Monte Carlo technique to simulate respectively lignin degradation and amylose acid hydrolysis using the lunetic information obtained from model compounds

CELLULOSE ACID HYDROLYSIS PROCESS

Hydrolysis of cellulose is generally considered as a firstorder reaction with respect to the concentration of β (1-4) bonds between β-anhydroglucose monomers (Sharples, 1968; Ladish 1989). The cleavage of a glycosidic bond in acid media has been studied and many mechanisms have been proposed (BeMiller, 1967). It is now generally accepted that the reaction starts with a rapid protonation of the glycosidic oxygen atom, followed by a slow breakdown of the protolysed conjugate acid to the cyclic carbonium ion, which adopts the half-chair conformation. A fast reaction with water then gives the reducing glucose (Sjostrom, 1981; Fengel and Wegener, 1984). It is also well known that, in aqueous acid solution, glucose undergoes inter- and intra-molecular elimination of water between the hemiacetal and mainly the hydroxyl groups.
Therefore, the main products of the reverse condensation reactions are essentially isomaltose, gentiobiose and 1:6-anhydro-β-D-glucopyranos (levoglucosan). However, cellobiose and higher oligosaccharides were also detected (Sugisawa and Edo, 1964). During our experiments with glucose degradation, the only measurable product was glucose. Therefore, the kinetic constant *(k_D)* estimated from the experimental data included all the glucose degradation and reverse reactions.

On the other hand, the peak that was related to some unidentified saccharides of higher molecular weight than cellobiose was more important during experiments with cellobiose acid hydrolysis than the peak detected during pure glucose experiments. This could be an indication that the dehydration reactions were more important during cellobiose acid hydrolysis than during pure glucose acid degradation. This fact was supported by the necessary increase of 10% of the rate constant of glucose degradation for the deterministic simulation of glucose yield versus time during cellobiose acid hydrolysis (Dadach and Kaliaguine, 1993). Moreover, as indicated by the data presented in the first part of this work (Dadach and Kaliaguine, 1993), the rate of rupture of the glycosidic bonds is also affected by the ease by which the glycon rings are reached by the acid ions (Segal, 1971; Feller et al., 1986). Therefore, the accessibility of the glycon rings, located in the crystalline regions could be a limiting factor to the rate of rupture of the glycosidic bonds. The drastic conditions necessary to produce significant saccharification of cellulose also result in the undesirable secondary decomposition of glucose into such products as furfurals and levoglucosan (Conner et al., 1986).

STOCHASTIC SIMULATION OF A POLYMER DEPOLYMERIZATION PROCESS

The basis of Monte Carlo simulation is to construct a deterministic kinetic model based on the probabilistic one by considering its reaction constants not as reaction "rates" but as reaction "probabilities per unit time". Therefore, reaction occurs with a certain probability (Gillespie, 1976).

This concept has been surveyed in an extensive review paper by McQuarrie (1967). In order to understand the stochastic approach to a polymer degradation process, a random reaction trajectory of a linear oligomer with a degree of polymerization of 10 (9 bonds) is illustrated in Figure 1.

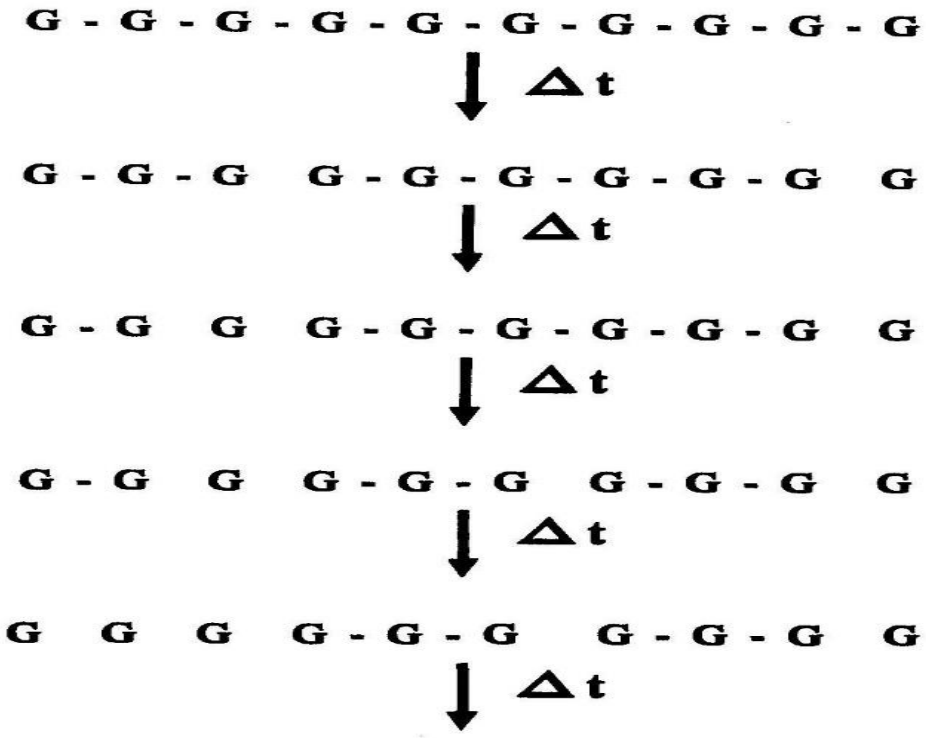


Figure 1 – Random trajectory of the depolymerization of a linear polymer.

The real reaction time is divided into small time increments Δt and each downward arrow represents the passage of one Δt for the simulated depolymerization process. Assuming that the polymer linkages are ruptured independently with a first order rate constant k, the transition probability that each bond, in state (i) at time t, is in state (j) at time $(t + \Delta t)$, depends not only on its rate constant k, but also on the length of an allowed transition step Δt (McQuarrie, 1967):

$$Pr_{i\_j}(t, t + \Delta t) = k\Delta t + o(\Delta t) \quad \text{.....(1)}$$

where $o(\Delta t)$ is a function of Δt satisfying

$$\lim_{\Delta t \to o} [0(\Delta t)/\Delta t] = 0 \quad \text{..... (2)}$$

In the limit as $\Delta t \rightarrow 0$, equation (1) could be expressed as (Trivedi, 1982):

$$Pr_{i\_j}(t, t + \Delta t) = 1 - \exp[-k\,\Delta t] \quad \text{..... (3)}$$

After the passage of each Δt, the rupture of each polymer bond is tested by comparing the transition probability for each bond to a randomly selected number. One or more bonds are ruptured when a selected random number comprised between 0 and 1 has a value less than the calculated transition probability for the bond tested. The final result after each Δt represents the new state of the chain (Train and Klein, 1988).

To simulate this reactive system as a Markov chain, the polymer could be considered as a group of parallel subsystems, each one being composed of a single bond (Pinto and Kaliaguine, 1991). The markovian assumption is equivalent to specifying that the physical system has an extremely limited memory, that is, given the "present" of the process, the "future" is independent of its "past" (Wolff, 1989). Therefore, the time evolution of the system proceeds by allowing fixed time intervals, Δt to pass in series and the simulated process takes the form of a markovian random walk in the N-dimensional space of the population of the N different bonds (Gillespie, 1976). Since the reaction of a single polymer chain would not provide statistically significant results, when the final reaction time is reached, other identical polymers are randomly reacted using the same procedure. Averaging individual conversions at each time over a fixed number N_0 of Markov chains produces the Monte Carlo simulation.

STOCHASTIC SIMULATION OF CELLULOSE ACID HYDROLYSIS

The FORTRAN progam used in this work for the stochastic simulation of cellulose acid hydrolysis is based on the Monte Carlo technique developed by Pinto (1992) for the simulation of the acid hydrolysis of polysaccharides using the kinetic information obtained from the model compound, cellobiose. For the simulation of amylose acid hydrolysis at temperatures where glucose degradation was neglected, Pinto and Kaliaguine (1991) used two different approaches. In the first simulation procedure, based on Gillespie's classic work (1976), the calculated rate of glucose formation was in poor agreement with the values observed experimentally. On the other hand, the rate of glucose formation calculated by the second stochastic procedure, based on the work of McDermott et al. (1990) and described in the previous section of this paper, were in excellent quantitative agreement with their experimental data.

In the present study related to the acid hydrolysis of cellulose at temperatures higher than 110°C, experimental information including the morphology of cellulose and the rate constant of glucose degradation are therefore considered in the FORTRAN procedure. As reported in the experimental part of this investigation and shown in Figure 2, the model for cellulose chains used in our simulation will include the crystalline and the amorphous regions of cotton fibers as well as the regions of intermediate crystallinity. Therefore, the new parameters involved are the length of the three kinds of regions, namely the amorphous (LA), semi-amorphous (LSA) and crystalline or non-amorphous (LNA) regions.

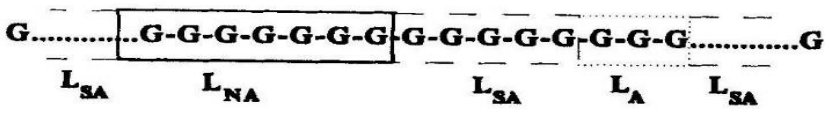


Figure 2 – Morphological model of cellulose chains.

The parameter L_{NA} is estimated from our experimental levelling-off degree of polymerization (L_{NA} = LODP =200). Our IR spectra indicated that the crystallinity index of the cotton fibers is 79.0% (Dadach and Kaliaguine, 1993). The crystallinity of cotton fibers varies considerably depending on the experimental technique used for its determination (Young, 1986). According to Scallan (1971), 90% is a typical degree of crystallinity of nontreated cotton linters and nontreated cotton fibers. In the present work, a crystallinity of 90% is considered and the length of the amorphous, semi-amorphous and crystalline regions could then be estimated from the following equation:

$$Cr = [L_{NA}/(L_A + L_{SA} + L_{NA})] \text{ .....(4)}$$

Therefore, the values introduced in the program procedure are: (L_A) = 14; (L_{SA}) = 7; (L_{NA}) = 200. The experimental average degree of polymerization of the cotton sample (DP=2200) is also introduced in the input data of the program. Many models for the depolymerization of linear chain molecules have already been considered in the literature (Simha, 1941; Sillen, 1943; BeMiller, 1967). In these models, three different hypotheses have been made:

1. The rate of disintegration is the same for all bonds, independent of their position in the chain.

2. There is a preferred breaking at the ends of the chain (one or both ends) and a common hydrolysis rate for all other bonds.

3. There is a progressive change in the rate of disintegration as a function of the distance from ends of the chain.

In the present study, the value of the ratio (M = 2) between the kinetic constant of the non-reducing end (k_2) and the one of the reducing end (k_1), used by Pinto and Kaliaguine (1991) to simulate the experimental results of Kamiyama and Sakai (1979) for the hydrolysis of xylooligosaccharides of DP ranging from 3 to 5, will be considered. As a result, in each of the three zones, two rate constants are considered: k_2 for the nonreducing ends and k_1 for all other bonds. Therefore, at each time step Δt, six types of bonds are tested for rupture using Equation 3 and the corresponding rate constants are related in the following manner:

$$(k_2 / k_1)_A = (k_2 / k_1)_{SA} = (k_2 / k_1)_{NA} = 2.0 \text{ .....(5)}$$

Moreover, we assume that the rate constant k_2 of the nonreducing ends in the amorphous regions is equal to our experimental hydrolysis rate constant of cellobiose k_2'. The values of the rate constant at the nonreducing ends of the crystalline regions of cotton ($k_{2,NA}$ = 1/1100 min^{-1}) is estimated from the experimental ratio of the slope of the decrease of the average degree of polymerization of cotton fibres during the first and last stages of the cellulose acid

hydrolysis process (Dadach and Kaliaguine, 1993). In the same way, the rate constant for the semi-amorphous regions ($k_{2,SA}$ = 1/50 min^{-1}) was estimated from the average value of all intermediate stages observed during our experiments. Therefore, the rate constants of the all nonreducing ends of cellulose are related to the cellobiose hydrolysis rate constant by:

$$(k_{2,A} / k_2') = 1;\ (k_{2,SA}/k_2')=1/50;\ (k_{2,NA}/k_2') = 1/1100 \ldots..(6)$$

Furthermore, since the cellulose acid hydrolysis experiments were conducted at high temperatures, where glucose is thermally degraded, the FORTRAN program should also include the transition probability related to the pseudo first-order rate constant for glucose degradation, k_3'; determined from experiments of glucose described in the first part of this study:

$$P_{glucose-degrad}(t, t + \Delta t) = 1 - \exp[k_3' \Delta t] \ldots\ldots.(7)$$

In our model of cellulose acid hydrolysis, we have considered the rupture of the β(1, 4) bonds and the degradation of glucose as two first order irreversible reactions. Therefore, the rupture of any glycosidic bond adjacent to a ruptured bond may be followed by a degradation of the glucose formed:

$$A \xrightarrow{k_{AB}} B \xrightarrow{k_{BC}} C \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

However, according to Peat and his coauthors (1958), when a glycosidic linkage of a polysaccharide is severed by acid, the two saccharide fragments may combine with water or, alternatively with each other or with other fragments. In the latter case, the energy associated with the original linkage could be available to accelerate the formation of reversion products. Therefore, in order to consider all the reactions related to a possible combination between the glucose formed and reducing ends of other oligomers or between oligomers, the pseudofirst-order rate constant k_3' determined from experiments of pure glucose was replaced in our model by an overall glucose disappearance rate constant.

A Monte Carlo simulation of this simplified model of cellulose acid hydrolysis is complicated by the fact that the use of Markov chain formulation allows only one reaction per molecule per discrete time step Δt. Therefore, the glucose formed (B) will not react in the same Δt in which it was formed. An erroneous overestimation of the glucose yield could be especially large during the rupture of the glycosidic bonds located in the non-amorphous regions, where the glucose degradation rate is much higher than its formation rate. This situation was analysed by McDermott et al. (1990). To allow more than one reaction of the same molecule in one

simulation time step Δt, the authors introduced the transition probability (P_{AC}) that a molecule (A) at time t, is transformed into (C) at time $(t + \Delta t)$:

$$P_{AC} = - [k_{BC} / (k_{AB} - k_{BC})] P_{AB} + [k_{AB} / (k_{AB} - k_{BC})] P_{BC} \quad \ldots\ldots (9)$$

Therefore, for a hypothetical transition of a molecule (A), a randomly selected number (RN) is compared to the transition probabilities:

1-If $RN < P_{AC}$; A reacted to C.

2-If $P_{AC} \leq RN < P_{AB}$; A reacted to B.

3-If $RN \geq P_{AB}$; A did not react.

The authors have shown that the use of P_{AC}, related to the possibility of two consecutive reactions in the same Δt, describes the lunetics accurately for all values of $k_{AB}\Delta t$. On the other hand, the stochastic results related to only one transition per Δt approach the deterministic data only for values of $k_{AB}\Delta t < 0.01$ (McDermott et al., 1990).

For the stochastic simulation of the acid hydrolysis of cellulose however, the use of the transition probability P_{AC} is more complicated. First the degradation of a glucose molecule is possible only after the rupture of two adjacent glycosidic bonds (with the obvious exception of terminal monomers in the initial chain). Therefore for each transition time step Δt, P_{AC} could be used for a potential glucose molecule only, which is represented by any glycosidic bond adjacent to a ruptured bond. As a result, after each Δt, the location of the potential glucose molecules should first be codified and for the next reaction step Δt, the program should first identify, for each glycosidic bond, the type of glucose molecule (potential or not potential) before using the appropriate transition probability (P_{AC} or P_{AB}). Furthermore, the use of P_{AC} for the cellulose acid hydrolysis is even more complicated by the fact that P_{AB} represents the transition probability of both the reducing and nonreducing ends defined by Equations (3) and (5). From the fact that the number and the lengths of all oligomers formed in one reaction time step Δt can be known only at the end of the reaction step, a new test is then necessary to define if a glycosidic bond, related to a potential glucose, is at a reducing or a nonreducing end. Therefore, the increase of the CPU time required for these two tests cannot be neglected.

Moreover, in the first part of this investigation we have shown that, during cellulose acid hydrolysis, the rate of rupture of a glycosidic bond will depend on both the accessibility and the reactivity of the glycon ring. Therefore for each potential glucose molecule, an appropriate value of P_{AC} should be calculated depending on the corresponding glycosidic bond location in the amorphous, semi-amorphous or crystalline regions of the cellulose chain. Thus, for the potential glucose molecules for which the constant rate of glucose formation may be

considered as equal to the rate of glucose disappearance ($k_{AB} = k_{BC}$), Equation (9) should be replaced by (McDermott et al., 1990):

$$P_{AC} = P_{AB} + (1 - P_{AB}) \log (1 - P_{AB}) \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

The required computation time is therefore also increased by the effects of cellulose morphology on the transition probability P_{AC}. We conclude that, for the simulation of cellulose acid hydrolysis, the use of P_{AC} might impose a large increase of the CPU time required for the simulation. On the other hand, for the cases where the rate of rupture is the same for all bonds, whatever their position in the chain, the transition probability P_{AC} could be considered when the computation time is not too high.

The procedure of the Monte Carlo approach used in this investigation (Figure 3) also includes using the kinetic rate constant k_2' preliminarly derived from the model compound reactions. However, in the FORTRAN routine used in this investigation, the glycosidic bonds of cellulose are first tested for reaction using Equations (3)-(6) and the data of the produced glucose concentrations are stored at each time. This part of the program was already used and discussed in a previous work (Pinto and Kaliaguine, 1991). Therefore at each time increment, all the stored glucose molecules are tested for degradation by comparing the transition probability of Equation 7 to a random number. A glucose molecule is degraded if the selected number is lower than the calculated probability. The remaining glucose molecules will represent the corrected glucose concentration. The number of glucose molecules of the next step should first be corrected by eliminating the number of glucose molecules that have reacted in the previous step, before the same procedure is repeated until the final reaction time.

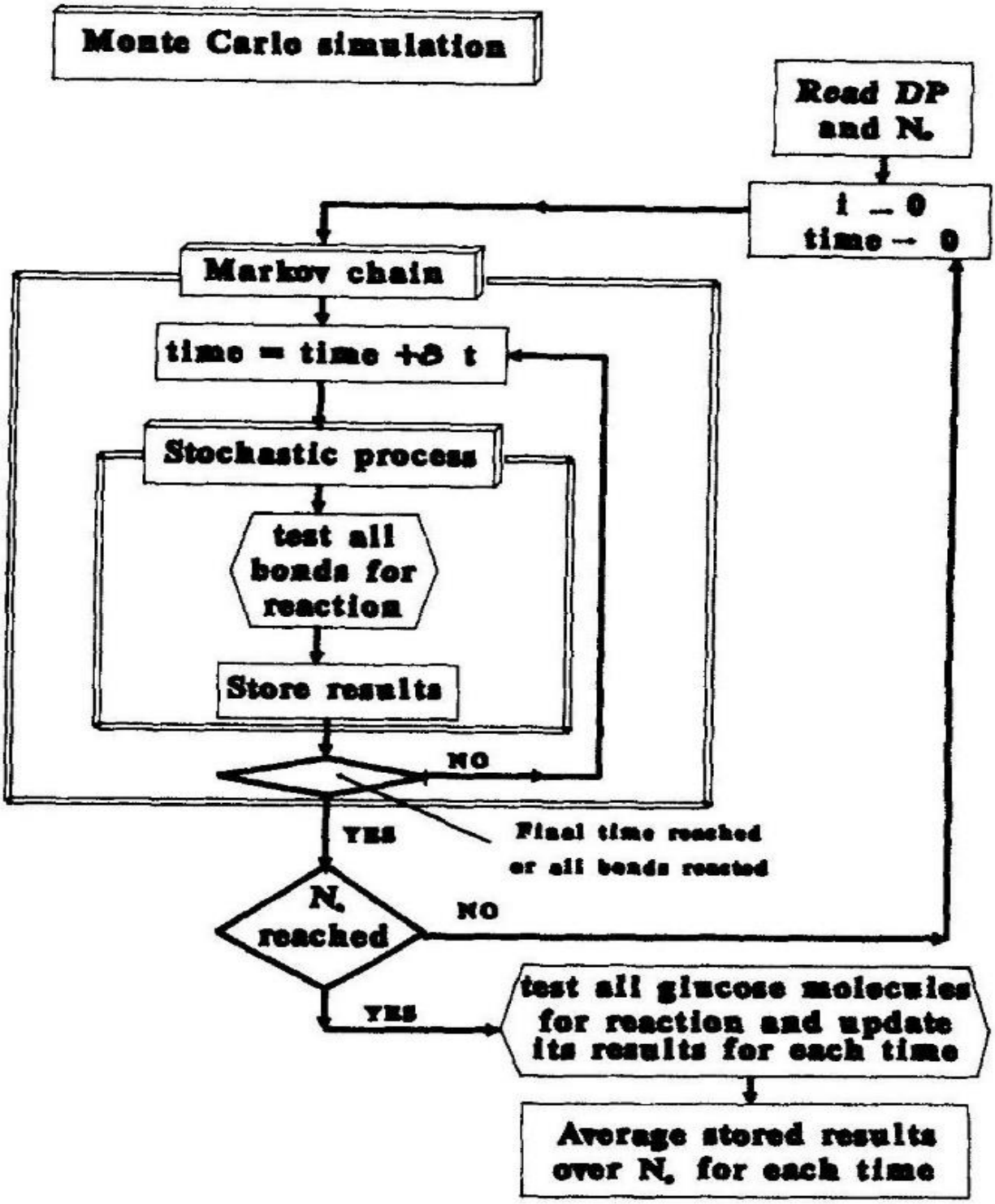


Figure 3 — Depolymerization simulation algorithm.

RESULTS AND DISCUSSION

The simulated values of glucose concentration, as a function of time, calculated using the stochastic procedure described in the previous section are compared **to** the experimental values obtained and presented in the first part of this study (Dadach and Kaliaguine, 1993). For convenience, we have chosen a reaction time step size Δt less than the inverse of the largest reaction rate constant. Figures 4-6 indicate an excellent quantitative agreement between the simulated values and the experimental data at all studied reaction temperatures. The small gap observed at 120°C between the simulated and experimental values could be related to the experimental difficulties of measuring glucose concentrations lower than 0.01 g/L.

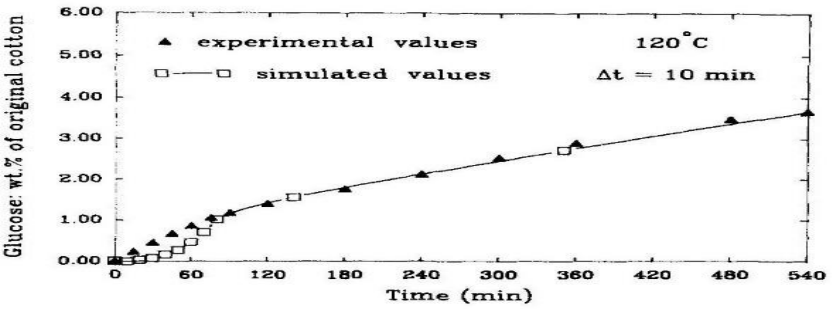


Figure 4 — Monte Carlo simulation of glucose build up in cotton sample hydrolysis in 0.015 mol/L sulfuric acid at 120°C

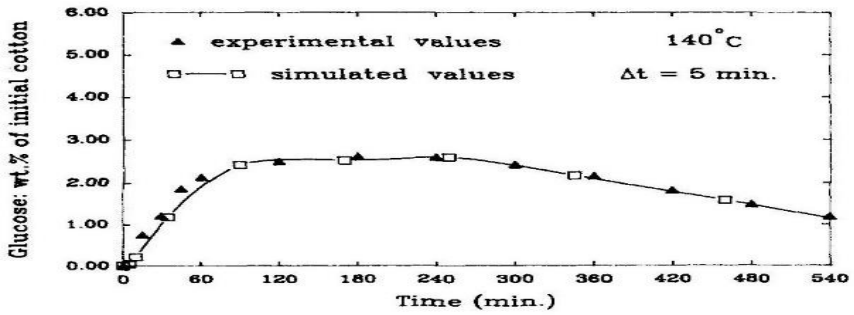


Figure 5 — Monte Carlo simulation of glucose build up in cotton sample hydrolysis in 0.015 mol/L sulfric acid at 140°C.

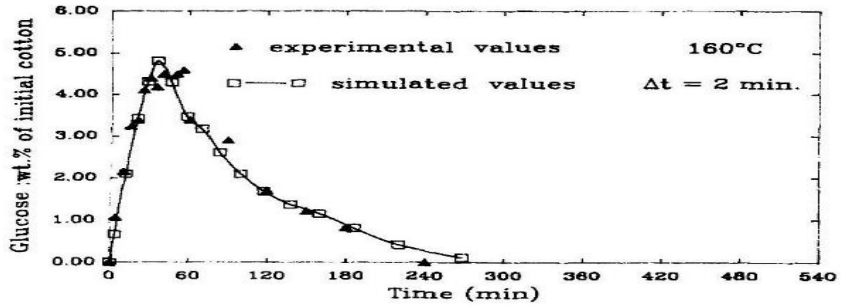


Figure 6 — Monte Carlo simulation of glucose build up in cotton sample hydrolysis in 0.015 mol/L sulfuric acid at 160°C.

As shown in Figure 7, the kinetic information obtained from experiments with the model compound cellobiose was used for the simulation procedure (Dadach and Kaliaguine, 1993). However, since we have considered cellulose acid hydrolysis as two first order irreversible reactions in series, it was necessary to use an overall glucose disappearance rate constant which considers all the possible condensation reactions between glucose and oligomers and between oligomers in solution.

The value of the overall glucose disappearance rate constant was always higher than the value of the experimental rate constant observed at the same temperature for pure glucose degradation. Both the preexponential factor and the activation energy of the two constants are obtained from an Arrhenius plot (Figure 8):

$k_{D,e} = 2.62 \times 10^{17} \exp (- 140.7 / RT)$.....(11)

$k_{D,s} = 2.56 \times 10^{17} \exp (- 137.6 / RT)$.....(12)

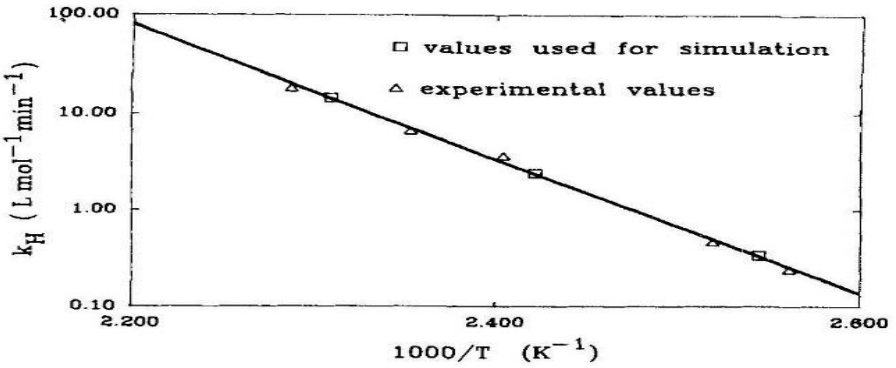


Figure 7 — Arrhenius plot for experimental data and values used for the simulation of the pseudofirst order k_H during cellulose acid hydrolysis.

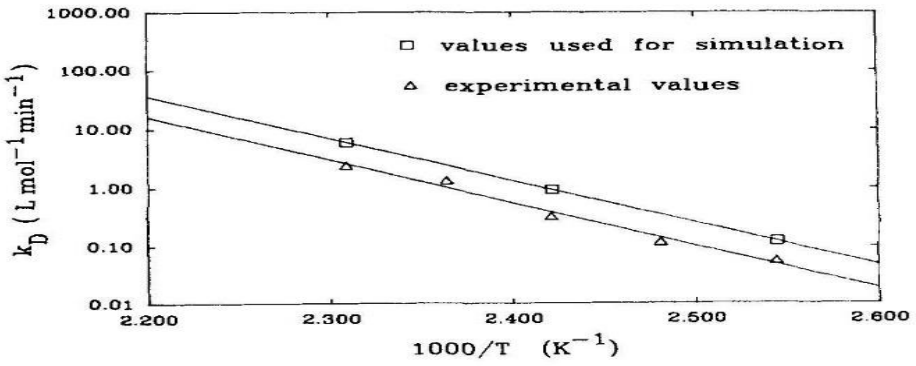


Figure 8 — Arrhenius plot for experimental data and values used for the simulation of the pseudofirst order k_D during cellulose acid hydrolysis.

where RT is in kJ/mol and k_{De} and k_{Ds} are in L/mol.min.

The higher values of the overall glucose disappearance rate constant could be an indication that the recombination of oligomers and the formation of reverse products from the glucose, during cellulose acid hydrolysis, are more important than the reverse products obtained from pure glucose acid degradation. The same phenomenon, however less important, was also observed during cellobiose acid hydrolysis. Indeed in the last case, in order to obtain a good fit of the experimental values of glucose yield during cellobiose acid hydrolysis, the degradation rate constants, used in the mathematical formulation had to be higher than the experimental rate constants of glucose obtained from pure glucose acid degradation (Dadach and Kaliaguine, 1993). Figures 9-11 compare the simulated results and the experimental data of glucose concentration, as a function of time, for the acid hydrolysis of milled cotton samples. For each temperature, we have used the same values for cellobiose acid hydrolysis rate constant and the overall glucose disappearance rate constant described previously. The effects of milling were investigated in the first part of this study.

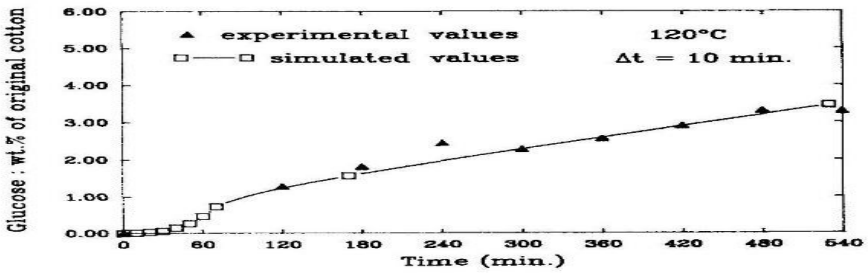


Figure 9 — Monte Carlo simulation of glucose build up in milled cotton sample hydrolysis in 0.015 mol/L sulfuric acid at 120°C.

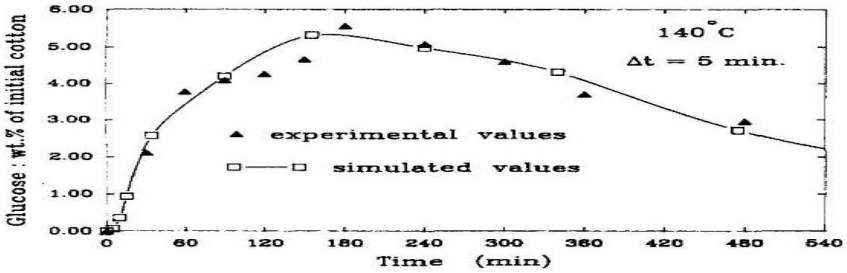


Figure 10 — Monte Carlo simulation of glucose build up in milled cotton sample hydrolysis in 0.015 mol/L sulfuric acid at 140°C.

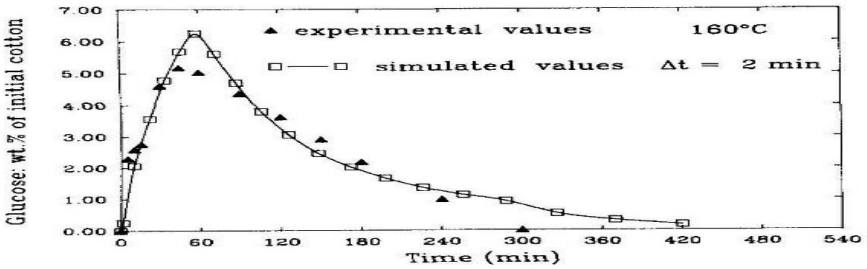


Figure 11 — Monte Carlo simulation of glucose build up in milled cotton sample hydrolysis in 0.015 mol/L sulfuric acid at 160°C.

Our experimental results allowed us to conclude that milling increases the accessibility of the glycosidic bonds located in the non crystalline regions and decreases the crystallinity of the cotton sample. The length of the crystalline regions (LODP) was decreased by milling from 200 to 110. These changes were introduced in the FORTRAN program first by increasing the percentage of the amorphous regions of cotton from 10% to 13%. As a result, the new values of the length of the amorphous, semi-amorphous and crystalline regions are: (L_A) = 11; (L_{SA}) = *5;* (L_{NA}) = 110. The kinetic constant of the rate of rupture of the glycosidic bonds located in the semi-amorphous regions were also corrected by increasing the ratio ($k_{2,SA}/k_2'$) from 1/50 to 1/5.

As shown and discussed in the first part of this investigation, the effects of milling on the yield of glucose during cellulose acid hydrolysis depend on the temperature. At 120°C, milling had no influence on the glucose yield. At 160°C, the yield of glucose was mostly affected by the decrease of the size of the crystalline regions from 200 to 110. However, at 140°C, the effects of both the increase of the kinetic constant related to the rupture of the glycosidic bonds located in the semi-amorphous regions and the decrease of the crystallinity of the milled cotton sample were detected (Dadach and Kaliaguine, 1993).

Therefore, the good agreement observed, for all the temperatures, between the simulated values and the experimental data of the milled cotton acid hydrolysis (Figure 9-11), indicates that the influence of the changes made in the input data of the program, in order to reflect the effects of milling, depends also on the temperature. These simulation results demonstrate clearly that the competition between the accessibility and the rate of rupture of the β(1, 4) glycosidic bonds during cellulose acid hydrolysis is well described by our model.

CONCLUSION

The utilization of a predictive stochastic Monte Carlo technique allowed us to simulate the cellulose acid depolymerization by considering the rupture of a β(1, 4**)** bond and the degradation of glucose as two irreversible first order reactions in series. Therefore, the FORTRAN procedure used to allow two reactions per molecule per discrete time step Δt was successfully applied. The experimental information related to the acid hydrolysis of the model compound cellobiose and the morphological aspect of cotton sample were directly used in our model. On the other hand, an overall glucose disappearance rate constant was introduced in our model in order to consider the fact that the acid hydrolysis of the highly cristalline cellulose is a complex reactive system where recombination between oligomers and between glucose and oligomers take place. To obtain a good agreement between the experimental time evolution of glucose concentration in a batch reactor and the predictions of the stochastic procedure, the values of the overall glucose disappearance rate constant introduced in the FORTRAN program were always higher than the experimental rate constants obtained from pure glucose experiments. These results indicate that the glucose reverse reactions are highly enhanced during cellulose acid hydrolysis. Furthermore, the good agreement observed between the simulated values and the experimental data of the milled cotton sample acid hydrolysis show that our model can easily simulate the effects of cotton pretreatments on cellulose acid hydrolysis by introducing the corresponding values in the input data of the program. We may conclude that Monte Carlo simulation associated with a Markov chain was therefore found to be a helpful and flexible tool for the connection between the model compound (cellobiose) reaction information and the production of glucose during cellulose acid hydrolysis.

NOMENCLATURE

Cr = crystallinity of cellulose chains.
k = first-order kinetic constant, min^{-1}
k_1 = pseudofirst-order constant for reducing ends, min^{-1}
k_2 = pseudofirst-order constant for non-reducing ends, min^{-1}
k_{De} = experimental second order kinetic constant for glucose degradation, L/mol · min
k_{Ds} = simulated second order kinetic constant for glucose degradation, L/mol · min
k_H = second order kinetic constant for cellobiose hydrolysis L/mol · min
k^1_2 = pseudofirst-order constant for cellobiose hydrolysis, min^{-1}
k^1_3 = pseudofirst-order constant for glucose degradation, min^{-1}
Pr = transition probability value
RN = picked random number
t = time, min
Δt = time increment, min

Subscripts

A = amorphous state
SA = semi-amorphous state
NA = crystalline state

REFERENCES

1. BeMiller, J. N., “Acid-Catalysed Hydrolysis of glycosides”, Adv. Carbohyd. Chem. 22, 25-32 (1967).
2. Dadach, Z. and S. Kaliaguine, “Acid Hydrolysis of Cellulose, Part 1: Experimental Kinetic Analysis”, Can. J. Chem. Eng., 71 (6), 880-891 (1993).
3. Conner, A. H., B. F. Wood, C. G. Hill Jr. and J. F. Harris, ‘‘Kinetic Modeling of the Saccharification of Prehydrolyzed Southern Red Oak” in ‘‘Cellulose: Structure, Modification and Hydrolysis”, R. A. Young and R. M. Rowell Eds. John Wiley & Sons, New York (1986), pp. 281-296.
4. Feller, R. L., S. B. Lee and J. Bogaard, “The Kinetic of Cellulose Deterioration”, Advances in Chem. Series 212,329-397 (1986).
5. Fengel, D. and G. Wegener Wood: Chemistry, Ultrastructure, Reactions, W. De Gruyter, Berlin (Germany), 1984.
6. Gillespie, D. T., “A General Method of Numerically Simulating the Stochastic Time Evolution of Coupled Chemical Reactions”, J. Comp. Phys. 22, 403-434 (1976).
7. Gillespie, D. T., “Exact Stochastic Simulation of Coupled Chemical Reactions”, J. Phys. Chem. 81, 2340-2352 (1977).
8. Kamiyama, Y. and Y. Sakai, “Rate of Hydrolysis of Xylo-Oligosaccharides in Dilute Sulfuric Acid”, Carbohydrate Res. 73, 151-159 (1979).
9. Ladish, M. R. , “Hydrolysis”, in “Biomass Handbook”, 0. Kitani and C. W. Hall, Eds., Gordon and Breach, New York (1989), pp. 434-451.
10. McDermott, J. B. and M. T. Klein, “Chemical and Probabilistic Modeling of Complex Reactions: A Lignin Depolymerization Example”, Chem. Eng. Sci. 41, 1053-1060 (1986).
11. McDermott, 3. B., C. Libanati, C. LaMarca and M. T. Klein, “Quantitative Use of Model Compound Information: Monte Carlo Simulation of the Reactions of Complex Macromolecules”, Ind. Eng. Chem. Res. 29, 22-29 (1990).
12. McQuarrie, D. A., “Stochastic Approach to Chemical Kinetics”, in “Methuen’s Monographs on Applied Probability and Statistics”, Vol. 8, M.S. Barlett, Eds., Methuen, London (1967).
13. Peat, S., W. J. Whelan, T. E. Edwards and *0.* Owen, “Quantitative Aspects of the Acid Reversion of Glucose”, J. Chem. SOC. 586-592 (1958).
14. Pinto, J. H. Q., “Etude Cinetique des Transformations Hydrolytiques des Polysaccharides”, PhD Diss., Universitk Laval, *Qukbec* (1992).
15. Pinto, J. H. *Q.* and S. Kaliaguine, “A Monte Carlo Analysis of Acid Hydrolysis of Glycosidic Bonds in Polysaccharides”, AIChE J. 37 905-914 (1991).

16. Scallan, A. M., “Quantitative Picture of Fringed Micellar Model of Cellulose”, Textile Res. J. 41 647-653 (1971).
17. Segal, L., “Cellulose and Cellulose Derivatives”, Wiley Interscience, New York (1971).
Sharples, A., “Degradation of Cellulose and its Derivatives. A. Acid hydrolysis and alcoholysis”. In “Cellulose and Cellulose Derivatives”. Bikales, N. M., and. L. Segal, Eds., Wiley Interscience, New York, N.Y. (1968).
18. SillCn, L. *G.,* “Uber die Zerfallsgesetze beim Abbau Hochpolymerer Ketten”, Svensk Kemiish Tidskrift 55, 221-230 (1943).
19. Simha, R., “Kinetics of Degradation and Size Distribution of Long Chain Polymers”, J. Appl. Phy. 12, 569-578 (1941).
20. Sjostrom, E., “Wood Chemistry; Fundamentals and Applications”, Academic Press, New York (1981).
21. Sugisawa, H., and H. Edo, Thermal Polymerization of Glucose Chemistry and Industry, 843 (1964).
22. Train, P. M. and M. T. Klein, “Chemical Modeling of Lignin: A Monte Carlo Simulation of Its Structure and Catalytic Liquefaction”, ACS Symp.Ser. 376, 241-263 (1988).
Trivedi, K. S., “Probability and Statistics with Reliability, Queuing and Computer Science Applications”, Prentice-Hall, Englewood
Cliffs, NJ (1982).
23. Turner, K. S., “Discrete Simulation Methods for Chemical Kinetics”, J. Phys. Chem. 81, 2379-2408 (1977).
24. Young, A. R., “Structure, Swelling and Bonding of Cellulose Fibers”, in “Cellulose: Structure, Modification and Hydrolysis”, R. A. Young and R. M. Rowell, Eds. John Wiley & Sons, New York (1986), pp. 91-128.
25. Wolff, R. W., “Stochastic Modeling and the Theory of Queues”, Prentice-Hall, Englewood Cliffs, NJ (1989).