MECHANISM OF PURIFICATION OF CELLULOSE IN ACIDIFIED AQUEOUS ACETONE

by

SALAH EL-DIN EL-SIDDIQUE AWAD EL-KARIM

M.Sc., Leningrad Technical Forestry Academy, 1976
M.Sc., University of Manchester, Institute of Science and Technology (UMIST), 1981

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Department of Wood Science

The University of British Columbia
Vancouver, Canada

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ABSTRACT

This project deals with solvent purification, a new approach for the preparation of high-yield dissolving pulp with characteristics similar to those recommended by the standards. At the same time, the solvent purification technique aims at removing and recovering chemically unmodified, low molecular weight sugars that could further be processed as by-products. In addition, the process offers a reduction in waste water amounts associated with dissolving pulp purification and economical reuse of the solvent. Thus, environmental abatement is also taken into account. The current technology is unable to achieve these goals.

The major objective of this work is the elucidation and characterization of the mechanism of the solvent purification process, i.e., the acetonation mechanism. In this thesis a detailed study on the mechanism of purification of cellulose in acidified aqueous acetone has been carried out. The mechanism has been proved to be of a physico-chemical character. The physical phenomenon has been found to be based on the H-bond disruption/destruction in crystalline cellulose by acetone as a solvent. On the other hand, the chemical hypothesis of the mechanism is verified to be the formation of isopropylidene groups on carbohydrate chains that leads to disproportionation of the polymer and protection of the sugar ring. The validity of these

hypotheses has been investigated as follows; cotton has been used throughout this study as a model compound and different techniques such as DRIFT, GC, HPLC, C-13 CP/MAS solid state NMR, X-ray diffraction, GPC, and viscosity measurements have been employed.

Factors affecting solvent purification treatment such as acidity, residence time, temperature, type of acid, and acetone concentration have also been investigated. The investigation of those factors was conducted in a manner that has helped elucidation of the acetonation mechanism rather than optimization of the solvent purification technique. Their impact on hydrogen bonding (1^{st} hypothesis) and isopropylidenation (2^{nd} hypothesis) has been observed to vary considerably.

Results obtained on hydrogen bonding, sugar derivatives, crystallinity, molecular weight distribution, and viscosity of cotton residues are in accord with the above assumptions.

Based on the experimental findings of this work, a mechanism of purification of cellulose in acidified aqueous acetone is described.

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LIST OF ABBREVIATIONS

DP	-	Degree of Polymerization
CP	-	Centipoise
CP/MAS	-	Cross Polarization/Magic Angle Spinning
NMR	-	Nuclear Magnetic Resonance
GPC	-	Gel Permeation Chromatography
IR	-	Infrared
DRIFT	-	Diffuse Reflectance Infrared Fourier Transform
GC	-	Gas Chromatography
HPLC	-	High Performance Liquid Chromatography
M_w	-	Weight-average Molecular Weight
M_n	-	Number-average Molecular Weight
CTH	-	Control Temperature and Humidity
TFA	-	Trifluoroacetic Acid
AOX	-	Adsorbable Organic Halides
HBD	-	Hydrogen Bond Donor
HBA	-	Hydrogen Bond Acceptor
Å	-	Angstrom
μ	-	Micron
Hz	-	Hertz
CrI	-	Crystallinity Index
λ	-	Wavelength
DMF	-	Dimethylformamide
r.t.	-	Retention Time
HMF	-	Hydroxymethylfurfural
CuEn	-	Cupriethylenediamine

FWHM	-	Full Width at Half Maximum Height
S.D.	-	Standard Deviation
MWD	-	Molecular Weight Distribution
M_w/M_n	-	Polydispersity
Me	-	Methyl
L	-	Litre
mL	-	Millilitre
μL	-	Microlitre
g	-	gram
hr	-	hour
cm_{-1}	-	wavenumber
C	-	Celsius
DMSO	-	Dimethylsulphoxide
I	-	Intensity
mg	-	Milligram
ppm	-	Parts Per Million
Ac	-	Acetyl
M	-	Molarity
psi	-	Pound Per Square Inch
N	-	Normality
o.d.	-	oven dry
XRD	-	X-ray Diffraction
G	-	Glucose
TAPPI	-	Tecnhnical Association of the Pulp and Paper Industry
THF	-	Tetrahydrofuran
GC-MS	-	Gas Chromatography-Mass Spectrometry

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DEDICATION

to my wife, Awatif

and

to the memory of my parents

1 INTRODUCTION

North American dissolving pulp producers, in recent years, have been hurt by high production costs and environmental pressures at many older prehydrolysis kraft and sulphite mills that are not economical to clean up. Competition from growing acceptance of low-cost synthetic fibers and films is another major concern. Rayon staple, for example, is under enormous competitive pressure from polyster, while plastic films (oriented polypropylene) are displacing cellophane (Mikulenka, 1989). U.S. dissolving pulp production declined from a level of 1.4 million metric tons in the mid seventies to a low of 991000 tons in the 1982 recession. The Canadian dissolving pulp markets followed a similar trend; declining from a peak of about 0.5 million metric tons in 1969 to around 0.2 in 1990 (Durbak, 1993). Today, the U.S. dissolving pulp capacity is about 1.5 million tons, and the Canadian around 0.3 million metric tons, largely under utilized. Dissolving pulp manufacture has remained more expensive than synthetic fibers because of the stringent purity requirements and low processed cellulose yields (Durbak, 1993).

Although dissolving grade pulps are prepared by different pulping processes and under varying bleaching conditions, at the end, the product cellulose should possess the following characteristics:

1- high alpha-cellulose content

2- low hemicellulose content

3- relatively high degree of polymerization (DP)

4- low ash content

5- good molecular uniformity.

In this respect, the feasibility of manufacture and competitiveness of dissolving pulp is largely dependent on the yield of purified pulp. In other words, alpha-cellulose content represents an important parameter of pulp purity. However the total amount of alpha-cellulose originally in wood remaining in the pulp is in the range of about 15-18% higher than the 28-32% retained in purified pulps (i.e, 43 to 50%). In this respect, the losses during pulp purification (pulping and bleaching) operations account for a remarkable shrinkage in industrial revenue due to the considerable yield loss not only from removal of hemicellulose and lignin but also cellulose itself. These losses are reflected in the dissolving pulp price.

At the present time, the lack of appropriate technology applicable to the manufacture of high-yield dissolving pulp appears to be the main reason for the appreciable losses in alpha-cellulose yield and quality of pulp in general. The acid sulphite pulping process, for a long time, has been used in manufacture of dissolving pulp. In this process, delignification and hemicellulose removal are accomplished under harsh acidic cooking conditions. Within such conditions also a considerable amount of degraded cellulose is removed in the spent cooking liquor. As a consequence, the final pulp yield of high alpha-cellulose content is

around 28-32% of that of the original wood (Golden, 1955). During the last decades the acid sulphite pulping industry has witnessed a decline in the number of mills all around the world. This is due to the fact that there has been a sharp switch to the prehydrolysis kraft pulping in dissolving pulp manufacturing because the kraft process proved to be suitable for all types of raw materials (including resinous species) that the acid sulphite process was unable to pulp (Rydholm, 1965).

Prehydrolysis in kraft pulping is a pretreatment of the raw material to achieve the following:

1- to lower the hemicellulose content in the substrate, and

2- to give a better pore opening in the cell wall for easier liquor penetration during subsequent treatments (bleaching and alkali extraction). Hemicelluloses, particularly the xylans respond well to removal by prehydrolysis (Rydholm, 1965).

Methods for attainment of high alpha-cellulose purity in wood pulps are complex and a number of schemes for alkali extraction of high brightness bleached pulps have been proposed for removal of alkali-soluble impurities (Schempp, 1971; Kleinert, 1956). However, brightness and low alkali solubility alone do not ensure high quality viscose and acetate pulps. Other factors such as accessibility during acetylation, filterability, and determination of haze have been found to qualify the pulp products (Rydholm, 1965. Golden, 1955). As for alpha-cellulose content in dissolving pulp manufacture, it is accepted to be in the range of 89-

97%. Desirable parameters of dissolving pulps are illustrated in Table 1 (Golden, 1955).

Table 1. Desirable Characteristics of Dissolving Pulps (Golden, 1955).

Pulp type	Bleached pulp yield %	α-cellulose %	Pentosans/ Mannan %	Viscosity CP
Acetate	28 - 32	95 - 97	< 2.1	30 - 70
Viscose	32 - 36	89 - 94	< 4.5	5 - 20

To reduce such losses (i.e 2/3 of wood) resulting from the current technological operations, solvent purification, a novel technique, appears to offer numerous advantages. These can be summarized as follows;

1. high alpha-cellulose yield by provision of selective simultaneous carbohydrate hydrolysis (no cellulose unit degradation) and delignification of conventional unbleached pulps,
2. maximum exploitation of the chemical value of the released products - sugar and lignin, facilitated by dissolution (hydrolysis) without modification - (due to the formation of protecting groups),
3. cutting down bleaching costs,

4. elimination of chlorine and chlorine compounds as reagents in bleaching operations,
5. reduction of process effluents by recovery of the solvent, and
6. more uniform molecular weight distribution of the purified cellulose.

Obviously, such gains will be consistent with the new sustainable development principle and "making more from less", whereby, a significant increase in the industrial revenue could be achieved.

The mechanism of solvent purification has been proposed to be of a physico-chemical character. The physical phenomenon is based on the hydrogen bond disruption in the crystalline cellulose by acetone as a solvent. On the other hand, the chemical hypothesis of the mechanism is suggested to be the formation of isopropylidene groups on carbohydrate chains that lead to disproportionation of the polymer and protection of the monomer sugar thus generated.

Hence, the study pursues the following major hypotheses; each one being supported by a number of sub-set of hypotheses;

1- H-bond disruption/destruction by the interaction of acetone with the cellulose hydroxyls

a- acetone, as a major volume fraction in the solvent (acetone/water) has the ability to deactivate the water molecules and brings about irreversible weakness in the hydrogen bonding system of the cellulosic material.

b- interaction of acetone with cellulose leads to stereochemical changes (i.e, rotational). This phenomenon brings about rearrangement in hydrogen bonding that leads to considerable disruption of the H-bonding system of the cellulosic material.

c- acetone, aided with high temperature and acid catalyst, is able to interact with cellulose and give rise to further stereochemical alterations (i.e, configurational and conformational) that subsequently disrupt/destroy the H-bond of the cellulose system.

d- accessibility of cellulose is affected by temperature, reaction time, acetone concentration, type of acid catalyst and acid concentration and provides conditions for selective purification of dissolving pulps.

2- Formation of isopropylidene intermediates on the cellulosics by the reaction of acetone with cellulose molecules

a- acetone, in the presence of an acid catalyst, is capable of interacting uniformly with cellulose and forming isopropylidene groups along the chains.

b- material removed by solvent purification consists largely of reducing and non-reducing sugars.

c- formation of isopropylidene groups on cellulose chains produces a cellulosic material with high molecular uniformity.

d- a major volume fraction of acetone, in the presence of an acid catalyst, leads to significant degradation (i.e., drop in CuEn viscosity) of the cellulose.

e- isopropylidene intermediates contribute simultaneously to decrystallization of the original cellulosic material and enhancement of the residues crystallinity.

f- temperature, acetone concentration, reaction time, type of acid catalyst and acid concentration contribute differently to the removal of cellulose.

To investigate the validity of these hypotheses cotton has been used throughout this study as a model compound. Cotton consists of glucose units mainly; however, trace amount of other substances are found in cotton (Hudson et al., 1948). The following methods have been employed:

1- Infrared (DRIFT) study - changes in hydrogen bonding, i.e., hydrogen bond disruption/destruction during the solvent purification treatment.

2- Cotton hydrolysis during solvent purification treatment.

2.1- Gas chromatographic (GC) investigation - isopropylidene derivatives of sugars identification during solvent purification treatment.

2.2- High performance liguid chromatography (HPLC) analysis - i. deacetonation, ii. quantitation - the predominance of acetonation sugar products, and iii. changes in weight loss during the solvent purification treatment.

3- C-13 cross polarization/magic angle spinning (CP/MAS) NMR structural investigation - formation of isopropylidene intermediates in the solid state during solvent purification treatment.

4- X-ray diffraction analysis - changes in crystallinity and crystallite breadth during solvent purification treatment.

5- Gel permeation chromatographic (GPC) analysis - changes in molecular weight distribution (molecular uniformity) during solvent purification treatment.

6- Viscosity analysis - changes in viscosity, i.e., degree of polymerization during solvent purification treatment.

Factors affecting treatment such as acetone concentration, residence time, temperature, type of acid catalyst and acid concentration have also been investigated. Since, the main objective of this study is the elucidation and characterization of the mechanism, the investigation of the factors will be carried out in a way that would help elucidate the mechanism of the solvent treatment rather than optimization of the process.

2 LITERATURE REVIEW

2.1 Trends of Current Dissolving Pulp Purification Processes (Pulping and Bleaching Operations)

The current pulp purification processes (i.e., pulping and bleaching operations) are known to be tremendous chemical by-product generators. Consequently, 65-70% of the original wood is lost during processing for this purpose (Golden, 1955). These losses have adverse effects on the economics of dissolving pulp production and represent potential reduction in revenue. In this respect, a new purification process of high specificity in delignification and hemicellulose removal is vitally needed.

Conceptually, higher yield dissolving pulps can be achieved by the application of solvent purification to conventional pulps. This treatment is expected to increase the alpha-cellulose content in pulps by the selective removal of hemicellulose and lignin without leading to further cellulose fragmentation. On the other hand, such a process offers the potential for recovery of chemical by-products without chemical modification, ensures solvent recovery, and enhances the properties of the dissolving pulp (e.g., accessibility, molecular uniformity etc.).

Dissolving pulps are highly purified grades of wood cellulose with alpha-cellulose content of about 89-97% (Golden, 1955). They are used to produce man-made fibres

(rayon and acetate), films (cellophane), plastics (cellulose acetates), and chemicals (methyl cellulose and carboxymethylcellulose). Two pulping processes are used to produce dissolving pulps, mainly, from soft- and hardwoods. These are the acid sulphite and prehydrolysis kraft pulping processes (Rydholm, 1965). By means of these processes different pulp grades of varying quality can be prepared, each one suitable for a specific end-use.

The quality required of a dissolving pulp for a specific purpose depends on its purity and reactivity. For example, acid sulphite dissolving pulps are considered as "reactive" pulps, suitable for production of rayon and cellophane prepared under lenient rayon (viscose) processing conditions. Prehydrolysis kraft pulps, in general, are assigned to produce stronger rayon fibres for uses such as high-wet-modulus textile rayon and high tenacity rayons for tire cords (Mikulenka, 1989). Cotton linters are also used to produce cellulose acetates and cellulose plastics (Mikulenka, 1989).

Dissolving pulp products can be divided into two major groups based on the conversion products, i.e., esters, and ethers. Rayon and acetate cellulosic fibres are believed to consume 77% of dissolving pulp production (Durbak, 1993). The products constitute viscose rayon staple, filament yarn, acetate staple, and acetate fibres (tow) which are used primarily for textiles, tire cords, various industrial products and cigarette filters (Durbak, 1993).

Cellulose ethers are widely used in pharmaceutical, cosmetics, detergents, food products, superabsorbants, and additives for oil well drilling muds. Finally, cellulose nitrates are used in printing inks, laquers and rocket fuels (Mikulenka, 1989).

The objectives of dissolving pulp purification processes are as follows;

1- maximum removal of the lignin contained in the pulp before excessive cellulose degradation takes place,

2- depolymerization of hemicelluloses in order to facilitate their removal either during cooking (prehydrolysis) or in subsequent bleaching and steeping operations (sulphite),

3- control of cellulose depolymerization in order to achieve the required viscosity levels, and

4- attainment of required quality levels for various end-uses.

2.1.1 Acid Sulphite Pulping

The sulphite dissolving pulp processing conditions are considerably different from those for paper pulp production. The retention of hemicelluloses in paper pulps is an advantage, while in dissolving pulps they have an adverse effect on the quality, i.e the presence of hemicelluloses and lignin impair the molecular uniformity of the dissolving pulps.

The sulphite cooking conditions for dissolving pulps are generally, characterized by fast temperature rise times,

high maximum temperatures, high acidity and low combined sulphur dioxide . The energies of activation of the sulphite dissolving pulp cooks have been found to be as follows;

1- for delignification about 22 Kcal/mol (Yorston, 1942; Morud, 1958)

2- for hemicellulose hydrolysis around 28 Kcal/mol (Konkin et al., 1959)

3- for cellulose hydrolysis about 28-44 Kcal/mol (Wise et al., 1952).

The action of acid sulphite liquors on hemicellulose removal during dissolving pulping corresponds to hydrolysis reactions of carbohydrates. These include the acidic hydrolysis of glycosidic bonds to form low molecular weight fragments (reduction of DP) leading to their ultimate solubility in the cooking liquor and degradation to oligomeric and monomeric sugars. The hydrolysis of hemicelluloses usually precedes that of cellulose. Investigations of spent sulphite liquor composition during the course of a softwood cook, showed that arabinose and galactose were the first sugars dissolved (Wenzl, 1970). Usually, this takes place at a temperature of about 100 ^{o}C. Xylose appears next followed by mannose and small quantities of glucose at a higher cooking temperature of 130 ^{o}C. This has been substantiated by analysis of the sugars in the side relief condensate (Wenzl, 1970). Arabinose and xylose constitute more than 60% of the total sugars found in the

pulping effluent stream. In softwoods, the arabinose originates from the acid labile arabinofuran (L-arabinofuranose) side unit on a 4-O-methylglucuronoarabinoxylan (Wenzl, 1970). Similarly, galactose originates from galactoglucomannan. In contrast, in the spent liquor, arabinose constitutes only 15-25% of the total sugars detected (Wenzl, 1970). The polymeric nature and reaction mechanism involving the carbohydrates has been studied by Hamilton (Hamilton, 1962). Furanosidic bonds are cleaved much more easily than those of pyranosides. This accounts for the rapid dissolution of arabinose in the sulphite cook. However, morphological factors prevail over chemical considerations, in that the rate of hydrolysis of glucomannan and xylan is about 15-30 times greater than that of cellulose, or about 4-5 times that predictable with model compounds.

In addition to glycosidic hydrolysis reactions, acetyl groups on the hemicelluloses are also hydrolyzed (split off) yielding acetic acid.

Other carbohydrate reactions taking place in the sulphite cooking liquor include conversion of aldoses into alpha- hydroxysulphonic acids, as well as aldonic acids. The alpha- hydroxysulphonic acids represent a large proportion of the loosely combined sulphur dioxide in spent liquors. Under sulphite pulping conditions xylose can be dehydrated to furfural, while glucose, at relatively high temperature, is decomposed to levulinic and formic acids from

hydroxymethylfurfural as the intermediate dehydration product. Dehydration reactions are favoured by low pH and high temperature such as are normally found in dissolving pulp-type cooking. Details of the decomposition reactions occurring in the spent liquor are shown elsewhere (Ingruber et al., 1970).

2.1.2 Prehydrolysis Kraft Pulping

Earlier, before 1950, dissolving grade pulps were produced exclusively by the acid sulphite pulping process (Rydholm, 1965). Although the sulphite process is still the method of choice for the production of certain types of dissolving pulps (Schempp, 1971), partly because of the recent remarkable decline in the number of sulphite mills and worldwide change in the raw material base, sulphite pulping for dissolving grade pulps has now been considerably replaced by the prehydrolysis kraft process (Simmonds et al., 1953; Richter, 1956). This process is vital for pulping resinous species such as pines, Douglas-fir, larches and non-woody materials (e.g., jute and kenaf) which are not suitable raw materials for pulping by the acid sulphite process.

In addition, the conventional kraft process is known to stabilize residual hemicelluloses against further alkaline reaction, whereas it is not possible to obtain acceptable quality dissolving pulp through subsequent treatment in the

bleach plant. In order to prepare a dissolving grade pulp by the kraft process, it is of importance to give the chips an acidic pretreatment before the alkaline pulping stage (Rydholm, 1965).

During prehydrolysis treatment, a considerable amount of material, in the order of 10% of the original wood, is removed in the acidic solution. Under these conditions (100-130 ^{o}C, 2 hr), the cellulose is fairly resistant to attack (Bernardin, 1958). However, the hemicelluloses have been greatly degraded to a much shorter chain length (i.e about 30% of the original DP) (Bernardin, 1958) and can, therefore, be easily removed in the subsequent kraft cook by means of peeling and other alkaline hydrolysis reactions. Primary delignification also takes place during the kraft cook. However, because of possible lignin condensation reactions during the prehydrolysis treatment, the residual lignin in unbleached prehydrolysis pulps is difficult to solublize during bleaching as compared to conventional kraft pulps (Rydholm, 1965).

Prehydrolysis in kraft pulping is assigned primarily as a pretreatment of chips to reduce not only the residual hemicellulose content in the final pulp, but also to provide a better pore opening in the fibre wall matrix in wood chips for easier penetration of the alkaline liquor (Rydholm, 1965). It is also worth mentioning that the prehydrolysis treatment is designed to afford xylose recovery from high hemicellulose content species. This could be of economical

value. While recovery of hemicellulose values from sulphite waste liquor by fermentation to ethanol and single cell protein is a well known process (Sjolander et al., 1938), similar processes based on kraft prehydrolysates although proposed by Sulzer (Switzerland) have not been implemented as yet. In conclusion, the final purified (bleached and alkali extracted) high alpha-cellulose pulp yield by prehydrolysis kraft pulping process is in the range of 32-36% from the original wood (Simmonds et al., 1953).

2.1.3 Bleaching

The object of bleaching in dissolving pulp manufacture is the removal of residual lignin, residual hemicelluloses and resins. For this reason, bleaching is considered to be a continuation of the cooking process. The bleaching operation used is completely dependent upon the characteristics of the cooked pulp and the end-use (e.g., cellophane, nitrate, acetate, etc.).

Bleaching results in removal of residual lignin and colouring materials from pulps. However, with the current conventional purification processes (i.e., pulping and bleaching operations), the bleached product contains hemicelluloses, ash, degraded cellulose and other impurities, which make it unsuitable for chemical conversion. Pulps intended for conversion to viscose or cellulose derivatives must also meet exacting specifications

with respect to alpha-cellulose content and viscosity. A low content of ash and resin is also desirable.

In current kraft pulping technology partial removal of hemicelluloses is achieved by prehydrolysis treatment. Purification of dissolving pulps by alkali treatment, and by additional steps in some cases, is carried out in connection with the bleaching operations. In these processes the attack on the cellulose and consequent yield losses, are severe. Jayme (1938) stated that an increase of the alpha-cellulose content of pulp from 88 to 96% by the hot alkali refining process will result in a weight loss of 25-30% of the pulp. Richter (1940) pointed out that the upper limit of alpha-cellulose obtainable by hot refining was 95%, although 97% alpha-cellulose could also be reached under harsher processing conditions. Those treatments, however, also led to considerable degradation of the cellulose chains and were associated with a decrease in viscosity.

Currently, chlorine compounds are in wide use in pulp bleaching. This is because they are most effective oxidizing agents (i.e selective delignification), offering a highly stable brightness and leaving a pulp relatively rich in alpha-cellulose content. On the other hand, pulp delignification proved to occur at the expense of the cellulose yield since significant hydrolytic degradation also took place on the cellulose fibres. In addition, these chlorine compounds are highly toxic and contribute to serious environmental problems (e.g., dioxins, and

adsorbable organic halides (AOX)). As a result millions of dollars have been spent on pollution control projects by the pulp and paper industry to eliminate toxic organochlorine compounds from bleach plant effluents.

Typical bleaching sequences for dissolving pulps are illustrated in Table 2.1 (Ingruber et al., 1983).

Table 2.1 Bleaching Sequences for Dissolving Pulps (Ingruber et al., 1983).

End Use	Cook Type	Bleach Sequence
Plastic Filler	Sulphite	CEDED, CEDPD,
	Prehydrolyzed Kraft	CEHDED
Nitration	Sulphite Prehydrolyzed Kraft	$CE^{O}CH$, $CE^{O}CH$
Textile Rayon	Sulphite Prehydrolysis Kraft	$CE^{O}CHD$, $CE^{O}HD$, $CE^{O}CH$ CEHDED CHEDED
Regular Acetate	Sulphite Prehydrolyzed Kraft	$CE^{O}CHD$, $CE^{O}HD$ ECEHD XDEDH, CEHXDED XCEHDED
Tire Cord	Prehydrolyzed Kraft	CEHXD, CEHDX, XDEDH, CHEDX XCEHDED
Plastics	Sulphite	$ECE^{O}HXD$

Where:

C	=	Chloronation
E^{O}	=	Pressure hot caustic extraction (HCE)
E	=	Mild (less than atmospheric HCE)
D	=	Chlorine Dioxide
P	=	Peroxide
X	=	Cold caustic extraction
H	=	Hypochlorite

It must be noted that nearly all bleaching sequences in the above series start with chloronation (C), a step now definitely linked with dibenzofurane and dioxin formation in bleach plants (Rotluff, 1989). At the same time it is realized that a compromise on this first bleaching stage (such as a C/D) is less acceptable for dissolving pulp purification because of the decisive effect of bleaching on the final quality of dissolving pulps. Thus the lack of suitable alternative bleaching sequences which can guarantee the same high purity as the CED, CEDED, CEH sequences will certainly put new pressures on dissolving pulp manufacturers to take a look at new pulp processing systems (e.g., solvent pulping and purification), known to be environmentally benign.

In line with these efforts, solvent purification of conventional chemical pulps could be a practical and desirable new approach in this respect. The specificity of treatment in removing lignin and low molecular weight polysaccharides offers higher pulp yield with high alpha-cellulose content. Residual colour in solvent purified pulp can easily be readily bleached with mild, less toxic oxidizing reagents such as hydrogen peroxide and chlorine dioxide. Further, solvent pulping is known to produce pulps of low extractives (Quinde, 1990) and ash content (Behera, 1985).

2.2 The Hydrogen Bond - Development

In this work, acetone is used as the solvent of purification due to the fact that acetone has the ability to penetrate into the cellulosic material and bring about considerable stereochemical changes. At the same time, acetone is classified as a dipolar aprotic hydrophilic solvent, i.e., HBA, (Frey-Wyssling, 1953; Bax et al., 1972; Isaacs, 1974)). Thus, the irreversible changes caused in hydrogen bonding of the cellulose by acetone - hydrogen bond disruption hypothesis - prompted the following review on hydrogen bond theory and practices.

2.2.1 Hydrogen Bonding - H-bond Donor/Acceptor Solvents

Hydrogen bonding is of significant importance for the stabilization and shape of large biological molecules in living organisms such as proteins, nucleic acids, and carbohydrates (Reichardt, 1988; Jeffrey et al., 1991). A general definition of the hydrogen bond is that when a covalently bound hydrogen atom forms a secondary bond to another atom, the second bond is referred to as a hydrogen bond (Joesten et al., 1974).

The interaction of different molecules (e.g., solute-solvent) in a system at certain reaction conditions might lead to changes in rate of the reaction and structure of the substrate. Consequently, these structural

(stereochemical) changes have a considerable impact on the modification of the hydrogen bonding of the substrate. In the pulp industry, mercerization (e.g., 18-30% NaOH) is used for the provision of accessible cellulose. In other words, the accessibility of cellulose can explicitly be understood as a new spatial rearrangement of the hydroxyls of the sugar residues, i.e., new positioning of hydrogen bonding within the cellulosic system. Thus, hydrogen bond disruption by acetone represents a major hypothesis in this study.

The concept of hydrogen bonding has been outlined in 1919 by Huggins (1971). The first publication on hydrogen bonding - applied to the association of water molecules - was in 1920 by Latimer and Rodebush (1920). However, earlier than this publication hydrogen bonding was pointed out to be the cause of association in ammonium salts whereby a proton links the ammonia molecule to the ion (Werner, 1903).

A hydrogen bond is formed by interaction between the R - X - H and :Y - R according to the following equation

$$R - X - H + :Y - R = R - X - H...Y - R$$

where:

R - X - H is the proton donor and :Y - R makes available an electron pair for the bridging bond. In this context hydrogen bonding can be regarded as a preliminary step in a Bronsted acid-base reaction which leads to a dipolar reaction product R - X...H - Y - R. X and Y are atoms of

higher electronegativity than hydrogen such as C, N, P, O, F, etc. Both inter- and intramolecular hydrogen bonding is possible, the latter when X and Y belong to the same molecule.

The most important electron pair donors (EPD) i.e hydrogen bond acceptors (HBA) are the oxygen atoms in ethers, carbonyl compounds, as well as nitrogen atoms in amines and N-heterocycles. Amides, hydroxy-, amino- and carboxyl groups are the most important proton donor groups (HBD). Strong hydrogen bonds are formed by the pairs O - H...O, O - H...N, and N - H...O, weaker ones by N - H...N, and weakest by Cl_2C - H...O, and Cl_2C - H...N (Reichardt, 1988). However, very strong hydrogen bonds are considered to be developed by carboxylic acids (13 Kcal/mol) (Biermann, 1993). Thus, the bond dissociation enthalpy for normal hydrogen bonds is between 1 to 10 Kcal/mol (Biermann, 1993)

When two or more equal molecules associate, homo-intermolecular hydrogen bond is formed as shown in Fig. 2.2.1.1. On the other hand, the association of different molecules for instance R - O - H...N is called a hetero-intermolecular hydrogen bond.

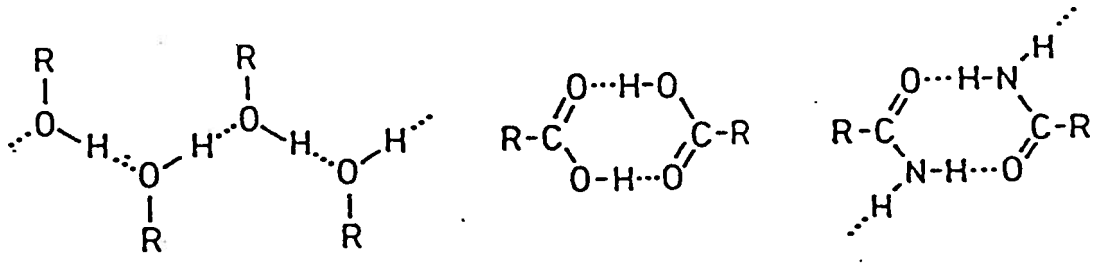


Figure 2.2.1.1. Homo-intermolecular hydrogen bond in alcohols, carboxylic acids and amides (the hydrogen bonds are denoted by dotted lines).

Hydrogen bonds can be either intermolecular or intramolecular. Both types of hydrogen bonds can be broken. For example 2-nitrophenol breaks its intramolecular hydrogen bond to form an intermolecular one with electron pair donor (EPD) solvents (e.g, anisole, hexamethylphosphoric acid triamide - HMPT etc.), see Fig. 2.2.1.2.

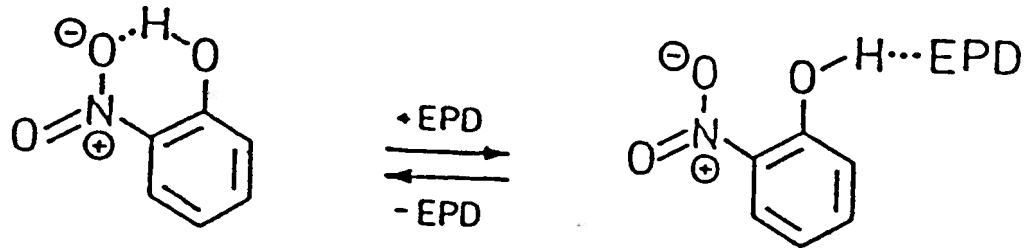


Figure 2.2.1.2. 2-nitrophenol breaks its intramolecular H-bond to form an intermolecular one.

Hydrogen bonds, generally, have the following structural and spectroscopic characteristics (Schuster, 1976);

1- The distance between the neighbouring atoms involved in the hydrogen bond (X and Y) are smaller than the sum of their van-der-Waals radii.
2- The X - H bond length is increased and hydrogen bond formation causes its IR stretching mode to be shifted towards lower frequencies.
3- The dipolarity of the X - H bond increases on hydrogen bond formation, in turn, this gives rise to a larger dipole moment of the complex than expected from vectorial addition of its dipolar components R - X - H and Y - R.
4- Due to reduced electron density at protons involved in hydrogen bonds, they are deshielded, resulting in remarkable downfield shifts of their ^{1}H-NMR signals.
5- In heteromolecular hydrogen bond, a shift of the Bronsted acid/base equilibrium R - X - H...Y - R = R - X...H - Y - R to the right hand side with increasing solvent polarity is found.

Similar conclusions on the hydrogen bond energy were already drawn by Coulson at the symposium held in Ljubljana in (1957). He found that the theoretical net hydrogen bond energy for ice develops as the result of the following four terms, each being of the order of magnitude of the bond energy itself. The contributions are as follows:

a- electrostatic	+6 Kcal/mole/bond
b- delocalization	+8 Kcal/mole/bond
c- repulsive overlap of electron clouds	-8.4Kcal/mole/bond
d- dispersion	+3 Kcal/mole/bond
Total	+8.6Kcal/mole/bond

Coulson noted that the experimental value for ice was +6.1 Kcal/mole/bond. He attributed the difference between the experimental and the theoretical values to the variation in length of the hydrogen bond.

Regarding the nature of the forces in the hydrogen bond (Vinogradov et al.,1971; Kortum, 1972), the hydrogen bond can be considered as dipole-dipole or as a resonance interaction. Since hydrogen bonding prevails only when the hydrogen bond is bound to an electronegative atom, the first speculation concerning the nature of the hydrogen bond is that it consists of a dipole-dipole interaction such as R - X - H...Y - R (Vinogradov et al., 1971. Kortum, 1972). This assumption is supported by the fact that the strongest hydrogen bond is formed in pairs in which the hydrogen is bound to the most electronegative element (e.g., F - H...F, H=155 KJ/mol). The greater strength of the hydrogen bond compared with nonspecific dipole-dipole interaction is due to the much smaller size of the hydrogen atom, relative to any other atom. This allows it to approach another dipole more easily. In conclusion this dipole assumption accounts for the linear geometry of the hydrogen bond, because a linear arrangement maximizes the attractive forces and minimizes the repulsive ones (Reichardt, 1988).

Furthemore, the shortness of hydrogen bonds indicates considerable overlap of van-der-Waals radii and this would give rise to repulsive forces. Also the existence of symmetrical hydrogen bonds of the type F...H...F can not be

explained in terms of electrostatic modelling. When the X - Y distance is extremely short, an overlap of the orbitals of the X - H bond and the electron pair of :Y could lead to a covalent interaction (Simmering, 1964) as shown below:

$$R - X - H...Y - R = R - X...H - Y - R$$

According to the above equation, this situation can be described by two contributing protomeric structures, which differ only in the position of the proton.

Solvents containing proton-donor groups are called protic solvents or HBD (Parker, 1962). Solvents having proton-acceptor groups are designated HBA solvents (Taft et al., 1976). The abbreviations HBD and HBA refer to hydrogen bond donor and acceptor, respectively and not to electron pairs involved in hydrogen bonding.

Aprotic solvents are those which are without proton-donor groups.

Typical protic solvents (HBD) are water, ammonia, alcohols, carboxylic acids and primary amides. On the other hand dipolar aprotic (HBA) solvents are ethers, amines, ketones, and sulphoxides (i.e., CH_3CN, CH_3NO_2, $(CH_3)_2CO$, $(CH_3)_2SO$).

In the case of protic solvents (HBD), the solute acts as HBA - base and the solvent as HBD - acid while for dipolar solvents the reaction is reversed (Taft et al., 1976).

2.2.2 Hydrogen Bonding in Cellulosic Material

The hydroxyl groups of the cellulose units involved in hydrogen bonding with neighbouring ones and with those of adjacent chains, have been the centre of investigations for many years. Cellulosic materials from various sources and treatments differ considerably in their degree of crystallinity, as evidenced by a large number of investigative methods. Since the super-structure of cellulose (i.e., hydrogen bonding system) has important consequences for the pulping, purification and papermaking processes as well as for the cellulose reactivity in the end use, this part of the review will focus on it at some length.

In 1937, Meyer and Misch (1937) in their elucidation of the supermolecular structural nature of cellulose proposed a model of a unit cell. It is illustrated in Fig. 2.2.2.1. The arrangement of the crystalline region was deduced from X-ray data. The dimensions of their monoclinic unit cell are as follows:

$a = 8.3$ Å
$b = 10.3$ Å
$c = 7.9$ Å
$\beta = 84^{o}$

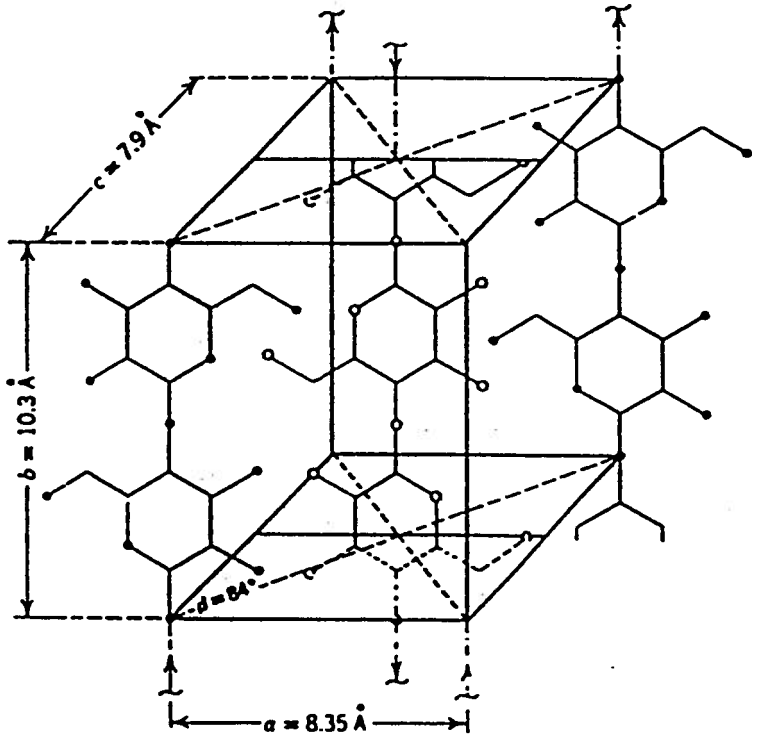


Figure 2.2.2.1. Unit cell of native cellulose according to Meyer and Misch (Meyer et al., 1937).

Meyer (1942) has also been able to give, in his book about natural and synthetic polymers, different structures for Celluloses I, II, III and IV as shown in Fig. 2.2.2.2.

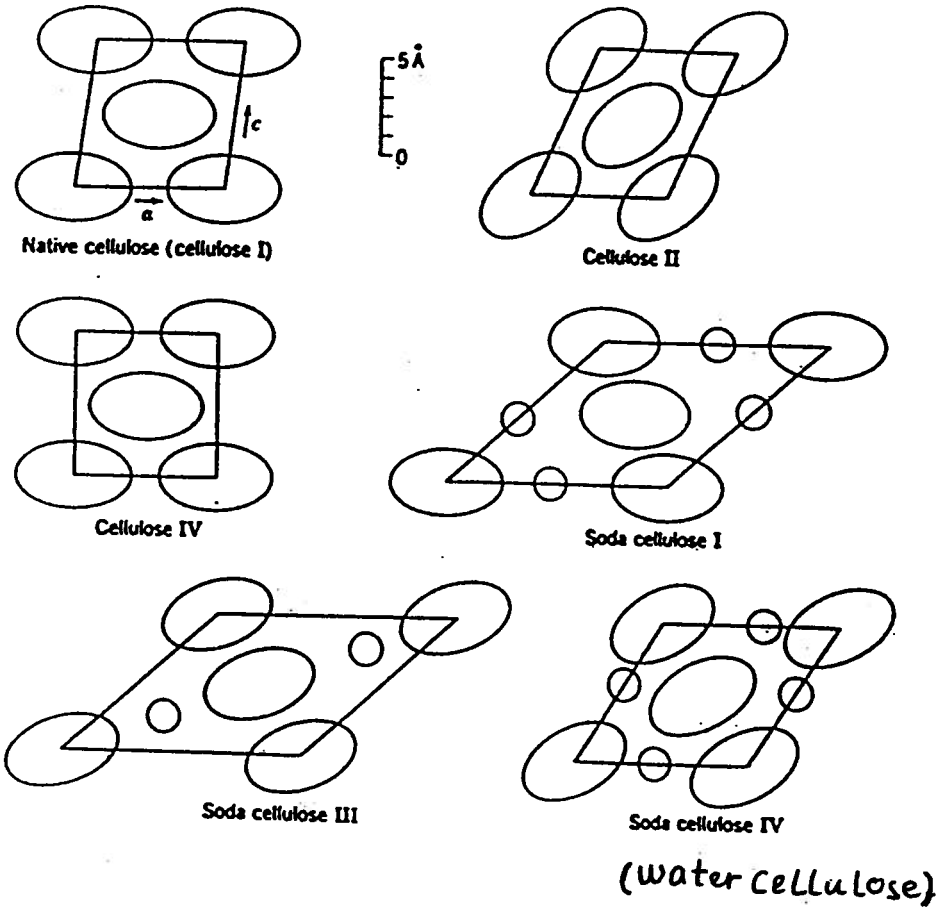


Figure 2.2.2.2. Schematic cross-sections of cellulose chains according to Meyer (1942) - ovals are glucose rings, and small circles are soda molecules.

It is of importance to point out that in the late forties Hermans (1949), in his book, "Physics and Chemistry of Cellulose Fibers", published diagrams illustrating many possibilities for intra-chain hydrogen bonds in the solid state. This was the first attempt in this area. Fig. 2.2.2.3

shows the possibility of intra-chain hydrogen bond in the cellulose.

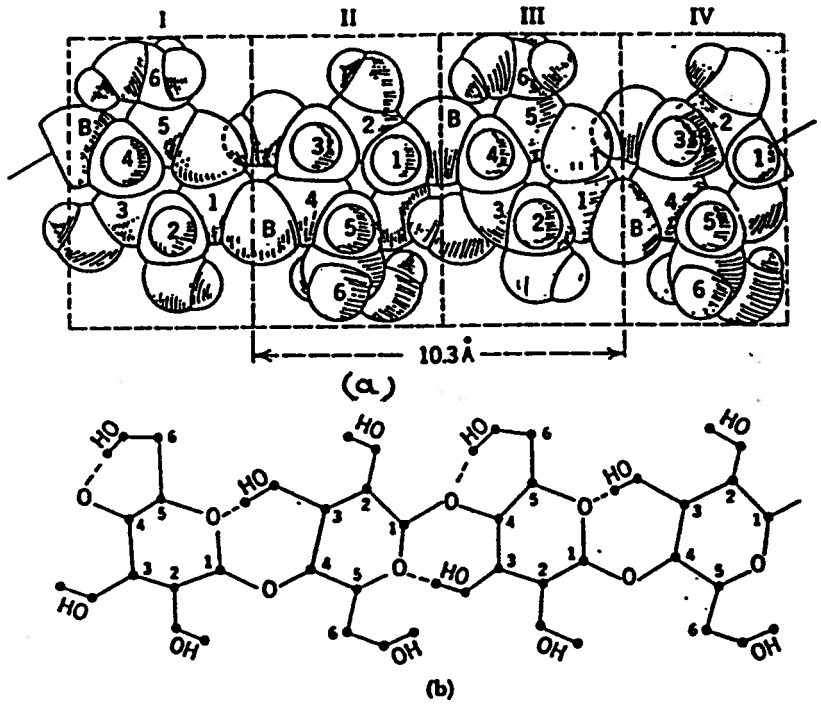


Figure 2.2.2.3. Intra-chain hydrogen bonds in cellulose (Hermans, 1949).

Later in 1959, particularly after Hermans and other workers (Petitpas et al, 1956; Carlstrom, 1957; Honjo et al, 1958) postulation of intra-molecular hydrogen bonds imposing a twist in the molecules (Liang and Marchessault, 1959; Liang et al., 1959) questioned the Meyer and Misch unit cell because it is unable to show this twist. Based on their infra-red spectral analysis, they proposed the crystal

lattice model for Cellulose I, which demonstrates both intra- and intermolecular hydrogen bonds (see Figs. 2.2.2.4 and 2.2.2.5).

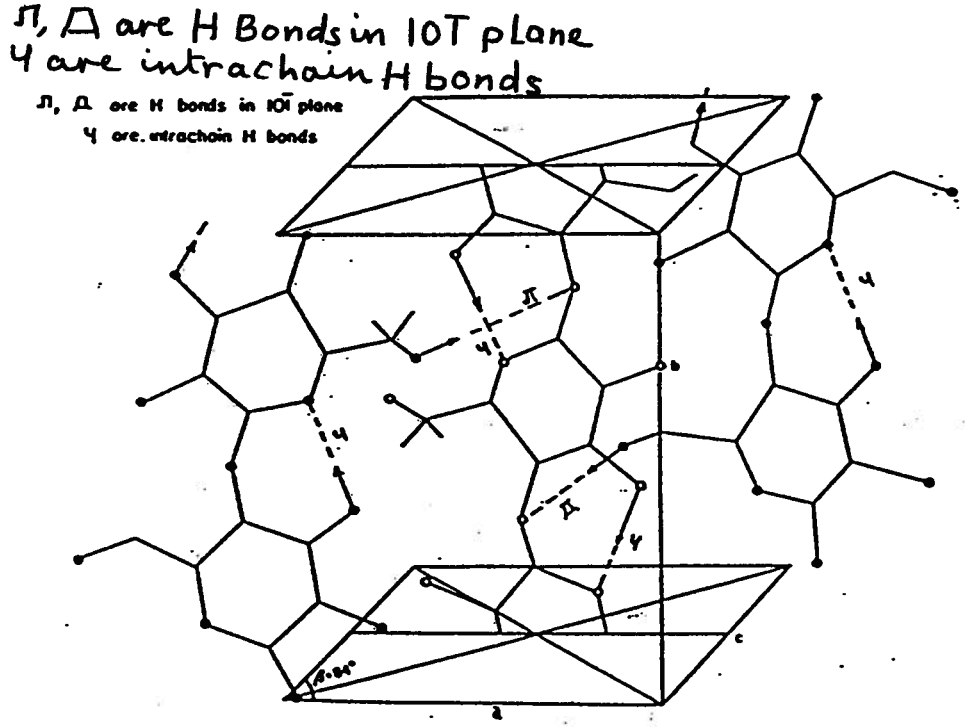


Figure 2.2.2.4. View of chain segments in cellulose I crystal (Liang et al., 1959).

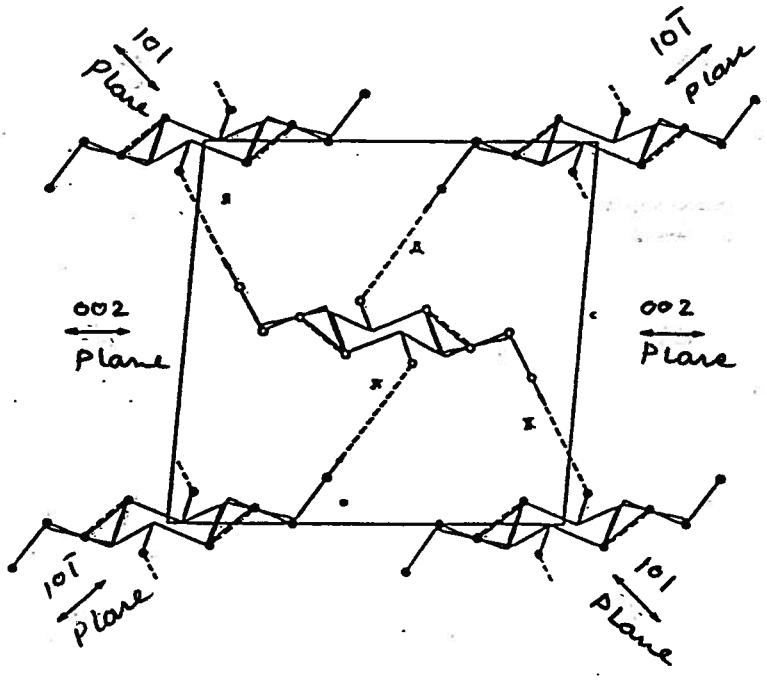


Figure 2.2.2.5. End view of cellulose chains in a unit cell (Liang et al., 1959).

The intramolecular hydrogen bonds are responsible for the stiffness and rigidity of the cellulose molecule and for the stabilization of the two-fold helical structure. In addition, this intramolecular hydrogen bonding also sustains the 1.03 nm crytallographic repeating distance which is in accord with the conformational energy considerations in relation to bond rotations for the C-1 - O-1 and the C-4 - O-4 glucosidic bonds (Sarko, 1978).

The relative positioning of the cellulose molecules with respect to one another in the unit cell determines the possibility for the formation of intermolecular hydrogen bonds. The development of van-der-Waals forces between the

neighbouring molecules inside the same crystal lattice plane is also influenced by this positioning. Intermolecular hydrogen bonds are a significant factor for the internal packing of the cellulose chains in the crystal lattice. The density of the interchain hydrogen bonding inside and between the planes affects to a great extent the swelling action and the accessibility of the crystalline domains.

Later, Nishimura and Sarko (1987) studied the conversion of Na-cellulose I from the cellulose I crystal structure. The analysis of crystallite sizes of cellulose I and alkali cellulose I during the transformation indicated that the change took place in two steps; the first is a fast step and resulted in conversion of 65% of cellulose I into Na-cellulose I. The crystallite sizes for cellulose I and alkali cellulose I were 62 and 35 Å, respectively. At the second step it was observed (Nishimura et al., 1987) that the conversion process was slow and the crystallite size of cellulose I decreased gradually until disappearance, while that of Na-cellulose I increased steadily to reach 50 Å. It was also noted (Nishimura et al., 1987) that during mercerization a simultaneous change in unit cell parameters of cellulose I took place. In this communication, a mechanism for mercerization (see Fig. 2.2.2.6), in which the conversion process was assumed to start in the amorphous zone of the cellulose, was proposed (Nishimura et al., 1987).

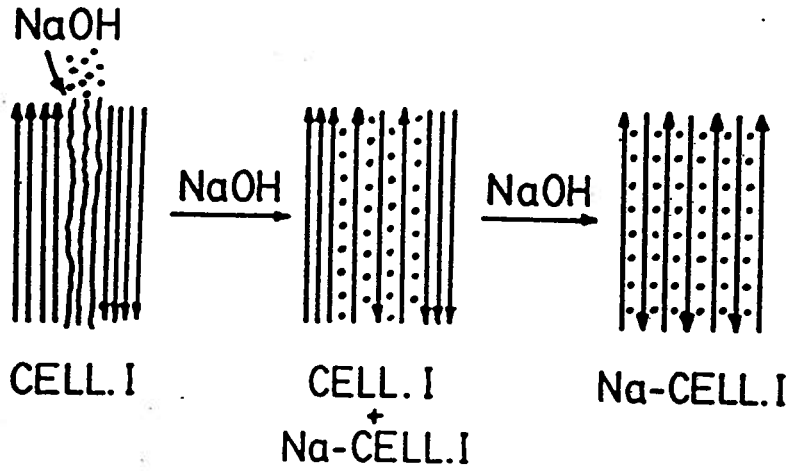


Figure 2.2.2.6. The two-part mechanisms of conversion of cellulose I into Na-cellulose I (Nishimura et al., 1987).

Currently, for obtaining a purified cellulose with suitable accessibility, molecular uniformity and improved dimensional stability mercerization is usually carried out on bleached pulps. During this process, both the inter- and intramolecular H-bonds are weakened. The transformation of native cellulose to mercerized cellulose (from cellulose I to II) is an irreversible exothermic phenomenon because of the modification of the crystalline network (Petitpas, 1948; Petitpas et al., 1950; Lal, 1974).

General procedures for mercerization vary depending on the aim to be achieved. Mercerization is usually carried out at NaOH concentrations of 18-25%, for different time

intervals and at different temperatures. In this process the treated pulp is subjected to degradation and results in an appreciable loss of fibrous material.

To attain accessibility, molecular uniformity, enhancement of crystallinity and to reduce such losses solvent purification could be the practical answer in this respect.

2.3. Solvent Effect on Stereochemistry and Mechanism

In this work the influence of acetone as a solvent on the structural transformations (i.e., stereochemical alterations) may be quite profound. The substantial physicochemical changes which are expected to be brought about on both soluble and insoluble portions of cotton by acetone (i.e., as a major volume fraction of the solvent composition) could well be demonstrated in the following chapter (Results and Discussion).

It has been verified (Tchoubar, 1966; Lemieux et_al., 1968; Stoddart, 1971; Amis, 1966; Reichard, 1988) that solvents have considerable effect on the mechanism and stereochemistry of the reaction course. In other words, the solvent can influence both the rate and the mechanism of a reaction. Lemieux et al (1968) studied the changes in conformational equilibria of the methyl 2-deoxy-β-L- and 3-deoxy-β-L-erythro-pentopyranosides by dissolving them in different solvents such as acetone, chloroform,

dimethylsulphoxide, water etc. It was noted (Lemieux et al, 1968) that marked changes in optical rotation had taken place. These changes were attributed to the specificity of solvation of the substrate by different solvents. This specific solute-solvent solvation has brought about some change in electron density of the system, i.e., the change in the electronic state of the oxygen atoms involved in the hydrogen bonds with a solvent appears to have a considerable influence on the conformational equilibrium. Using nuclear magnetic resonance and polarimetry techniques Lemieux et al. (1969) studied the effect of dimethylsulphoxide (DMSO) concentration on the specific rotation at 25 ^{o}C of solutions of methyl 3-deoxy-β-L-erythro-pentopyranoside and 1,2-O-isopropylidene 4-O-methyl-β-D-sorbopyranoside in ethylene dichloride, see Fig. 2.3.1. It was noted (Lemieux et al., 1969) that with increase of DMSO the numerical rotation of sugar derivatives was increased and a gradual change in conformation had taken place. It was concluded (Lemieux et al., 1969) that the engagement of the hydrogen of hydroxyl groups in a hydrogen bond with a base (i.e., DMSO) results in a polarization of the H-O bond in the direction of the oxygen atom. This makes the oxygen atom a relatively better hydrogen acceptor in hydrogen bond formation. It was also added (Lemieux et al., 1969) that the dipole interaction between two opposing axial hydoxyl groups, both bonded to solvent, is much greater than when both of the hydroxyl groups are acylated by electron withdrawing acyl groups.

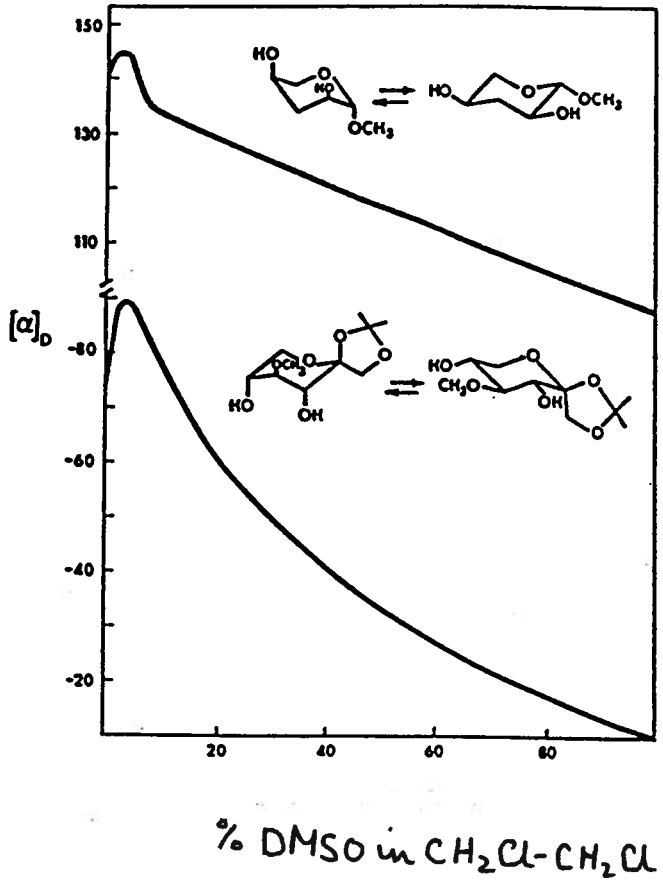


Figure. 2.3.1 Effect of increasing concentration of dimethylsulphoxide (DMSO) on the specific rotations at 25 °C of solutions (about 1%) of methyl 3-deoxy-β-L-erythro-pentopyranoside and of 1,2-O-isopropylidene 4-O-methyl-β-D-sorbopyranoside in ethylene dichloride (Lemieux et al., 1969).

Note: the publication error in Fig. 2.3.1 regarding the structure of 1,2-O-isopropylidene 4-O-methyl-β-D-sorbopyranoside, where the O-isopropylidene group is linked to C-1 only. However, the appropriate formation of the dioxolane ring is on both carbons in the position 1,2 of the sugar ring.

The importance of the nature of the solvent has also been emphasized by Stoddart (1971) in his informative book "Stereochemistry of Carbohydrates". The anomeric effect is large in solvents of low dielectric constant (e.g., carbon tetrachloride) and small in solvents of high dielectric constant (e.g., water) (Stoddart, 1971). However, the effect of the dielectric constant on the anomeric effect and hence on conformational equilibria, is often found not to be remarkable, such as the solvation effects involving hydrogen bonding. For example, methyl 3-deoxy-β-L-erythro-pentopyranoside exists predominantly as the C-1 conformation in solvents such as chloroform which do not form strong hydrogen bonds with hydrogen atoms of the hydroxyl groups. In this case, the C-1 conformation is stabilized by an intramolecular hydrogen bond involving the syn-axial hydroxyl groups. On the other hand, when hydroxyl groups are engaged in hydrogen bonding with solvents which are strong hydrogen acceptors such as pyridine or dimethylsulphoxide (DMSO) 1-C conformation is favoured (Stoddart, 1971).

Amis (1966) noted that the properties of the solvents such as solvation, nucleophilicity, electophilicity, cohesion, ionising power, influence on hydrogen bonding, etc., have impact on both rate and mechanism of the reaction. For instance, in the hydrolysis of secondary and tertiary alkyl halides two mechanisms of substitution were identified. These were a bimolecular mechanism involving attack by the hydroxide ions, and a unimolecular mechanism

kinetically dependent on the ionization of the alkylhalide (Amis, 1966). If R represents the alkyl radical and X represents the halide, these mechanisms can be illustrated as follows:

$$RX + OH^- = ROH + X^- \quad \text{bimolecular}$$

$$RX = R^+ + X^-$$

followed by

$$R^+ + OH^- = ROH \quad \text{(instantaneously), unimolecular}$$

The changeover was attributed to the reaction medium, concentration, and the alkyl group involvement (Amis, 1966).

Tchoubar (1966) ascertained that the difference between the electronegativities of oxygen and carbon and the mobility of Π electrons results in the fact that the carbonyl group is strongly polarized. In line with the high polarisability of the pi bond, this polarity is the cause of many heterolytic reactions taking place at the carbonyl group. In contrast to carbonyl groups in unsaturated hydrocarbons, the polarisation direction of the C=O group is independent of the nature of the substituents taken by the carbon atom, i.e., in the case of addition of polar molecules to the carbon-oxygen double bond, the negative end of the molecule attaches itself to the carbon, while the positive one to the oxygen (Tchoubar, 1966).

Regarding the literature reviewed on the importance of hydrogen bonding and the solvent effect on this area, it is

likely that acetone has the ability to penetrate into the cellulosic material under suitable conditions. At the same time acetone is classified as a dipolar aprotic protophylic solvent (HBA). This means, the high ratio of acetone in the solvent composition (> 80%) might bring about the following consequences; predominance of acetone in the reaction with cellulose, and stereochemical changes. Hence, both inter- and intramolecular hydrogen bonds are expected to be affected due to these reactions.

On the other hand, it is been known that ketals can be prepared by condensation of sugars with acetone in the presence of an acid catalyst (Stanek et al., 1963). Depending on the stereochemistry of these sugar derivatives, pentoses or hexoses form either five- or six-membered acetal ring which can easily be distinguished by NMR, GC, and GC-MS (Buck et al., 1965; Kiso et al., 1976). Thus reaction of acetone with cellulose is anticipated to offer similar isopropylidene derivatives as with sugars.

2.4 Isopropylidene Chemistry - Formation of Ketals

It has been known for some time that isopropylidene acetals can be formed by condensation of sugars with acetone in the presence of an acid catalyst (Stanek et al., 1963). Throughout the course of numerous studies in this field, many workers, using different techniques such as GC-MS and NMR have repeatedly proven that the hydroxyl groups of

sugars have been replaced by isopropylidene ones (Stanek, 1963). The formation of isopropylidene groups on the sugar ring of the soluble portion (solution) and insoluble one (solid state) of the cellulose is one of the major hypotheses in this work.

A ketal is an acetal derived from a ketone. Isopropylidene ketals are prepared by condensation of sugars with acetone in the presence of a Lewis acid catalyst. Five-membered fused ring systems are preferred and adjacent cis-hydroxyls are necessary (Stanek et al., 1963). Mild hydrolysis will cleave ketals fairly easily. There is enough difference in stability between the ketals involving the primary alcohol function (C-6) and that at C-1 so that selective acid hydrolysis is possible.

It is known that the reaction of carbonyl compounds with sugar alcohol in the presence of acid catalyst may yield acetals or ketals (Stanek et al., 1963). This reaction is not restricted to monohydric alcohols, but proceeds with polyol to form a five-membered dioxolane or six-membered 1,3-dioxane ring.

The first reaction of this type was carried out by Wurtz (in Stanek et al., 1963), who prepared 2-methyldioxolane by heating ethylene glycol with acetaldehyde in the presence of hydrogen chloride, (see Fig. 2.4.1).

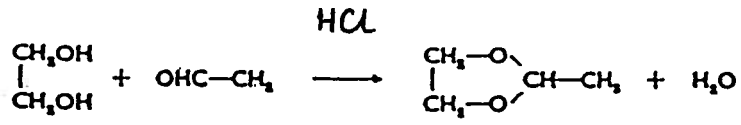


Figure 2.4.1. Preparation of 2-methyldioxolane.

These condensations are acetalized by acidic dehydrating agents such as sulphuric acid, anhydrous zinc chloride , etc. This reaction was introduced into sugar chemistry by Fischer (1895) who was guided by the presence of vicinal hydroxyl groups in the molecule of sugar alcohols to the idea of condensing these groups with acetone. Thus, the condensing effect of hydrogen chloride was utilized to prepare isopropylidene derivatives of saccharides, which together with other alkylidene derivatives assume a remarkable position mainly from the view point of synthesis.

Besides the isopropylidene derivatives of sugars, a long line of other condensation products of carbonyl compounds were studied. In this way methylene derivatives have been prepared by means of aldehyde and ethylidene or benzylidene derivatives by means of acetaldehyde or benzaldehyde, respectively. Cyclohexylidene, furfurylidene, etc. derivatives are likewise known as products of the

reaction between a sugar and cyclohexene, furfural or other oxo-compounds (Stanek et al., 1963).

The most significant, and also most thoroughly investigated products formed by condensation of carbonyl compounds with sugars, are the isopropylidene derivatives, designated in the older literature as acetone sugars. They are prepared in a similar way as other alkylidene derivatives, namely by the reaction of acetone with the sugar in the presence of condensation agents, (i.e., an acid catalyst).

At the most two isopropylidene groups can be introduced into the molecule of pentose or hexose sugars. A condition for the entrance of these groups into the sugar molecule, apart from a few exceptions such as xylose or sorbose, is the presence of vicinal cis-hydroxyl groups. It is clear from the given examples of D-glucose and D-mannose that the furanoid form of both sugars permits the introduction of two acetone molecules. Only pyranoid structures can in this case form monoisopropylidene derivatives.

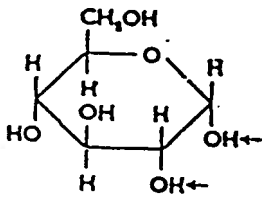


Fig. 2.4.2. α-D-glucose (pyranoid form)

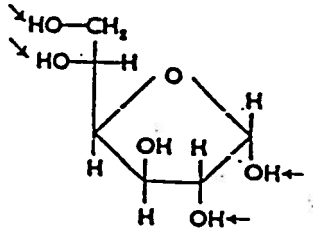


Fig. 2.4.3. α-D-glucose (furanoid form)

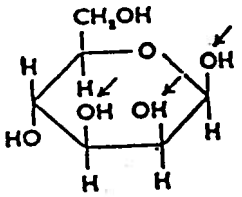


Fig. 2.4.4 β-D-mannose (pyranoid form)

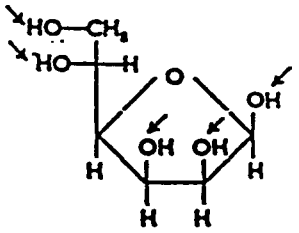


Fig. 2.4.5 β-D-mannose (furanoid form)

Note: the arrows indicate those hydroxyl groups at which a dioxolane ($C_3\ HO_2$) ring can be formed.

On the basis of the established structures of isopropylidene derivatives of various sugars, the empirical rule has been postulated that the sugar reacts with acetone always in such a structure as to permit the formation of a di-isopropylidene derivative. This rule is in agreement with the fact that the pyranoid structures of arabinose, galactose or fructose present no obstacle to the introduction of two isopropylidene groups and that consequently the di-isopropylidene derivative of these sugars exists in the form of pyranose.

The existence of various types of isopropylidene compounds of sugars and their stability are well established. From this it follows for instance that the dioxolane ring on furanose structures is relatively stable, whereas the ring attached to the side-chain is more labile and preferentially hydrolyzed and hydrogenolised (as exemplified by the conversion of 1,2:5,6-di-O-

isopropylidene-D-glucofuranose into 1,2-O-isopropylidene-D-glucofuranose).

Another result of conformation analysis is that in the bicyclic system composed of two five membered rings which contains the least number of endo-substituents, formation of the isomer is always stable. For this reason, 2,3-O-isopropylidene-D-ribose is favoured over 1,2-O-isopropylidene-D-ribose. Some inconsistencies, however, have as yet not been explained. For example, that the di-O-isopropylidene derivative of D-galactose has a pyranoid structure which is obviously more stable than the thus unprepared but theoretically likewisely advantageous 1,2:5,6-di-O-isopropylidene-D-galactofuranose.

The furanoid or pyranoid arrangement of isopropylidene derivatives of sugars is unambiguous in those cases in which it is predetermined. For instance, methyl-α-D-glucopyranoside (see Fig. 2.4.6) can not assume a furanoid structure during condensation. In this case, however, the formation of a six-membered 4,6-dioxane ring is encountered which otherwise is rare among isopropylidene derivatives.

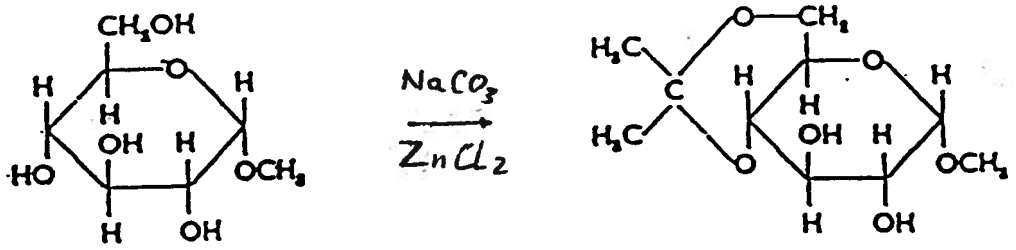


Figure 2.4.6. The formation of a six-membered 4,6-dioxane ring.

Considering these stereochemical effects it must be emphasized that the question of which form of the furanoid or pyranoid arrangement of an isopropylidene, or other alkylidene sugar compound, is favoured depends on the form the sugar existed prior to its reaction with the carbonyl compound.

2.4.1 Derivatives of Pentoses

Isopropylidene derivatives of all common pentoses are known (Stanek et. al, 1963) namely 1,3-O-isopropylidene-D-ribofuranose, 1,2:3,4-di-O-isopropylidene-D-arabinose, 1,2:3,4-di-O-isopropylidene-L-arabinose, 1,2:3,5-di-O-isopropylidene-D-xylose, 1,2:3,5-di-O-isopropylidene-α-D-lyxofuranose.

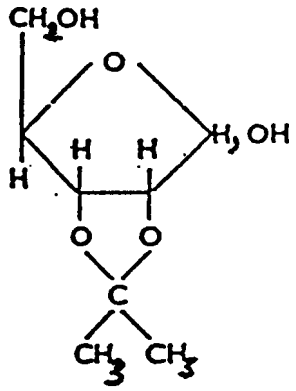


Figure 2.4.1.1. 2,3-O-isopropylidene-D-ribofuranose.

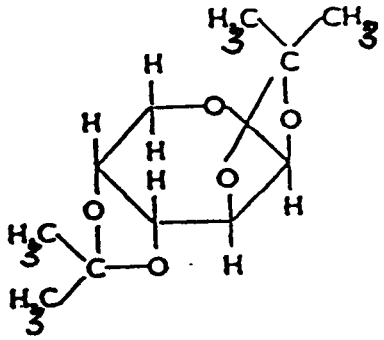


Figure 2.4.1.2. 1,2:3,4-di-O-isopropylidene-D-arabinose.

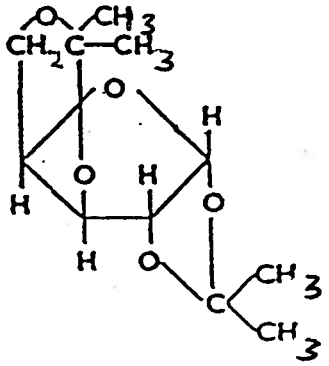


Figure 2.4.1.3. 1,2:3,5-di-O-isopropylidene-D-xylose.

By partial hydrolysis, the di-isopropylidenes of D and L-xyloses can be easily converted into corresponding 1,2-O-isopropylidene-D-L-xylofuranoses respectively. The 5-deoxy derivatives of these compounds have also been prepared. Careful isopropylidenation of arabinose may also lead to 3,4-O-isopropylidene-D or 3,4-O-isopropylidene-L-arabinopyranose. Moreover, the 5-deoxy-1,2-O-isopropylidene derivative was indirectly prepared from a 5-substituted L-arabinose.

Di-isopropylidene derivatives of pentoses containing a free aldehyde group were also formed. Thus, 2,3:4,5-di-O-isopropylidene-D-arabinose was obtained by oxidation of 1,2:3,4-di-O-isopropylidene-D-mannitol with tetra-acetate (Wiggins, 1946) or 3,4:5,6-di-O-isopropylidene-D-mannitol with periodate (Bourre et al., 1952). The same substance can be obtained from 2,3:4,5-di-O-isopropylidene-D-arabinose diethyl dithioacetal by action of mercuric chloride (Gatzi et al., 1938). Further 2,3:4,5-di-O-isopropylidene-D-xylose can be formed by the oxidation of 1,2:3,4-di-O-isopropylidene-L-iditol with sodium periodate (Bourre et al., 1952).

2.4.2 Derivatives of Aldohexoses

The formation of cyclic acetals or ketals comes as a result of the condensation of 1,2 and 1,3-diols with aldehydes and ketones if the diol is itself cyclic, the

acetal or ketal forms only when two OH groups are cis, for geometric reasons.

Since aldohexoses are polyhydroxy compounds, they also undergo similar reactions. The reaction is in general complicated by the fact that the ring size in the product is not the same as in the free sugar. This actually takes place when the more stable pyranose form does not have cis vicinal hydroxyl groups, but the furanose form does. Thus galactose reacts with acetone to give the diketal shown below because, in the Â form, which is present under acidic conditions of the reaction, there are two pairs of vicinal OH groups to yield the diacetal.

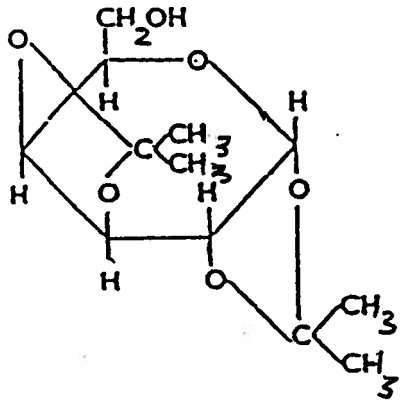


Figure 2.4.2.1. The formation of 1,2:3,4-di-O-isopropylidene-α-D-galactopyranoside.

On the other hand, α-glucose reacts by way of the furanose form, since this is the only glucose structure possible with a pair of cis-hydroxyl groups, as follows:

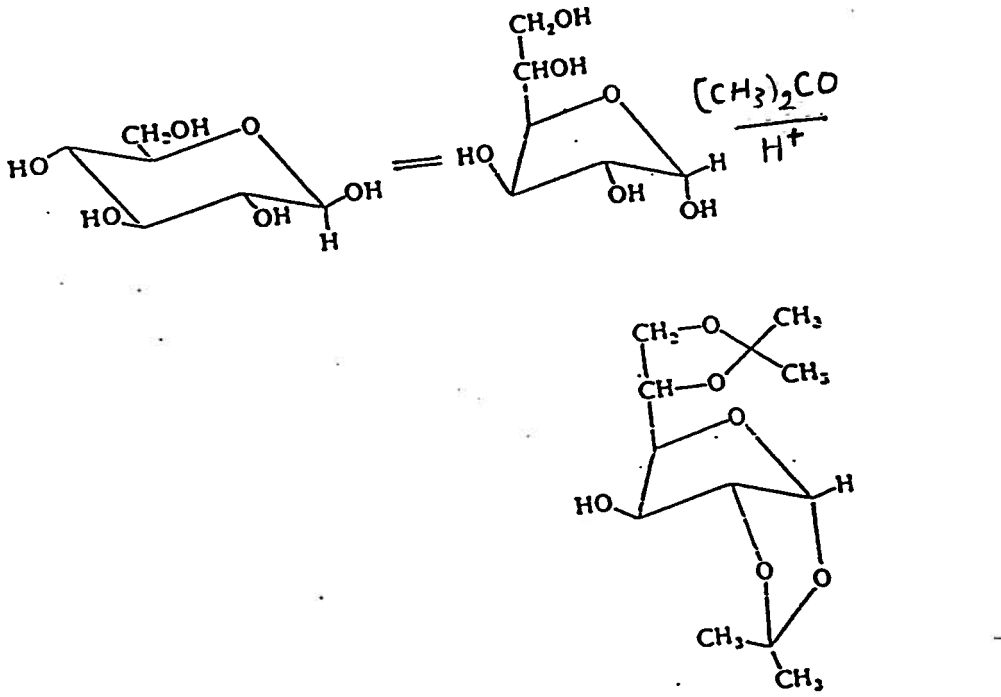


Figure 2.4.2.2. The formation of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose.

Partial hydrolysis of 1,2:5,6-di-O-isopropylidene-D-glucofuranose (see Fig. 2.4.2.3) yields 1,2-O-isopropylidene-D-glucofuranose, as:

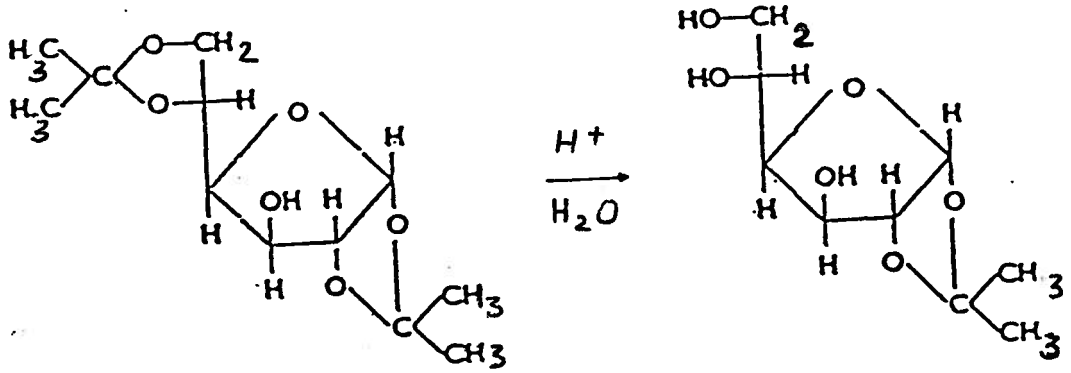


Figure 2.4.2.3. Partial hydrolysis of 1,2:5,6-di-O-isopropylidene-D-glucofuranose.

This removal of one of two isopropylidene groups from the molecule of 1,2:5,6-di-O-isopropylidene is made possible by the fact that the 5,6-O-isopropylidene group is accessible to hydrolysis more readily than the O-isopropylidene group in the position 1,2. On the other hand, the reverse conversion of 1,2-O-isopropylidene-D-glucose into its di-isopropylidene derivative proceeds readily and can be effected by means of anhydrous copper sulphate in acetone (Ohle, 1922).

An isomeric di-O-isopropylidene-D-glucose with the isopropylidene residue in the position 1,2:3,5, however, is also known (Fig. 2.4.2.4). Derivatives of this substance are formed by the reaction of acetone with 6-substituted derivatives of D-glucose, as:

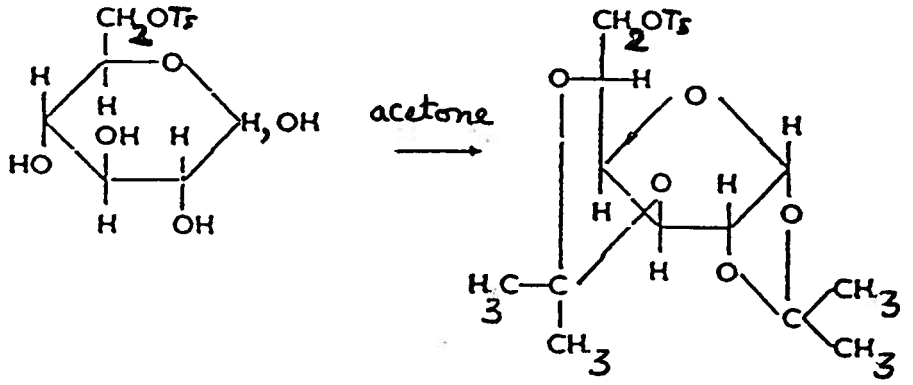


Figure 2.4.2.4. Formation of an isomeric di-O-isopropylidene-D-glucose in the position 1,2:3,5.

The same type of compound is obtained by the action of phosphorous pentachloride upon 1,2:5,6-di-O-isopropylidene-D-glucofuranose, which instead of the expected 3-chloro-3-deoxy derivative gives the 6-chloro-6-deoxy derivative with simultaneous rearrangement of the isopropylidene groups (see Fig. 2.4.2.5):

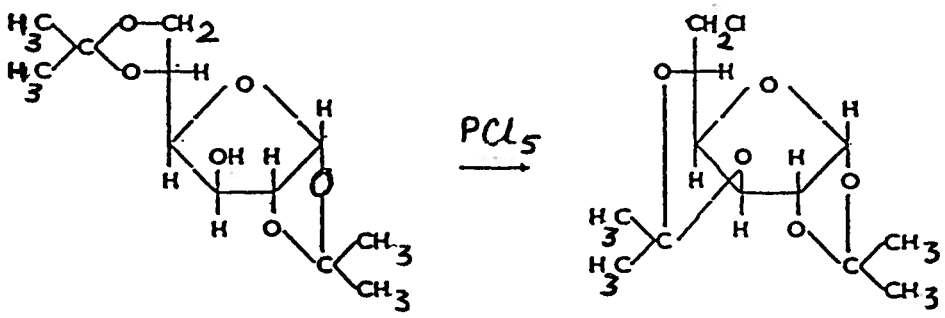


Figure 2.4.2.5. Formation of 6-chloro-6-deoxy-1,2:3,5-di-O-isopropylidene-D-glucofuranose.

An interesting product is formed in the reaction of D-glucose with acetone in the presence of boric acid. It is the 1,2-O-isopropylidene-D-glucofuranose 3,5-boric acid ester. This compound is split of the borate residue, thus permitting a convenient preparation of 6-substituted 1,2-O-isopropylidene derivative of D-glucofuranose (see Fig. 2.4.2.6).

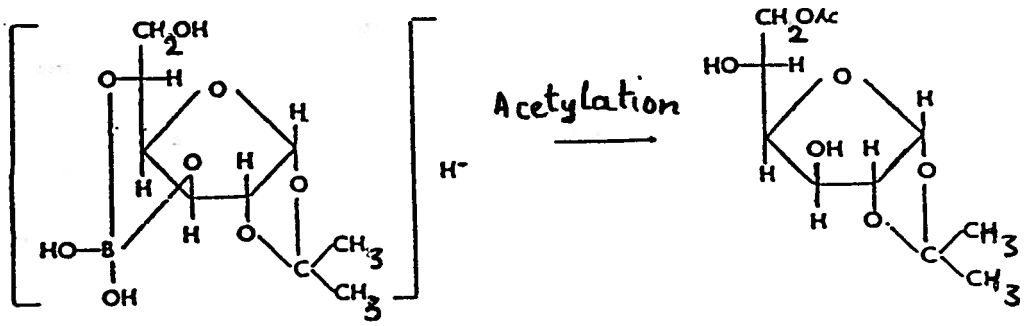


Figure 2.4.2.6. 6-acetyl-1,2-O-isopropylidene-D-glucofuranose.

Isopropylidene derivatives of L-glucose have also been prepared (Stanek et al., 1963).

The di-O-isopropylidene derivative of D-mannose (see Fig. 2.4.2.7) is remarkable in that its solution exhibits mutarotation and may be oxidized to 2,3:5,6-di-O-isopropylidene-D-mannonic acid. This supports the assumption that the hemiacetal hydroxyl group of this compound is unsubstituted, and that here 2,3:5,6-di-O-isopropylidene-D-mannofuranose is concerned. The proof of the structure was carried out by converting di-O-isopropylidene-D-mannose into its di-O-isopropylidene-D-mannonic acid, or into its lactone, which is identical with the product prepared by direct isopropylidenation of -D-mannose with acetone, as:

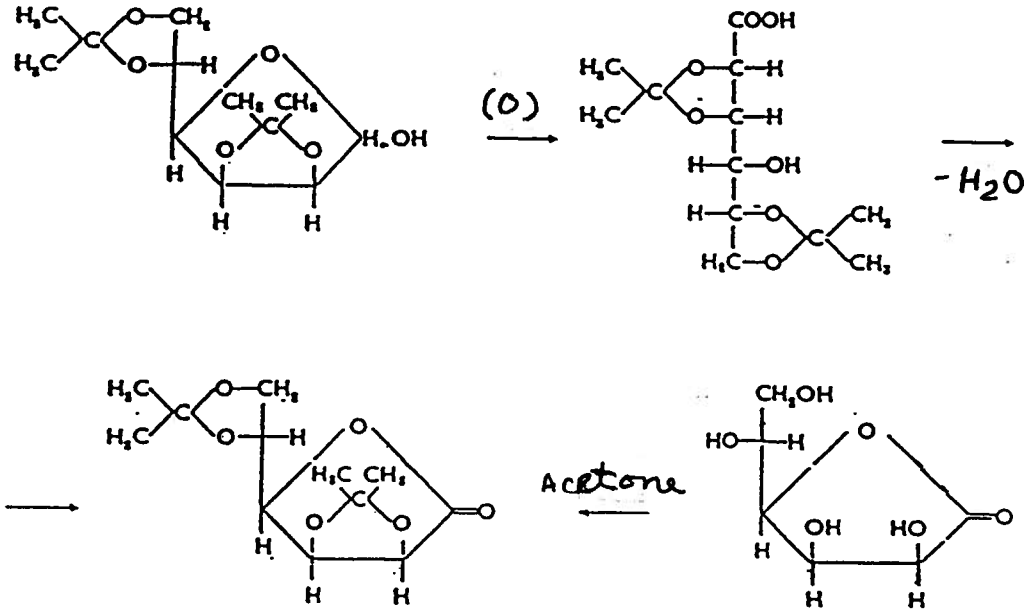


Figure 2.4.2.7. Formation of 2,3:5,6-di-O-isopropylidene-D-mannofuranose.

D-galactose is the only easily accessible aldohexose whose di-O-isopropylidene derivative has a pyranoid structure. Partial hydrolysis of 1,2:3,4-di-O-isopropylidene-D-galactopyranose yields 1,2-O-isopropylidene-D-galactopyranose. However, with regards to the almost equal ease of splitting both isopropylidene groups, this reaction is less advantageous than the analogous procedure in the glucose series. The

monoisopropylidene derivative has also been obtained as intermediate in the preparation of the di-isopropylidene derivatives, as:

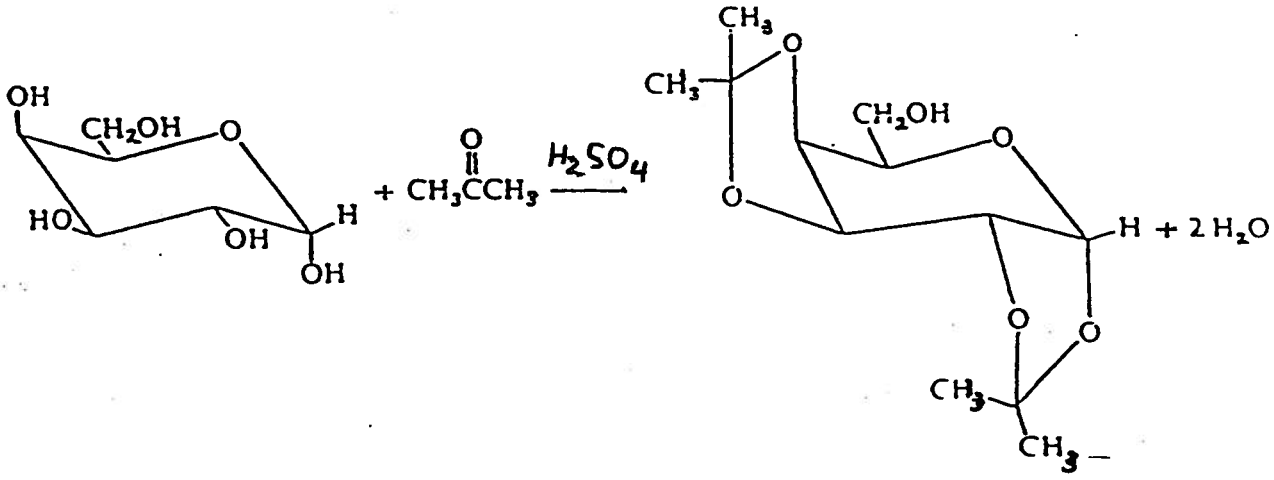


Figure 2.4.2.8. 1,2:3,4-di-O-isopropylidene-D-galactopyranose.

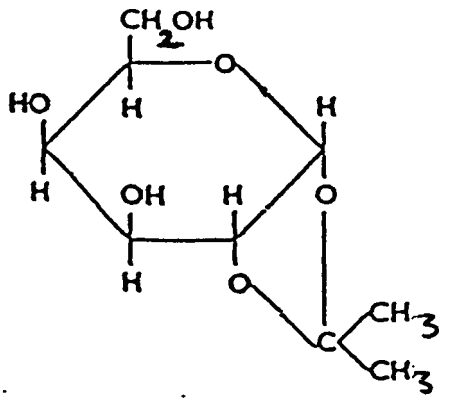


Fig. 2.4.2.9 1,2-O-isopropylidene-D-galactopyranose.

2.4.3 A Study of Sucrose - Disaccharide

Using a combination of 2,2-dimethyoxypropane, N,N-dimethylformamide, and toluene-p-sulphonic acid Khan and Mufti (1975) studied the synthesis of sucrose. Treatment of sucrose with acetalation reagents afforded a mixture which, after treatment with acetic anhydride and pyridine followed by chromatography on silica gel, gave the crystalline 1,2:4,5-diacetal Fig. 2.4.3.1 in 15% yield. In the NMR spectrum of Fig. 2.4.3.1, the signals due to H-1 and H-4 appeared at relatively higher field (τ = 6.15 and 6.25, respectively). The signals for these protons usually appear in the region t 4.5-5.4 for acetylated derivative of sucrose

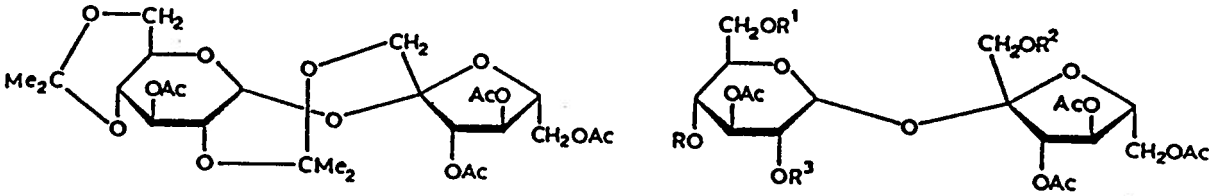
(Khan et al., 1975). The shift to higher field therefore, suggested that C-4 and C-2 were involved in the presumed acetal linkages. It was stated (Khan et al., 1975) that the p.m.r. spectrum of Fig. 2.2.3.1 showed four methyl peaks at 8.56, 8.64, 8.77, and 8.85 due to two isopropylidene groups. Further proof of the presence of cyclic acetal groups in Fig. 2.4.3.1 was supplied by the information of tetra-acetate Fig. 2.4.3.2 on treatment with 60% acetic acid at 90 ^{o}C for 10 minutes. Although the signals due to H-2 and H-4 were not allocated in the p.m.r. spectrum of Fig. 2.4.3.2, they were shown by spin-decoupling experiments to be in the region of 5.55, 6.5 in deuteriochloroform and 5.2, 5.5 in deuteriobenzene. The shift of these signals to higher field would be expected if C-2 and C-4 carried free hydroxyl instead of acetoxyl groups (Khan et al., 1975). Reacetalation of 3,3',4',6'-tetra-O-acetylsucrose (Fig. 2.4.3.2) afforded the diacetal Fig. 2.4.3.1 in 80% yield, which confirmed that no acetyl migration occurred during the deacetalation of 1',2:4,6-di-O-isopropylidenesucrose tetra-acetate (Fig. 2.4.3.1) to give 3,3',4',6'-tetra-O-acetylsucrose (Fig. 2.4.3.2).

The position of the remaining two hydroxyl groups in Fig. 2.4.3.2 were established by the following sequence of reactions (Khan et al., 1975). Treatment of Fig. 2.4.3.2 with trityl chloride and pyridine at 88 ^{o}C for 4 hr, gave the ditrityl ether compound (Fig. 2.4.3.3) as the minor, and the monotrityl ether Fig. 2.4.3.4 as the major product. The

trityl group at C-6 in Fig. 2.4.3.4 was established by converting 3,3',4',6'-tetra-O-acetyl-6-O-tritylsucrose (Fig. 2.4.3.4) into the known, 6-O-tritylsucrose hepta-acetate (Otake, 1970), using acetic anhydride and pyridine. It was noted (Khan et al., 1975) that when tritylation was conducted at 90 °C for 24 hr, it afforded 3,3',4',6'-tetra-O-acetyl-1',6-di-O-tritylsucrose (Fig. 2.4.3.3) in 85% yield. The slow tritylation treatment given to Fig. 2.4.3.3 indicated that the second primary hydroxyl group was at C-1'. This was verified by treatment of 3,3',4',6'-tetra-O-acetylsucrose (Fig 2.4.3.2) with methane-sulphonyl chloride and pyridine to give the tetra-sulphonate Fig. 2.4.3.5 which, with a refluxing solution of sodium iodide in butanone, gave the 6-deoxy-6-iodo derivative Fig. 2.4.3.6 in high yield. The structure of Fig. 2.4.3.6 was identified by its p.m.r. spectrum.

The involvement of C-4 in Fig. 2.4.3.1 in cyclic acetal formation was also studied (Khan et al., 1975). Treatment of 3,3',4',6'-tetra-O-acetyl-1',6-di-O-tritylsucrose (Fig. 2.4.3.3) with methane-sulphonyl chloride in pyridine afforded 2,4-disulphonate compound Fig. 2.4.3.7. Detritylation of 3,3',4',6'-tetra-O-acetyl-2,4-di-O-mesyl-1',6-di-O-tritylsucrose (Fig. 2.4.3.7), using hydrogen bromide in acetic acid, in a mixture of chloroform and acetic acid at 0 °C, gave 1',6-dihydroxy compound Fig. 2.4.3.8. The structure of the latter Fig. 2.4.3.8 was established by its p.m.r. spectrum. Addition of

trichloroacetyl isocyanate to a solution of 3,3',4',6'-tetra-O-acetyl-2,4-di-O-mesylsucrose (Fig. 2.4.3.8) in deuteriochloroform generated two singlets at .72 and 1.02 in the p.m.r. spectrum, due to the imino protons of the resulting carbamate group, thereby confirming the presence of two hydroxyl groups in Fig. 2.4.3.8. The mass spectrum of Fig. 2.4.3.8 showed ions due to hexopyranosyl and ketofuranosyl cations at m/e 361 and 289, respectively. Acetylation of 3,3',4',6'-tetra-O-acetyl-2,4-di-O-mesylsucrose (Fig. 2.4.3.8) gave the corresponding hexa-acetate compound (Fig. 2.4.3.9). The p.m.r. result of sucroseocta-acetate showed that the signals for H-2 and H-4 in Fig. 2.4.3.9 appeared at slightly higher field, i.e at t 5.35 and 5.2, respectively. This was considered a further evidence that the two sulphonates in Fig. 2.4.3.9 were located at C-2 and C-4. The mass spectrum of Fig 2.4.3.9 (Khan etal., 1975) showed the expected ions at m/e 403 and 331 due to the hexopyranosyl and ketofuranosyl cations, respectively. Similar treatment to 2,4-di-O-mesylsucrose hexa-acetate (Fig. 2.4.3.9), using sodium benzoate in hexomethylphosphoric triamide, gave a product with inversion of configuration at C-4. The mass spectrum and p.m.r. data confirmed the ∝-D-galacto configuration and the $^4C_1$ conformation for Fig. 2.4.3.10.



1

Fig. 2.4.3.1

Fig. 2.4.3.2 R = R1 = R2 = R3 = H
Fig. 2.4.3.3 R = R3 = H, R1 = R2 = Tr
Fig. 2.4.3.4 R = R2 = R3 = H, R1 = Tr
Fig. 2.4.3.5 R = R1 = R2 = R3 = Ms
Fig. 2.4.3.6 R = R2 = R3 = Ms, OR1 = I
Fig. 2.4.3.7 R = R3 = Ms, R1 = R2 = Tr
Fig. 2.4.3.8 R = R3 = Ms, R1 = R2 = H
Fig. 2.4.3.9 R = R3 = Ms, R1 = R2 = Ac

Figure 2.4.3.1 to 2.4.3.9. Synthesis reaction of sucrose.

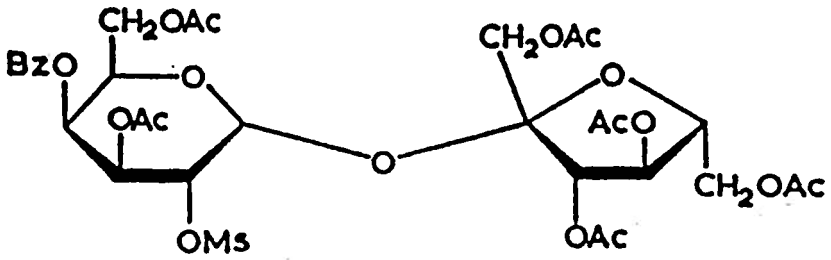


Figure 2.4.3.10. Acetylation of sucrose.

In conclusion, it is worth mentioning that all isopropylidene chemistry research (i.e formation, synthesis, kinetics etc.) has been accomplished at room or low temperatures and under anhydrous conditions. No hydrolysis of sucrose to glucose and fructose has been reported nder these conditions, i.e., acidified aqueous acetone and high temperature. However, in this work the presence of small amount of water in the reaction medium is vital for hydration of anhydrosugars that are cleaved during cellulose hydrolysis. This is fairly clearly demonstrated by Shallenberger et al. (1975), see Fig. 2.4.3.11. below:

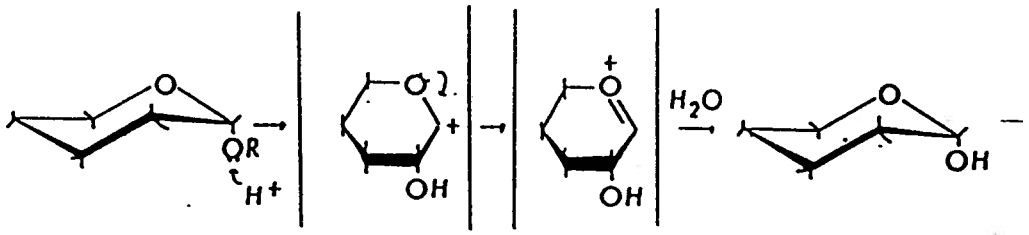


Figure 2.4.3.11. Scheme for hydration of anhydrosugars during the hydrolysis of glycosidic structures (Shallenberger et al., 1975).

2.5 Elucidation and Characterization of a Mechanism

A study of the reaction mechanism of the solvent purification of cellulose is extremely important in many practical aspects. In this context, understanding of the physico-chemical transformations that take place on the cellulose and the effect of other factors such as solvent composition, type of acid, temperature etc. appear to be crucial for better optimization of the organosolv hydrolysis process. The methods which are particularly suitable to provide answers for the elucidation and characterization of the mechanism are reviewed below.

2.5.1 Infrared Investigation

Measurement and interpretation of infrared (IR) absorption spectra represent means of qualitative identification of specific compounds (Marchessault, 1962), as well as quantitative estimation (O'Connor et al., 1958) of their relative proportions in mixtures, and are also regarded as an aid in elucidation of the molecular structure. Earlier applications of infrared absorption spectroscopy to cellulose were confined to studies of the cellulose molecule, investigations of physical, optical, and crystalline properties, i.e., crystallinity and crystal modifications of more or less pure celluloses.

One of the difficulties to be taken into consideration in a study of cellulose by IR spectroscopy is that only a limited number of absorption bands can be satisfactorily interpreted in terms of molecular vibrations. Another problem that could account for difficulties encountered in the study by IR spectroscopy of polymers, containing both crystalline and amorphous regions, such as cellulose, is the absorption overlapping of these two regions (Sutherland et al., 1950).

The hydrogen bonding system of carbohydrates (e.g., cellulose) in the solid state produces complex O-H stretch in the frequency range of 3600 to 3000 cm^{-1} region. Due to this complexity of -OH absorptions it is quite difficult to evaluate the significance of individual hydrogen bonds.

In this aspect, many workers (O'Connor et al., 1958; Hurtubise et al.,1960; Nelson et al, 1964) have used IR spectroscopy for quantification and characterization of modified celluloses with respect to hydrogen bonding. This was carried out by measurement of band absorbances at different treatments. O'Connor et al. (1958) used the ratio of the absorptivities at 1429 and 893 cm^{-1} to follow the changes in hydrogen bonding of different cellulose samples at various treatments. It was concluded (O'Connor et al., 1958) that both mechanical (grinding) and chemical (ethylamine) treatments had an impact on the decrystallization of the treated celluloses. Using IR spectroscopy Hurtubise et al. (1960) studied the changes in

the fine structure (lateral order) of cotton and unbleached sulphite birch and spruce pulps at different mercerization treatments. Their IR calculation (Hurtubise et al., 1960) showed that throughout various mercerization treatments cotton had maintained a relatively higher degree of lateral order than the other pulps and this was attributed to its high crystallinity.

Recently, using deconvolution processing of IR spectra, numerous studies (Fengel, 1992; Fengel, 1993) have focussed on quantification of changes brought about by different treatments on the structure of cellulose. Emphasis was also made to characterize the degree of crystallinity by relative heights of different bands (985 cm^{-1}, 1165 cm^{-1}, 1430 cm^{-1} etc.), and to find a correlation between hydrogen bonding and the system cellulose-water. Although deconvolution processing of IR spectra produced well-separated and much better resolved bands in the -OH region, much controversy still remains about the position of bands. This band shifting problem has been noted in both of Fengel's papers (Fengel, 1992; Fengel, 1993); bands 1280 cm^{-1}, 1460 cm^{-1}, 3350 cm^{-1}, 3418 cm^{-1}, 3466 cm^{-1} well shifted to 1270 cm^{-1}, 1470 cm^{-1}, 3378 cm^{-1}, 3440 cm^{-1}, 3506 cm^{-1}, respectively. It was also observed (Fengel, 1992) that during the transformation of cellulose I to cellulose II, the disappearance and appearance of some bands in the -OH region such as 3285 cm^{-1} and 3560 cm^{-1}, respectively, well observable.

These spectral changes in band positioning and heights are essentially due to alterations of the stereochemical character. Such variations occurring upon different treatments were found to be affected by a number of factors such as the temperature and nature of the solvent (Brewster, 1959; Durette et al., 1969). In conclusion, these changes in band positioning and the reconsideration (Fengel, 1993) of different bands in the cellulose-water system could justify the limitation of deconvolution processing of IR spectra in quantitative analysis.

Thus, the involvement of acetone, with its great H-bond acceptor potential, with cellulose molecules through the attraction of both inter- and intramolecular H-bond would lead to stereochemical changes in amorphous and crystalline zones. This type of alteration is expected to bring about irreversible H-bond disruption at both inter- and intramolecular hydrogen bonding level and cause permanent weakness in the hydrogen bonding system of the cellulose. In order to investigate the validity of this hypothesis diffuse reflectance infrared fourier transformer (DRIFT) is employed in this work. This technique is designed to provide enough information about the OH stretching. In other words, it is fairly sensitive to follow up any changes that may occur in hydrogen bonding system of a material.

2.5.2 Sugar Hydrolysis with the involvement of Acetone

The use of acetone as a solvent in wood hydrolysis dates back to 1933 when Dreyfus (1933) admixed concentrated sulphuric acid with acetone and ether in the ratio of 7 to 3, respectively. He also impregnated compressed wood with the solution in order to deposit and distribute small quantities of the acid within the wood matrix. The removal of the solvent system was achieved by distillation. Thereafter, the wood residue was boiled in water for dissolution of carbohydrates. The Dreyfus process was unable to produce directly soluble sugars but could effect strong acid hydrolysis at lower temperatures.

Later, Chang et al.(1976) developed a process which could dissolve the total wood biomass at high temperatures (180-210 ^{o}C) in acid catalyzed aqueous acetone. Kinetics of acid catalyzed organosolv saccharification was published in 1977 (Chang et al, 1977). Also a Canadian patent on this process has been released (Paszner et al, 1981). At that stage the process for total saccharification of wood used acidified acetone of concentration 50 to 70%. Recovery of the reducing sugars was in the range of 60 to 72% of the theoretical yield. Further improvement in sugar recovery (up to 95%) was attained by merely increasing the acetone concentration to greater than 80% (Paszner et al., 1986).

The Acid Catalyzed Organosolv Saccharification (ACOS) process chemistry that lead to a significant high-rate

hydrolysis and thermal stability of the dissolved sugars (Paszner et al, 1988) has not yet been verified. Ward and Grethlein (1988) suggested that the dissolved glucose was in the 1,6-anhydroglucose form which can be readily post-hydrolyzed to glucose.

However, Paszner et al. (1988), relying on isopropylidene chemistry concepts and the loss of acetone from the pressure vessel (for reasons other than leakage), disagreed with Ward and Grethlein's (1988) assumption. In addition, the formation of 1,6-anhydrohexopyranoses is known to occur in aqueous acidic solutions where high energies are applied (Stoddart, 1971).

In early investigations of Chang et al. (1976, 1977) in acetonation of cellulosic materials much of the focus was devoted to the kinetics and optimization of the process. It was noted (Chang et al., 1976; Chang et al., 1977) that hydrolytic dissolution of wood mass , at low temperature, (160-170 ^{o}C) occurred in two stages, i.e., bulk hydrolysis and main hydrolysis. At high temperature (200 ^{o}C) hydrolysis was found to be first order all the way to total dissolution. However, both Paszner et al.(1986, 1988) and Ward et al.(1988) observed total saccharification of biomass when acetone was used. It is noteworthy to mention that neither of these works was able to demonstrate structural changes resulting from the acetonation treatment. Nonetheless, Paszner et al (1988), managed to throw, hypothetically, some light on the mechanism of acetonation.

It was concluded (Paszner et al., 1988) that the possibility of isopropylidene derivatives of sugars as final products and transient (hemi) ketal formation on the cellulose, as shown in Fig. 2.4.1.1 might significantly weaken the glycosidic linkages in cellulose. This eventually leads to rapid depolymerization of cellulose to isopropylidenated glucose. Thus the high sugar yield obtained during acetonation of wood biomass was attributed (Paszner et al., 1988) to derivatization of cellulose residues, i.e., isopropylidene group formation on the sugar ring, thereby, avoiding dehydration to furfural and hydroxymethylfurfural otherwise possible under the prevailing saccharification conditions.

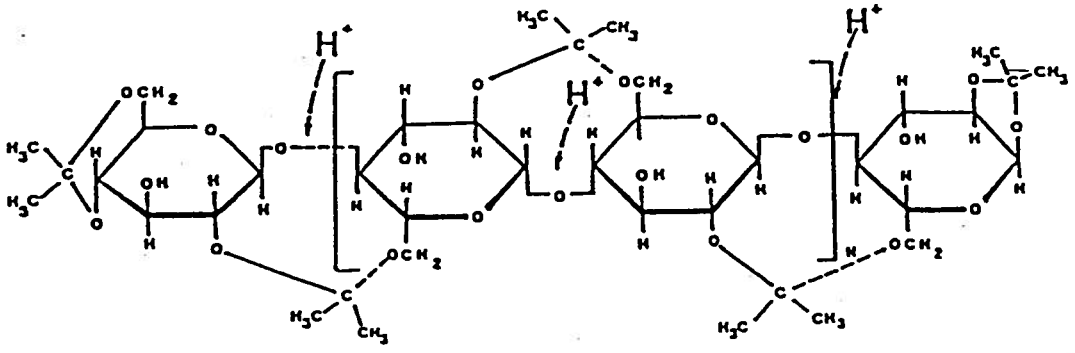


Fig. 2.5.1.1 Proposed O-isopropylidene intermediates for cellulose during high temperature in acidified aqueous acetone.

2.5.3 The C-13 CP/MAS NMR Spectrometric Investigation

Isopropylidene groups, in the form of cyclic acetals have found wide use in carbohydrate chemistry for their protective role of diol functions (De Belder, 1965; De Belder, 1977). In addition to their chemical value, there has been much interest in their conformational structures (Mills, 1955; Wolfrom et al., 1974; Barker et al, 1952).

C-13 NMR has frequently been used in structural studies of isopropylidene chemistry. Buchanan et al. (1980), using C-13 NMR, studied several carbohydrate isopropylidenes of unknown structure. It was noted (Buchanan et al., 1980) that the C-13 chemical shifts of the methyl groups were separated from each other by about 10 p.p.m. This large difference was attributed to the difference in environment of the equatorial and axial methyl groups in the chair conformation and that the higher field signal was due to the axial group which was more bulky. While the methyl groups of 5-membered acetals were slightly separated from each other. This could be (Buchanan et al., 1980) due to the conformational mobility of the system and to the fact that the methyl groups were pseudoequatorial and pseudoaxial.

Buchanan et al. (1982), in a continuation of their structural studies of isopropylidene acetals, were able to draw more conclusions on the acetal ring size; 1,3-dioxolane, 1,3-dioxane and 1,3-dioxepane. It was observed (Buchanan et al., 1982) that the chemical shift of the

acetal carbon of 1,3-dioxolane rings was in the range 108.1-115.7 p.p.m, while those of 1,3-dioxane rings were between 97.9 and 101.1 p.p.m. This was attributed to the flexibility of the former ring. In the case of 1,3-dioxepanes the acetal carbon chemical shift value was found (Buchanan et al., 1982) to be intermediate, nearer to that in the 1,3-dioxanes.

Christophe (1984), using large excess of 2,2-dimethoxypropane, acetone and sulphuric acid, was able to isopropylidenate 2-acetamido-4,6-O-benzylidene-2-deoxy-D-glucitol. The investigation of the latter compound by C-13 NMR spectroscopy showed that the benzylidene acetal carbon resonated at 101.2 p.p.m, while that of isopropylidene one gave a signal at 99.9 p.p.m. These values indicated that both acetal rings were 1,3-dioxanes. Also, C-13 NMR spectrum of this compound illustrated that the chemical shifts of methyl groups were separated by 10.9 p.p.m., which was within the expected range for dioxanes (Christophe, 1984).

The synthesis of 1,2:4,5-di-O-isopropylidene-3-O-(2,3,4,6-tetra-O-acetyl-β -D-glucopyranosyl)- β -D-fructopyranose was achieved (Couto et al., 1984) by codensation of tetra-O-acetyl-α-D-glucopyranosyl bromide with 1,2:4,5-di-O-isopropylidene-β -D-fructopyranose in 1:1 nitromethane-benzene in the presence of mercuric cyanide during 5 hr. The C-13 NMR spectrum of the disaccharide showed two signals at 112.0 and 108.9 p.p.m. for the dioxolane carbon atoms (Couto et al., 1984).

2.5.4 X-ray Diffraction Characterization

X-ray diffraction is the only technique used for the characterization of polysaccharides of ordered structures at an atomic resolution level. The structural information that can be deduced from x-ray diffraction analysis is dependent on the organization and packing arrangement of the specimen of interest (i.e., fiber). Fibrous materials contain ordered three-dimensional units (i.e., crystallites or micelles) of atoms within their elementary and microfibrils. Fibrils are the main structural components of the cell walls. Therefore, x-ray diffraction data can be used to assess the structural changes which have been brought about by a certain treatment of the cellulosic material.

The existence of a three-dimensional arrangement in celluloses has been verified by x-ray and electron-diffraction diagrams of such substrates as ramie (Mann et al., 1960), Valonia ventricosa cellulose (Honjo et al., 1958), cotton (Segal et al., 1959), and Fortisan (Mann et al., 1960). The diagrams of these cellulosic materials exhibited sharp reflections which could only be accounted for in terms of three dimensional co-ordinates. All the reflections from the typical cellulose II structure could be interpreted in terms of a monoclinic unit cell of approximate dimensions: a=7.92 Å, b=10.34 Å, c=9.08 Å, β =62.7^{o} (Wellard, 1954). The dimensions for ramie (i.e cellulose I) were determined (Wellard, 1954) to be as

follows; a=8.17 Å, b=10.34 Å, c=7.85 Å, β=83.6°. It was stated (Mann, 1962) that even though these observations illustrate the existence of three-dimensional crystalline orientation, they do not confirm that all regions which contribute to the sharp reflections of the diffraction diagrams show the same degree of crystallinity. This might be attained only if good agreement could be obtained between calculated intensities for a crystalline model and the observed intensities. However, today, by the appropriate use of computer model building to select reasonable three-dimensional models for comparison with x-ray data, many details of the ordered structures have been drawn for numerous cellulosic materials (Rees, 1977).

The lateral packing order, which is formed by hydrogen bonds with hydroxyls of adjacent cellulose chains, provides more structural information by bringing about various Bragg diffractions. With these diffractions unit cell dimensions and the space group can be determined.

Rozmarin (1977) studied the effect of acid hydrolysis on the supermolecular structure of cellulose (i.e variation in crystallinity index). He also investigated different parameters contributing to the hydrolysis reaction. It was pointed out (Rozmarin, 1977) that with the increase of acid concentration, the crystallinity index decreased rapidly and temperature exerted the largest effect on hydrolysis of cellulose.

Recently, in an interesting review on supermolecular structure of cellulose, Hayashi (1985) stated that the irreversible change from cellulose I to II could be due either to the difference of skeletal chain conformation or the difference in the chain packing polarity (i.e parallel vs. antiparallel). It was added (Hayashi, 1985) that it is not possible to establish the crystal structure of cellulose with the limited amount of x-ray data now available. To accomplish an accurate description of the crystal structure of cellulose, the x-ray information obtained should be strengthened by other chemical and physical methods of structural analysis.

2.5.5 Molecular Weight Distribution Characterization

Information concerning molecular weight distribution is essential in relation to our understanding of the physical properties of many industrially important celluloses and cellulose derivatives. Many different methods have been known so far for determining molecular weight distribution. Solutional and precipitational fractionations, especially, were very popular in the past for that purpose. Recently, many investigations have been carried out on the determination of molecular weight distribution of polymers by gel permeation (exclusion) chromatography (GPC). The traditional methods (e.g., solvent precipitation) are time-

consuming and accurate molecular weight distribution is not obtained.

Gel permeation chromatography is a relatively simple technique applicable to rapid determination of molecular weight distribution of polymers. Usually in this technique polymer molecules are separated according to their molecular size in solution. The polymer solution flows through a column packed with porous packing on which larger molecules are excluded (eluted first) while the smaller molecules are retained in the packing intersticial spaces. By using a suitable calibration technique, the molecular size distribution can then be obtained and converted into molecular weight distribution. In this procedure, two important steps must be taken into considerations;

1- to ensure that complete solubility (true solution) of the sample in the solvent is attained, and

2- to use suitable calibration standards.

In this regard, the major factor in determining the molecular weight distribution of cellulosic materials is in conversion of the polysaccharides to derivatives suitable for analysis. Two methods are available for derivatizing : nitration (Timell, 1965) and carbanilation (Hall et al, 1973). The drawbacks of the former method are the instability of the nitrates, insolubility of nitrated xylan and the impossibility of achieving complete nitration. On the other hand, carbanilation has repeatedly been verified

to provide complete substitution of polysaccharides without degradation (El Ashmawy et al., 1974). Carbanilated celluloses are readily soluble in tetrahydrofuran (THF), the solvent of choice for GPC. Analysis of carbanilated polysaccharides by gel permeation chromatography has usually provided satisfactory results (Danhelka et al., 1976).

The polydispersity of celluloses represents the extent of variation in molecular size, i.e., experimentally determined values for molecular weight distribution are obtained as averages, which are dependent on the method used. Commonly, molecular weight determination provides both weight-average M_w and number-average M_n molecular weight distributions. The ratio of weight-average molecular weight to number-average molecular weight (M_w/M_n) defines the polydispersity, i.e, generally, the greater the relative difference between M_w and M_n the wider is the spread in molecular weights (polydispersity) of the sample of interest. Values with narrow polydispersity are considered excellent for dissolving pulp manufacturing (Rydholm, 1965).

The degradation of cellulose may result from different mechanisms such as thermal, oxidative, enzymatic, acid-hydrolysis, base-catalyzed oxidation and mechanical. Their common impact on the cellulosic material is the diminishing molecular weight. Several parameters affect the course of the mechanism (i.e., the extent of degradation). Factors such as temperature, reaction time, catalysts, reaction media, gases

molecular weight distribution (MWD) were studied (Suleman et al., 1987). It was found that the lowest molecular weight distribution was produced in acidic medium when palladium chloride has been used as a catalyst. On the other hand, they concluded that the catalyst, dicobaltoctacarbonyl acted, through different reactions, as a cellulose stabilizer from further degradation.

Chang et al. (1973) investigated the molecular weight distribution of different celluloses after acid hydrolysis treatment. They observed that the total number of crystallites was decreased during hydrolysis while the chain length distribution remained constant. They also noted that the crystallites were broken down into molecular fragments.

In the present study gel permeation chromatography (GPC) is employed to investigate the molecular weight distribution (MWD) of treated and untreated substrates (cotton). Uniformity of molecular weight distribution is an important parameter for predicting the performance of acetonation treatment on cellulosic material and as an indicator for dissolving grade quality.

3 MATERIAL AND METHODS

3.1 Sample Preparation Procedures

3.1.1 Raw Material

100% pure cotton for pharmaceutical purposes has been used throughout the duration of this study as a model compound, obtained from the University Pharmacy at The University of British Columbia (UBC) premises. Its characteristics were determined as follows; the percentage of moisture free cotton was determined according to TAPPI standard T 258 os-76. Extractives were determined according to TAPPI standard 204 os-76. Alpha-cellulose was determined according to TAPPI standard 203 os-74. The results of this investigation are illustrated in the following chapter (Results and Discussion).

3.1.2 Raw Material Preparation for the Analysis

Cotton was extracted with alcohol-benzene (2:1) according to TAPPI standard T 204 os-76.

To remove any extractives that may interfere with the results, cotton was extracted with alcohol-benzene for 72 hr. Then it was extracted with only alcohol in order to remove the residual benzene. After alcohol extraction the cotton was left

overnight in the fumehood for evaporation of the solvent. The purified cotton was dried in a controlled temperature and humidity room (CTH), which maintained the following conditions; temperature 23 ±2 °C, and relative humidity 50 ±2%, for a week and by the end of this step it was ready for the analysis.

3.1.3 Solvent Extraction of Sugars

The hydrolysis runs of cotton were performed in stainless steel bombs equipped with glass liners similar to those described earlier (Chang et al., 1976; Chang et al., 1977; Paszner et al., 1983; Paszner et al., 1988). An oil bath served as a heating source. The bombs were charged for each cook with 5 gram of extracted cotton to which acidified organosolv liquor (acetone : water) was added. The bombs were then immersed in the oil bath at an assigned temperature for a specified length of time.

At the end of the sugar extraction run the bombs were chilled in water and the contents filtered on a Buchner funnel. The residue was washed with several portions of fresh liquor. The filtrate was stored in the fridge for further treatment and analysis. The pulp residue was neutralized with ammonia solution, thoroughly washed with distilled water and dried at 60 °C for weight loss determination and other treatments.

3.1.4 Isolation of Sugars from the Spent Liquor and their Preparation for HPLC Analysis

In the case of trifluoroacetic acid as a catalyst, sugars in the spent liquor (acetone, water and TFA) were isolated by evaporation of the acetone and partial removal of water. The contents of the flask (i.e viscous solution) were diluted with distilled water and filtered. The filtrate, once again, was rotary evaporated and filtered in order to remove the impurities that may negatively affect the sugar analysis results by HPLC analysis.

When hydrochloric acid (HCl) was used as a catalyst, neutralization with ammonia solution was done first. Filtration, evaporation and dissolution followed.

3.1.5 Secondary Hydrolysis of Nonreducing Sugars and Oligosaccharides

After the adjustment of the acid concentration of the primary hydrolysate (acetone, acidified water and sugars) to 3%, the contents were placed in a glass liner of a stainless steel bomb. The pressure vessel with the contents was heated in an oil bath at 120 °C for different specified times. The post-hydrolysate was neutralized with ammonia solution and left to stand at room temperature for 2 hr in order to allow the ammonium salt to precipitate. Then the hydrolysate was filtered and evaporated on a rotary evaporator. The viscous

solution was once again dissolved with distilled water and filtered to ensure high degree of purity for HPLC analysis.

3.1.6 Preparation of Hydrolysate for Gas Chromatographic Analysis

The spent liquor (acetone, acidified water and sugars) of cotton solvent treatment was neutralized with ammonia solution and left to stand for 2 hr in order to allow ammonium salt to precipitate. The contents were filtered, eluted through a column of ion exchange resin (XAD-16) in order to remove the impurities that might negatively affect the analysis of isopropylidene derivatives results by GC analysis. The filtrate was rotary evaporated. The viscous solution was extracted with chloroform. The chloroform extract was filtered through a microfilter prior to GC analysis.

3.1.7 Acetonation of Cotton Hydrolysate Reducing Sugars

The cotton hydrolysate was rotary evaporated and concentrated to a syrup. An amount of 100 mL of fresh acetone and 2 mL of concentrated hydrochloric acid were mixed and the mixture was added to the syrupy residue in the flask with the magnetic rod. The flask with the contents was placed over a magnetic stirrer and stirring was conducted at room temperature for 20 hr. Neutralization, filtration and purification steps were similar to those described in section 3.1.6.

3.1.8 Sugar Hydrolysis - Standards Preparation

The monomeric composition of cotton hydrolysate extracted with acid catalyzed aqueous acetone at various kinetic variables (i.e., temperature, reaction time, acid concentration etc.) was investigated using different standards of sugars . 25 mg of each sugar (glucose, galactose, mannose, arabinose and xylose) was weighed, transferred into a volumetric flask (25 mL cap.) and deionized water was added and adjusted to the mark. The contents were well shaken to ensure a uniform concentration throughout the solution. These standard sugar solutions were used for identification of different sugar retention times.

3.1.9 Sugar Hydrolysis - Mixture of Standards Preparation

20 mg of each sugar standard were weighed and all were mixed together to make up 100 mg. The mixture of standards preparation procedure was identical to that described in section 3.1.8.

3.1.10 Sugar Hydrolysis - Preparation of Isopropylidene Derivatives of Sugar Standards

1,2:5,6-di-O-isopropylidene-α-D-glucofuranose, 1,2-O-isopropylidene-α-D-glucofuranose, 2,3:5,6-di-O-isopropylidene-β-D-mannofuranose and 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose were obtained from Sigma Chemical Laboratories and used as standards for gas chromatographic (GC) investigation. Procedures for their preparation are quite similar to those of the simple sugars as described earlier in section 3.1.8 with the exception that chloroform was used as a volatile solvent for the solublization of the isopropylidene derivatives.

3.1.11 Solvent Extraction of Cotton using C-13 labeled Acetone

An extracted sample of cotton (140 mg (o.d)) was placed in a tube positioned in a glass liner with glass beads and dried for a week over phosphorous pentoxide in a desiccator. To the 1 g of C-13 labeled acetone an amount of acidified water (0.16 N HCl) (105 µL) was added. The fresh liquor (C-13 labeled acetone and acidified water) was transferred to the tube containing the cotton and the glass liner containing the sample was placed in the stainless steel bomb. The bomb was pressurized to 450 psi and heated to 150 °C for 2 hr. Neutralization, filtration and residue washing steps were carried out similar to those described in section 3.1.3. The

filtrate was collected in a vial and stored in the fridge for further analysis. The residue was dried in the CTH room for 48 hr. The residue was studied by C-13 CP/MAS solid state NMR.

3.1.12 Preparation of Cotton Residues for X-ray Diffraction Analysis

Sample preparation was conducted according to Nelson et al.(1964).

Samples, which were treated with acid catalyzed aqueous acetone, were prepared for X-ray diffraction (XRD) by placing the fibrous material in a 1 in (2.54 cm) square metal frame and the content was transferred onto a hydraulic press. Pressing of the fibrous material was carried out at 15000 psi (1050 kg/cm^2) for 5 min.

Samples such as untreated cotton and those which were treated with acetone and water without the acid catalyst were ground in a Wiley microgrinder to pass a 30-mesh (0.6 mm) screen prior to pressing. Pressing was conducted in a similar manner as described above.

3.1.13 Cotton Residue Carbanilation

Carbanilation of cotton fibrous material (i.e., solvent treated and untreated cotton) was done according to Schroeder et al. (1979) with some modifications.

The cotton sample equivalent to 0.1 g (o.d.) was dried in

a quick fit flask (250 mL cap.) at least overnight in an oven at 60 °C. Anhydrous pyridine (100 mL) and phenyl isocyanate (7.2 mL) were added to the flask. Then the reaction flask was capped, sealed with parafilm and placed in a circulating thermostated oil bath at 80 °C for 2 days. The mixture was allowed to cool slightly and methanol (4 mL) was added to react with the excess phenyl isocyanate. The mixture was mixed with an equal volume of dioxane, filtered through a glass filter paper in a Buchner funnel, and transferred to a beaker (1 L). A mixture of methanol (800 mL) and acetic acid (5 mL) was added to the contents of the beaker and the formation of white particles in the solution were immediately observed. The suspension was left over-night in the fumehood to settle, after which the clear solution was carefully decanted and the wet precipitated polymer left in the fumehood for 2 days to dry. Using a spatula, the sticky precipitated polymer was removed into a vial and kept over phosphorus pentoxide in a desiccator for further use.

3.1.14 Viscosity Determination

Viscosity of cotton residues was determined according to TAPPI standard T 230 os-76.

An amount of air-dry residue equivalent to 0.250 g o.d. was weighed and transferred into a dissolving bottle containing several 6 mm glass beads. After adding 25 mL of

distilled water, the bottle was capped and shaken for a few minutes. Then the bottle was allowed to stand for about 2 minutes while purging with nitrogen (N_2). 25 mL of cupriethylenediamine (CuEn) was added and purging with N_2 was continued for 1 more minute. The bottle was then capped and shaken until the fibers were completely dissolved (i.e., no fibers stuck on the walls of the bottle).

The viscometer was filled by immersing its small diameter leg into the solution and drawing the liquid into the instrument by applying suction to the other end. After drawing the liquid level to the second etch mark, the tube was removed from the solution, cleaned and returned to its normal vertical position. The viscometer was placed in a constant temperature water bath at 25 °C for at least 5 min for the solution to reach the temperature. The solution was drawn up into the measuring leg of the viscometer with a suction bulb, and allowed to drain so that the inner surfaces of the viscometer were wetted. The efflux time was then determined by drawing the liquid above the upper mark and measuring the time required for the meniscus to pass between the two marks. The measurement of efflux time was repeated three times. This procedure was carried out on all residues which were treated with acetone, water and acid catalyst.

In the case of untreated cotton and those treated with just acetone and water, 1 M cupriethylenediamine solution (CuEn) 25 mL was added first to the residue with a two-

minute nitrogen purging, after which the bottle was capped and shaken frequently for 10 min. Then 25 mL of distilled water was added to the bottle and shaking was continued for 20 min. The rest of the procedure was similar to that described above.

3.2 Analytical Methods

3.2.1 IR Analysis - Diffuse Reflectance Infrared Fourier Transformer (DRIFT)

The average absorbance peak height around 3400 cm^{-1} (gross hydroxyl range) of differently treated cotton specimens was obtained. This was conducted in a way that the intensity of the hydroxyl band could be read without being influenced by the intervening factors. Such factors that could be taken into consideration are the variations in peak location due to stereochemical changes and noise perturbation. The analysis was maintained on a Perkin-Elmer 1610 Fourier transform infrared spectrometer equipped with a Perkin-Elmer diffuse reflectance attachment, with the sample placed on ground potassium chloride. The spectrum of pure potassium chloride was ratioed against that of each sample. The spectra resulted from measurements involving 64 scans at a spectral resolution of 8 cm^{-1}.

The hydrogen bonding test is the mean for three measurements.

3.2.2 Detection of Isopropylidene Derivatives by Gas Chromatography (GC)

Gas chromatographic investigation of isopropylidene derivatives of sugars was carried out on a Hewlett Packard 5890A gas chromatograph, equipped with a flame ionization detector and an HP 3396A integrator. The reports generated on the HP 3396A printer, after each chromatographic run, were transferred to a computer for data storage.

The column used for the separation of isopropylidene derivatives was Supelcowax 10, 30 m x 0.25 mm I.D. The inlet pressure for the column was 10 psi. The carrier gas was helium and the flow rate was 1 mL/min. The injection and detector temperatures were 200 °C and 300 °C, respectively.

3.2.3 Sugar Analysis - High Performance Liquid Chromatography (HPLC)

The samples prepared as described in sections 3.1.5 and 3.1.6 were directly injected into the high performance liquid chromatograph (HPLC) column without any further treatment. A DIONEX HPLC (Dionex Corp., Sunnyvale, CA) equipped with autosampler, gradient pump and pulsed amperometric detector was used. The eluent was degassed by vacuum for 20 min and degassed again by DIONEX eluent degas module using helium, before the sample run.

The columns used were anion exchange resin columns, CarboPac PA1 (4x250 mm), and a guard column (4x50 mm) to protect the main analytical column from contamination. An NG1 guard column was also placed before the CarboPac PA1 column to remove any impurities such as phenolic materials that might form in the hydrolysate. The CarboPac column contained polymeric nonporous Microbead resins which exhibit rapid mass transport, fast diffusion , high pH stability (pH 0-14), and excellent mechanical stability (>4,000 psi).

The Pulsed Amperometric Detector (PAD) had a flow-through cell with a gold working electrode, stainless steel counter electode, and a silver/silver chloride reference electrode. The potential of the working electrode was cycled through three values to let the electrode surface be cleaned and the current be stabilized before sampling the oxidative current from the flow-through solution. Working electrode potentials were set as follows; E1=0.005 V (300 ms), E2=0.60 V (120 ms), E3=-0.80 V (300 ms) with a sampling time of 200 ms from 100 ms to 300 ms. The E2 and E3 pulses remove remaining sugars and then reactivate the gold surface, respectively. The response time was 1.0 sec and the output range was 100 nA.

The main analytical eluent used was degassed, distilled and deionized water prepared by a Millipore Mill-Q Water System. The column was regenerated after every injection with 250 mM NaOH which was prepared as follows; the distilled deionized water used was degassed first by helium gas for 15

min before mixing with the NaOH solution to avoid carbonate formation.

The flow rate was 1.0 mL/min and 500 mM NaOH was introduced into the mixing cell from a post-column pump (Varian 5000 HPLC) at the flow rate of 1.0 mL/min All samples before loading onto the column were filtered through a 0.4 um syringe filter (NALGENE^{tm}). All tubings used were made of metal free PEEK.

Regarding accuracy of sugar analysis, three injections were made for each sample and the standard solution was injected after different interval times to monitor possible variations in the column or detector conditions. Calibration curves were prepared by using standard solutions of arabinose , xylose, galactose, glucose and mannose at three different concentration levels. The data were processed by DIONEX AI-450 software using a DIONEX advanced computer interface. The computer used is Hewlett Packard 486 Vectra with Microsoft Window 3.1.

3.2.4 Solid State Cotton Study - C-13 CP/MAS NMR spectrometry

CP/MAS C-13 NMR spectra of cotton residues were obtained from a Bruker MSL-400 spectrometer operating at 100.6 MHz. The spectral conditions used were as follows:

a- spin contact time: 2ms, 90° proton pulse: 6.5 μsec., and the relaxing delay was 4 sec.

b- MAS spinning rate - 3500-4500 Hz.

The spectra were recorded by using a spectral width of 41.666 KHz.

3.2.5 X-ray Diffraction

X-ray diffraction technique was employed in this work to investigate the crystalline structural changes brought about by the solvent purification treatment on cotton cellulose. The X-ray diffraction data of the samples were recorded using a Siemens Diffractometer equipped with a D-5000 rotating anode X-ray generator. The wavelength of the Cu/Kax radiation source was 0.154 nm and the spectra were obtained at 30 mA with an accelerating voltage of 40 kV. Samples were scanned on the automated diffractometer from 9° to 40° of 2 (Bragg angle), with data acquisition taken at intervals of 0.04° for 1 sec.

A peak resolution program was used to calculate both the crystallinity index of cellulose and the dimensions of the crystallites (Hindeleh et al., 1978). This program allowed the resolution of the X-ray diffraction pattern into the contributions of each of the diffraction planes. The background was attributed to the amorphous part of cellulose. Generally, the Voigt function (Chung, 1989) resulted in the best fit of the X-ray diffraction patterns and was routinely used for the determination of both the crystallinity index of cellulose and the dimensions of the crystallites through peak

broadening (full width at half maximum height). The crystallinity index, which is defined as the ratio of the resolved peak area to the total area under the unresolved peak profile, was calculated using the the following equation;

$$CrI\ (\%) = \frac{\int I_T d\theta - k\int I_A d\theta}{\int I_T d\theta} .100$$

where CrI is the crystallinity index of the cellulose, I_T is the total intensity of diffraction in the diffractogram, I_A is the total intensity of diffraction due to the amorphous portion of the sample, θ is the diffraction angle, and k is the ratio of the crystalline and amorphous intensities at a particular 2θ value outside of the crystalline peak region (Wims, et al., 1986). In this work, the value of k was not determined for each sample used and was taken to be equal to one in all cases for convenience of calculations.

The crystallinity index of the cellulose was also calculated by the empirical method described by Segal et al. (1959), using the equation described below,

$$CrI\ (\%) = \frac{I_{002} - I_{AM}}{I_{002}} .100$$

where I_{002} is the maximum intensity of the 002 lattice diffraction (reflection attributed to the crystalline region of the sample) and I_{AM} intensity of diffraction at Bragg angle $2\theta = 18°$ (reflection attributed to the amorphous region of the sample). Nevertheless, the latter approach does not include any correction for the background (unresolved peak profile). Results obtained using both methods were in good agreement.

The apparent dimensions of the cellulose crystallites were determined by applying the Scherrer's equation to the data obtained by the peak resolution program. The average thickness of the crystallite (i.e., relative values) at each plane of diffraction was calculated using the following equation;

$$t(hkl) = \frac{K.\lambda}{B.\cos\theta}$$

where, t is the thickness of the crystal at the (hk1) plane of diffraction, λ is the wavelength of X-ray source, K is the Scherrer's constant (for pretreated cellulose, K = 0.9), and B is the peak full width at the half maximum height (Cullity, 1956).

The crystalline test (the crystallinity index and crystallite breadth) is the mean for three measurements.

3.2.6 Gel Permeation Chromatography

The gel permeation chromatograph (GPC) used, for the study of molecular weight distribution (MWD) of solvent treated cotton materials, was a Spectra-Physics SP8810 liquid chromatograph. Samples of cellulose tricarbanilate dissolved in tetrahydrofuran (THF) were filtered through a teflon membrane with a pore size of 0.45 μm and analyzed using a series of four TSK-GEL type H8 columns. Tetrahydrofuran was used as the eluting solvent at a flow rate of 1 mL/min. The samples in the eluent were detected by a UV spetrophotometer detector (Spectroflow 757) at the wavelength of 235 nm. The signal from the detector was fed to the integrator SP4229 for peak integration and illustration of integral and differential distributions of molecular weights.

Due to the lack of commercially available standards of cellulose tricarbanilate, the GPC calibration curve (i.e., the correlation of elution volume with molecular weight) was established from the elution profile of polystyrene standards with narrow MW distributions (Danhelka et al., 1976; Coll et al., 1970; Valtasaari et al., 1975). The following equation was used:

$$\ln M_C = \frac{(1+\alpha_P)\ln M_P + \ln (K_P/K_C)}{1+\alpha_C}$$

where M_c and M_p are the MW of cellulose tricarbanilate and polystyrene, respectively. The Mark-Houwink coefficients used in the present analysis for polystyrene in THF, $K_p = 1.18 \times 10^{-4}$ and $\alpha_p = 0.74$, and for cellulose tricarbanilate in THF, $K_c = 2.01 \times 10^{4}$ and $\alpha c = 0.92$, were those reported by Valtasaari et al. (1975).

3.2.7 Viscosity Measurement

This was measured according to TAPPI standard 230 os-76. The viscosity test in the following chapter (Results and Discussion) is the mean for 3 measurements.

4 RESULTS AND DISCUSSION

4.1 Mechanism of Purification of Cellulose in Acidified Aqueous Acetone: Elucidation and Characterization

4.1.1. Characteristics of the Raw Material used for the Elucidation of the Mechanism

100% pure cotton for pharmaceutical purposes has been used throughout the duration of this study as a model compound. Its characteristics were determined to be as follows: 1- the moisture content was 4.85%, 2- the extractives content was 0.02%, and 3- the alpha-cellulose content was 98.2%. Other characteristics determined such as absorbance (hydrogen bonding), viscosity, crystallinity index and crystallite breadth (full width at half maximum height, FWHM), etc. are discussed where appropriate in the text.

4.1.2. IR (DRIFT) Study - Hydrogen Bonding Changes (i.e., hydogen bond disruption/destruction) during Solvent Purification Treatment

The aim of studying residual cotton samples after acetonation, with the use of a Fourier transform infrared spectrometer equipped with a Perkin-Elmer diffuse reflectance attachment, is to verify, quantitatively, the effect of the treatment on the hydrogen bonding of the

cellulosic material (i.e., the hydrogen bond disruption hypothesis). Hydrogen bonds have occupied a key position in the interpretation of physico-chemical processes and the macromolecular structure of cellulose (Sarko, 1978; Nishimura et al., 1987) and because of their importance as the locus of interaction between molecules and between the nearby functions in the same molecule. Thus, the hydrogen bond provides special promise for the study of such interactions. It has been known for a long time (Hilbert et al., 1936; Ellis et al., 1940) that the observed stretching frequency of a covalently bound hydrogen atom is perturbed in a specific way when that atom gets involved in hydrogen bonding to an acceptor group. These infrared shifts have given us a broad knowledge of the structural requirements for hydrogen bonding, both at inter- and intramolecular levels (Liang et al., 1959; Marchessault et al., 1960). In this context, it has also been verified (Amis, 1966; Lemieux et al., 1968) that a change in solvent has a substantial impact on the mechanism and stereochemistry of the reaction course and hence on the hydrogen bonding of the specified system. Acetone as a solvent appeared to follow such a trend as has been confirmed in the present work.

4.1.2.1. Acetone Effect on Hydrogen Bonding of Cotton Residues during Solvent Purification Treatment

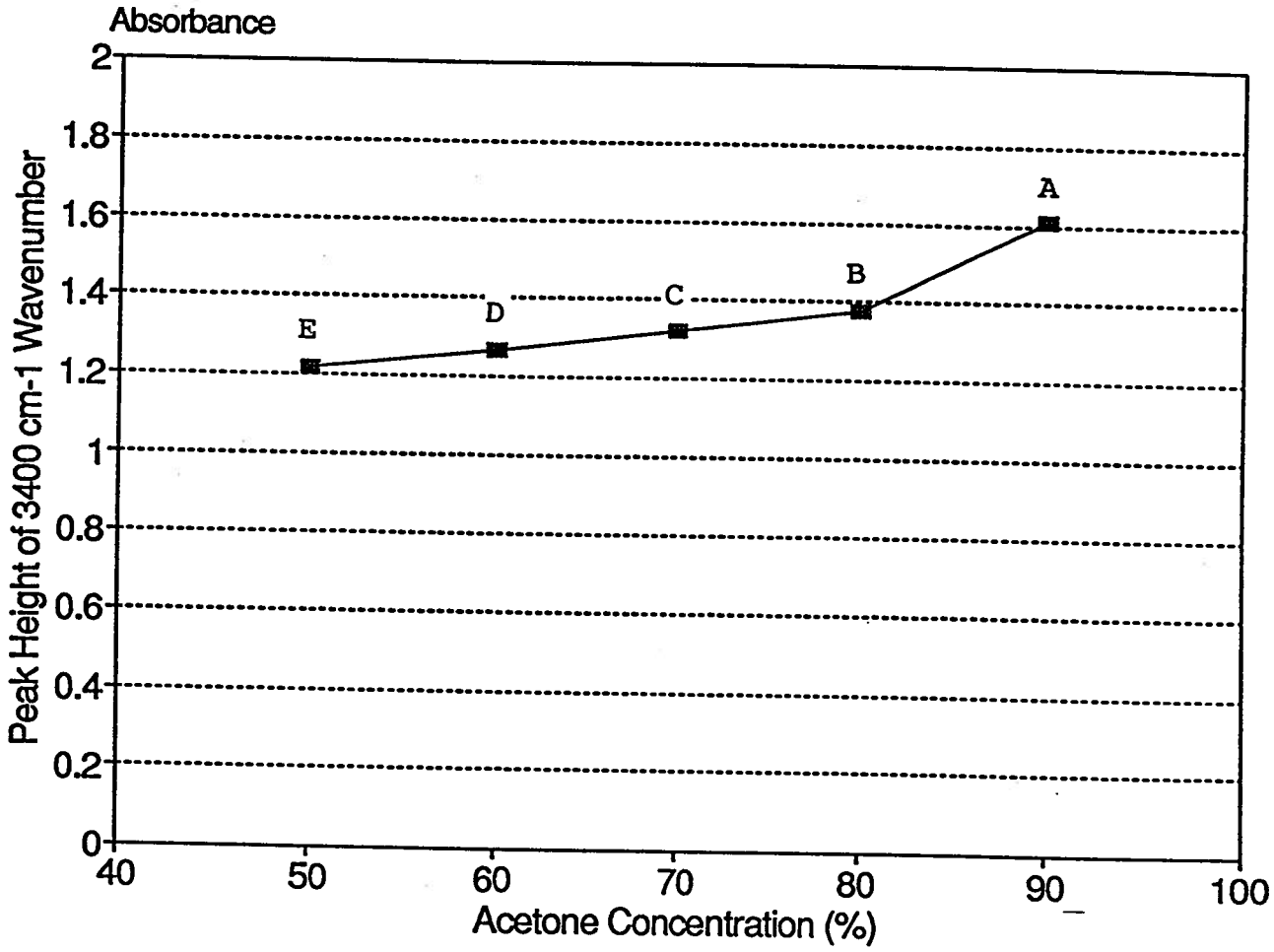


Figure 4.1.2.1. Effect of acetone on hydrogen bonding of cotton residues treated with different acetone concentrations (liquor/solid ratio: 10/1; 150 ^{o}C; 2 hr; no acid catalyst added).

* Means with the same letter are not significantly different.

** Significance at 95% confidence level.

The spectral changes in the vicinity of the O-H fundamental stretching range, that accompany the solvent effect on cellulose, are shown in Fig. 4.1.2.1. The results indicate that the average height of the O-H band (3400 cm^{-1}) has increased with the increase of acetone concentration in the solvent composition. Fig. 4.1.2.1 also shows that there is a sharp increase in band height especially in the 80 to 90% range in acetone concentration. The statistical analysis shows that the treatments of cotton with different acetone concentrations are significantly different, Fig. 4.1.2.1 (Duncan's multiple range test). The increase in the intensity of the O-H range band (3400 cm^{-1}) with the increase of acetone concentration is due to the fact that the reaction of acetone with the cellulose hydroxyls is expected to weaken the hydrogen bonding in the system. This attenuation of the hydrogen bonds leads to provision of spacings in the cellulosic material. These results are in accord with the earlier observations recorded on acetone-water pulping of wood species (Zarubin et al., 1989) when it was found that the physical/mechanical properties of paper were lowered due to acetone treatment. However, the decrease in physical strength of paper was attributed (Zarubin et al., 1989) solely to hydrolysis reactions. The extent of spacing (i.e., accessibility) in hydrogen bonding of a cellulose is dependent on a number of factors as will be discussed later in the text.

Fig. 4.1.2.1 illustrates that the solvent purification treatment has brought about, within the residual cotton, irreversible H-bond rearrangement that seems to cause permanent weakness in the H-bonded system. The most probable explanation for the hydrogen bond attenuation is due to the interaction of acetone (HBA) with the polar hydroxyl groups of the cellulose molecules (HBD). It is not well understood to what extent water can penetrate the crystalline cellulose, but in any case it is known that such penetration does not bring about any change of spacings in the crystallites (Libby, 1962).

On the other hand, the systematic increase of absorbance (attenuation of the H-bond) with the successive increase of acetone concentration in the acetone-water system (Fig. 4.1.2.1) appears to hold for an important phenomenon. The probable explanation for this phenomenon is that acetone is a dipolar aprotic protophylic solvent. Hence, this means that the behaviour of acetone with cellulose is similar to any other dipolar aprotic hydrophylic solvent such as dimethylsulphoxide (DMSO), dimethylformamide (DMF), dimethylacetamide (DMA), and hexamethylphosphoric triamide (HMPT). The solvation properties of these solvents are characteristic. It will suffice to state that owing to their molecular structure they are much better able to solvate cations than anions. In other words, they act as hydrogen bond acceptors with cellulose. Hence their role can also be confined to the

swelling of cellulose. It follows from these results shown in Fig. 4.1.2.1 that acetone can be considered as a swelling agent for cellulose. This interpretation is based on the fact that, earlier, Bax et al. (1972) emphasized that the proton-solvating property of acetone-water mixtures systematically increases with the rise in concentration of acetone reaching a maximum in pure acetone. They attributed the protophylicity of acetone to the charge density distribution in the acetone molecule, in conjuction with its spatial structure, which strongly favours solvation of positive ions over that of negative ones. Similar explanation about the protophylicity of acetone was also noted by Frey-Wyssling (1953) and Isaacs (1974). On the other hand, some previous works concerning the solvation properties of the acetone-water systems and their proton affinities surfaced differences of opinion. It was noted (Fong et al., 1969) that the enhancement of acidity with increasing acetone content in the acetone-water mixtures could be attained with up to 42 wt % acetone. Even though, this enhancement of acidity was interpreted (Fong et al., 1969) by the better anion solvation rather than the solvation of proton. Beyond this limit, any increase of acetone content in a water-acetone system will lead to the reduction of the dielectric constant, and hence it retards the dissociation constant of an acid. Later, Waggoner et al. (1982) claimed, in his investigation of medium effect on proton activity using acetone-water mixtures, that the

reason for the enhanced protophylicity of acetone in the range of 20 to 40 wt % acetone was due to the specific proton-solvating properties of acetone-water complexes that could be formed at these compositions. In other words, Waggoner et al. (1982) contended that the mutual interactions of the solvent constituents would possibly play a significant role in determining the proton affinities in the acetone-water systems.

The weakness of hydrogen bonds , resulting in the residual cotton during the acetonation, might be due to the length and nonlinearity of these bonds. In this concept, in a comprehensive comparative study Scheiner et al. (1985) investigated the geometry and energies of hydrogen bonds between carbonyl and hydroxyl oxygens. They stated that the instability developed into $(H_2CO...OH_2)^+$ by increase of the angle from 107^o to 180^o has in turn been attributed to the weakening of the H-bond caused by the nonlinearity of the O-H...O atoms. In the case of hydrogen bonds between two hydroxylic molecules (i.e., $H_2OH...OH_2)^+$ the H-bond was not weakened because the central proton remained along the O...O axis. Their results indicated that the rigidity of the (COH) angle in H_2COH prevented the central proton from following the water molecule as it rotated down to the angle of 180^o. The experimental results showed (Scheiner et al., 1985) that an energy of 16.3 kcal/mol was required to bring the hydrogen bond, formed between a carbonyl group and hydroxyl compounds, to linearity. However, the hydrogen bonds, formed

between hydroxyl compounds, consumed only 4.6 kcal/mol to maintain linear position. In addition, Jeffrey et al. (1991) noted that the carbonyl (C=O) bond length is much less sensitive to the changes in bond character than the single C-O bond length. It was also emphasized (Jeffrey et al., 1991) that the carboxylic acids offer very strong hydrogen bonds through their hydroxyl groups as hydrogen bond donors (HBD). However, on the contrary, they form with other molecules fairly weak hydrogen bonds through their carbonyl groups (C=O) as hydrogen bond acceptors (HBA). This was attributed (Jeffrey et al., 1991) to the rigidity of the carbonyl group. Apparently, this nonlinearity of hydrogen bonding in conjuction with the provision of longer hydrogen bonds, in the case of carbonyl groups, could be thought of as the mechanism of hydrogen bond disruption in the cellulosic material by acetone. In addition, the systematic, irreversible attenuation of hydrogen bonding, with the increase of acetone concentration, suggests a new orientation of the hydroxyls on the cellulose. However, such a phenomenon can be only attained through intramicellar swelling of the cellulose (Frey-Wissling, 1953; Sarko, 1978; Jeffrey et al., 1991). In other words, this intramicellar swelling is anticipated to be accompanied with a new type of crystal packing order, i.e., provision of a different set of unit cell dimensions.

Regarding the literature reviewed on the importance of hydrogen bonding, H-bond donor/acceptor solvents etc. (Huggins, 1971; Saenger, 1979; Simmering, 1964; Parker, 1962), and the results obtained in the present work, confirm that acetone has the ability to penetrate into the cellulosic material under suitable conditions. At the same time acetone is classified as a dipolar aprotic hydrophylic rather than hydrophobic solvent (i.e. HBA) (Frey-Wyssling, 1953; Bax et al., 1972; Isaacs, 1974). This means, the high ratio of acetone (around 90%) in the solvent composition (i.e., usually acetone + protic solvent) brings about the following consequences;

1- predominance of acetone in the reaction zone with cellulose, i.e., better solvation and
2- stereochemical changes produced by structural alterations such as the presence of isopropylidene intermediates in the solid state of the cellulose confirmed by C-13 CP/MAS NMR analysis. Consequently, the formation of those intermediates brings about considerable weakness in the hydrogen bonding (inter- and intramolecular bonds) system by formation of hydrophobic isopropylidene groups on the cellulosic material. This phenomenon can be explained by the fact that the electron density on hydrogen is reduced because of isopropylidene group formation on the sugar ring and the removal of some hydrogen in condensed water molecules as a

result of acetone and sugar movements out of the fibre structure.

In conclusion, for the hypothesis of disruption/destruction of H-bond of cellulose (carbohydrate) by acetone in the solvent purification of pulp, one relies on the following considerations:

a- deactivation of water molecules to interact with the cellulose when acetone comprises the major volume of the solvent composition,

b- penetration of acetone molecules into the cellulose fibres,

c- interaction of acetone with cellulose (carbohydrate) molecules through their hydroxyl groups. This presumably brings about stereochemical changes (i.e., rotational) at the beginning that disrupt and permanently weaken the H-bond of crystalline cellulose,

d- at high temperatures and in the presence of acid catalyst (hydrolysis), solvent interaction with cellulose molecules, now, is evident to cause further significant stereochemical alterations (i.e., rotational, configurational, and conformational). The validity of these assumptions has been proven by the results obtained by GC, HPLC, and C-13 CP/MAS solid state NMR analyses. These structural changes disrupt/destroy both inter- and intramolecular H-bond of the material (amorphous and crystalline regions),

e- at high acetone concentrations (around 90%), high temperature remarkably increases the rate of cellulose

(carbohydrate) dissolution (effect of overpressure of acetone at high temperature) by hydrolysis to low molecular weight fragments.

4.1.2.2. Other Factors Affecting Hydrogen Bonding of Cotton Residues during Solvent Purification Treatment

Further investigation into the solvent purification treatment has revealed that other variables such as type of acid, acid concentration, temperature and residence time have variable effects on hydrogen bonding of the treated material. However, the solvent's (i.e. type of acid catalyst) effect on hydrogen bonding appears to be the one most crucial among these parameters when other variables are kept constant as it is demonstrated in the following results.

4.1.2.3. Effect of Type of Acid Catalyst and Acid Concentration on Hydrogen Bonding of Cotton Residues during Solvent Purification Treatment

The effect of the type of acid catalyst on hydrogen bonding has been examined with different acid concentrations.Figs. 4.1.2.2 and 4.1.2.3 show the effect of acid concentration on hydrogen bonding with different acid catalysts.Both Figs. 4.1.2.2 and 4.1.2.3 show that there is a sharp fall of absorbance (i.e., from 1.61 to 1.05 and 0.86 for TFA and 1.06 for HCl) at low concentration of acid of

the solvent purification treatment. The second common phenomenon is the decrease in the peak height in the O-H stretching range with the use of different acid catalysts. Fig. 4.1.2.2 illustrates that the peak height goes down from 1.61 (no acid catalyst added) to 0.86 absorbance at 1.5 N TFA. However, the statistical analysis indicates that there is a difference in the behaviour of the two acids with regards to bydrogen bonding. According to Duncan's multiple range test, the treatments of cotton with different acid concentrations (TFA) are significantly different, see Fig. 4.1.2.2. While those treated with different acid concentrations (HCl) (except 0.0 N HCl) appear to be not significantly different (Fig. 4.1.2.3).

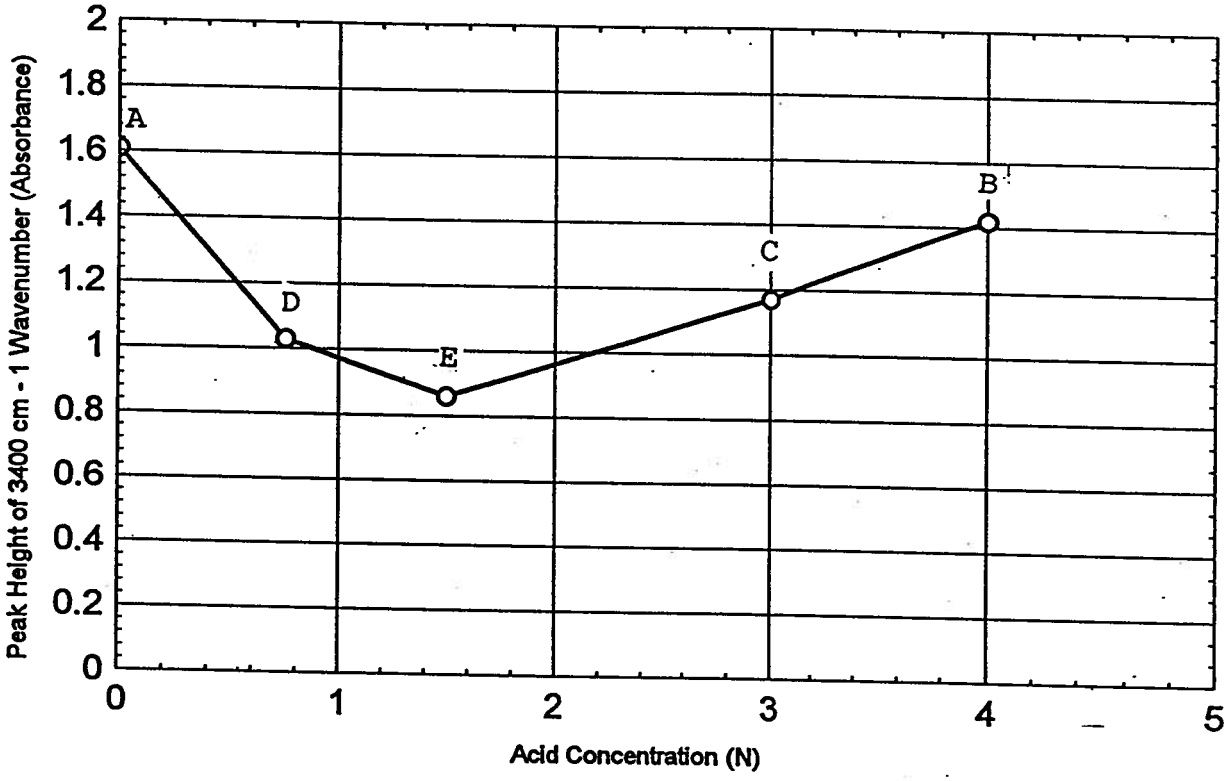


Figure 4.1.2.2. Effect of acid concentration on hydrogen bonding of solvent purified cotton when TFA was used as catalyst (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C).

* Means with the same letter are not significantly different.

** Significance at 95% confidence level.

However, at higher acid concentrations (3 and 4 N TFA) the band intensity of O-H range has successively increased to reach 1.42 absorbance. On the other hand, Fig. 4.1.2.3 shows that the peak height of the 3400 cm^{-1} has sharply decreased from 1.61 to 1.05 absorbance at 0.16 N HCl. Further increase in acid concentration (0.4 and 0.8 N HCL) resulted only in a very slight further decrease in absorbance.

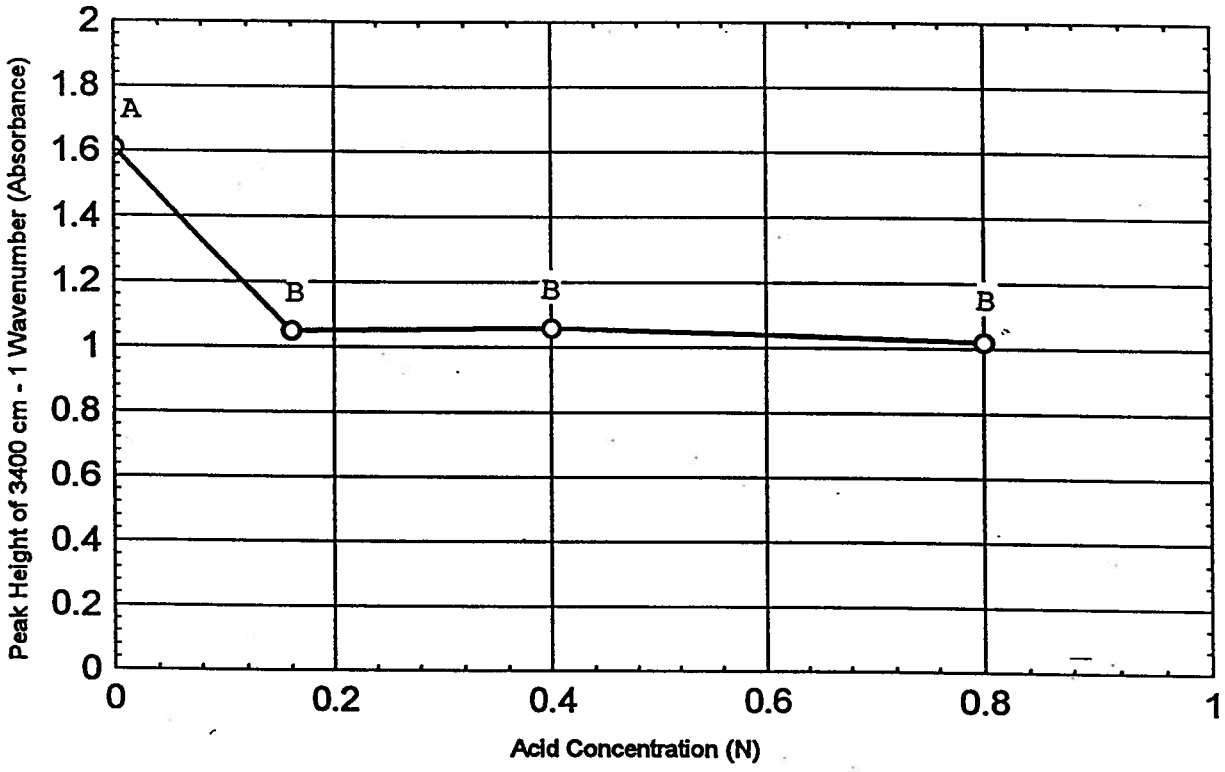


Figure 4.1.2.3. Effect of HCl acid catalyst concentration on hydrogen bonding of solvent purified cotton (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C).

* Means with the same letter are not significantly different.

** Significance at 95% confidence level.

Figs. 4.1.2.2 and 3 show much similarity in two aspects. The first trend is the sharp increase in the strength of hydrogen bond of the material at low concentration of acid of the treatment. This is probably associated with the ease of removal of considerable amounts of amorphous cellulose at the beginning of the treatment. On the other hand, the second observation is that the use of acid in solvent purification treatment gives rise, generally, to a stronger hydrogen bond in the residual material, no matter what type of acid catalyst is used. This can be attributed to the fact that the acid catalyst facilitates the process of structural transformations to take place by the protonation of already solvated molecules (i.e., isopropylidenated sugars). Hence, the strength of the hydrogen bond of the cellulose relies on the structural changes and the removal of sugar derivatives into the solution.

The result shown in Fig. 4.1.2.2 indicates that the variation of acid concentration of TFA in the presence of acetone has given cotton residues with different levels of hydrogen bond strength. Apparently, at lower acid concentrations (i.e., 0.75 and 1.5 N TFA) the formation of hydrogen bonding between TFA and the cellulose molecules dominates and renders even residual cotton with stronger hydrogen bonds (0.86 absorbance) than that of the untreated

cotton (1.08 absorbance) . In the case of higher acid concentrations (3 and 4 N TFA), favourable conditions are likely to develop for TFA-acetone suggested reactions (Geddes, 1956; Harris, 1965; March, 1985). In turn, reactions with high ratio of acetone in the solvent composition provide better chances for acetone to attenuate the hydogen bonds in the cellulosic material.

In conclusion, the variation in hydrogen bond strength is probably due to the different reactions associated with the use of TFA as a catalyst (i.e., protonation, formation of hydrogen bonding with both hydroxyl groups of the cellulose and water molecules, and TFA-acetone reaction). On the other hand, it was stated (Jeffrey et al., 1991) that the carbohydrates resemble water molecules in hydrogen bonding behaviour. They can, with their hydroxyl groups, have both donor and acceptor properties, i.e., amphiprotic depending on the reaction medium. In other words, cotton cellulose acts as hydrogen bond donor (HBD) in the abundance of acetone, while in lower concentrations of TFA in the presence of acetone it behaves as hydrogen bond acceptor (HBA).

Fig. 4.1.2.3 shows the changes in hydrogen bonding that have taken place at different concentrations in the residual cotton samples when HCl was used as an acid catalyst. The figure illustrates that the hydrogen bonding was stronger in the initial cellulosic material. A significant drop occurs on acidifying the system. Higher acid concentrations applied

have slight effect on hydrogen bond system. The strength of the hydrogen bond, in the case of HCl, could probably be attributed to the fact that HCl is known to be an efficient acid in hydrolysis and it seems that HCl is less involved in similar side reactions than TFA. Thus, the solvation of solvent-solute, more or less, proceeds much easier and hence leads to pronounced structural transformations in the cellulosic material. In turn, these acetonated sugars could easily be protonated, in the case of HCl acid as catalyst, and dissolved in the solution. Thus, the process of efficient hydrolysis with HCl will result in provision of cellulose with relatively stronger hydrogen bonds than that offered by the acetonation treatment in the absence of an acid catalyst.

The slight increase in the strength of hydrogen bonding associated with higher concentrations of HCl acid could only be attributed to further removal of amorphous cellulose in the solution. HCl is considered to form a weak hydrogen bond with other compounds. Hence one of the requirements for the formation of strong hydrogen bonds is that the element covalently bonded to the hydrogen must have a small atomic size (Mortimer, 1971). However, this is not the case in HCl. The chlorine atom is fairly large and, therefore, has a diffuse electron cloud. A similar explanation for the weakness of hydrogen bond formed by HCl acid with other compounds was given by Vinogradov et al. (1971). He stated

that the HCl molecule, even though it is a polar one, has weak dispersion forces.

4.1.2.4. Effect of Temperature on Hydrogen Bonding of Cotton Residues during Solvent Purification Treatment

Figs. 4.1.2.4 and 4.1.2.5 show the effect of temperature on hydrogen bonding of cotton residues during the solvent purification treatment. The statistical analysis indicates that the treatments of cotton at various temperatures (130, 150, and 180 ^{o}C) for hydrogen bonding are significantly different, in the use of TFA as a catalyst (Duncan's multiple range test). However, when HCl was used as a catalyst, the statisical analysis shows that the treatments at 130 and 150 ^{o}C are not significantly different. Fig. 4.1.2.4 shows that the solvent treatment at 130 ^{o}C, when TFA was used as a catalyst, has afforded a cellulosic structure with a weakened hydrogen bond. The absorbancies of the treated cotton samples (1.17, 1.41 and 1.52) are all higher than that of the untreated one (1.08). This can be explained by the fact that acetone as a low boiling point solvent (i.e., 56 ^{o}C) with a small molecule has the ability to penetrate and interact with the cellulose molecules (amorphous and crystalline) and bring about larger spacing in the hydrogen bond network as hydrogen bond acceptor (HBA). Nonetheless, the molecular size of water is normally smaller than that of the acetone (the diameter of

the water molecule is 2.78 A; Frey-Wyssling, 1953). However, the acetone effect (i.e., intramicellar swelling) is more pronounced than that of water. Hence, other important properties of a solvent affecting penetrability and swellability should be taken into account such as molecular structure and reactivity (Tchoubar, 1966; Bax et al.,1972; Isaacs, 1974). In addition, it was also emphasized (Bradley et al., 1993) that with the increase of temperature the molecules are more free and faster to reorient and interact. At 150 ^{o}C the treatment offers cellulose with much stronger hydrogen bonding (0.66, 0.86 and 1.14 absorbance). Apparently, at this temperature the formation of hydrogen bond, due to interaction of TFA (HBD) with the hydroxyl groups of the cellulose molecules, predominates. Nonetheless, the solvent treated cotton at 180 ^{o}C has yielded structures with stronger hydrogen bonding in general. This can be explained by the fact that at higher temperatures, favourable conditions are expected to develop for better diffusion of both acetone and acid catalyst into the cellulosic material. Hence, stereochemical alterations could proceed more effectively under more extensive solvent-solute solvation and bring about changes in the crystallinity index and the crystallite size.

Fig. 4.1.2.4 also shows that three points (two points (F, G) for 2 different treatments and one (H) for the 3 different treatments) are thermodynamically at equilibria.

Apparently, this means that the structures are similar for the treated samples at these points.

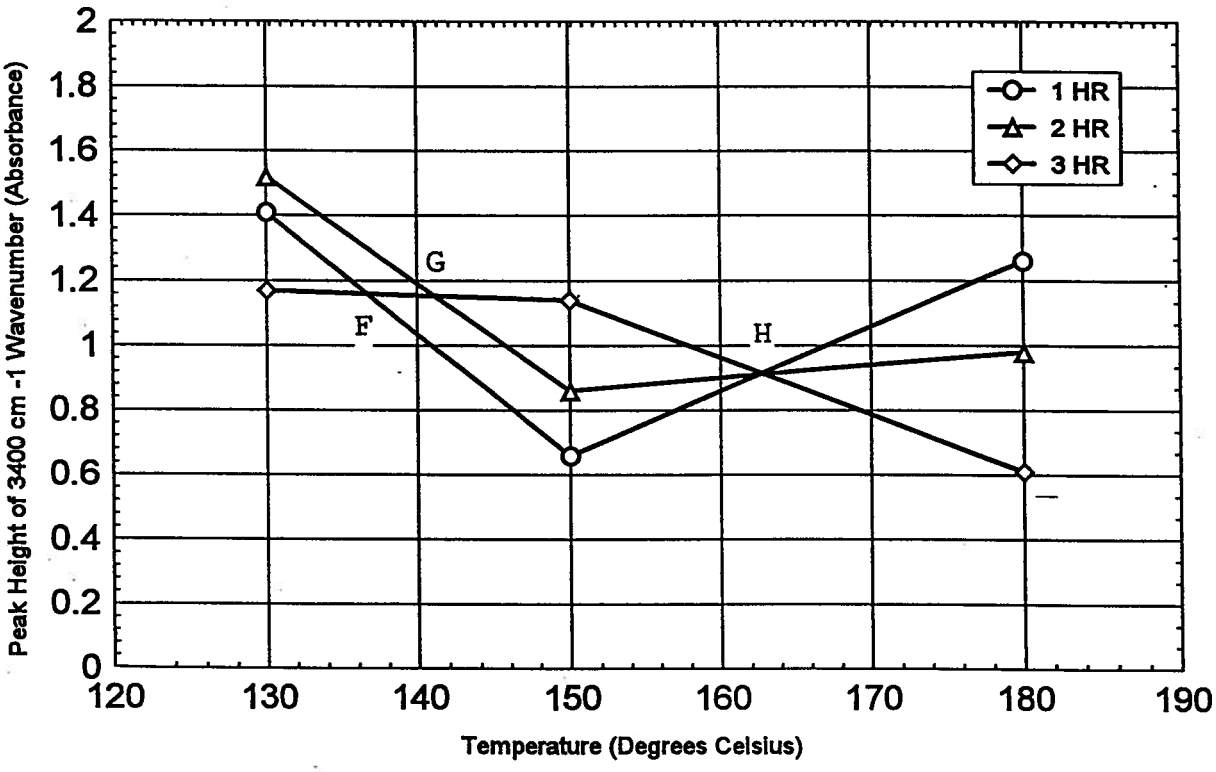


Figure 4.1.2.4. Effect of temperature on hydrogen bonding on cotton residues during solvent purification treatment (acetone:water: 90:10; liquor/solid ratio: 10/1; 1.5 N TFA).

However, Fig. 4.1.2.5 shows that the solvent purification treatment using HCl at all temperatures applied (except 180 ^{o}C) has generally rendered residual cotton with slight changes in hydrogen bonding. The interpretation for this phenomenon is twofold. First, it is possible that the increase of temperature may lead to an increase in the removal of both amorphous and crystalline cellulose.

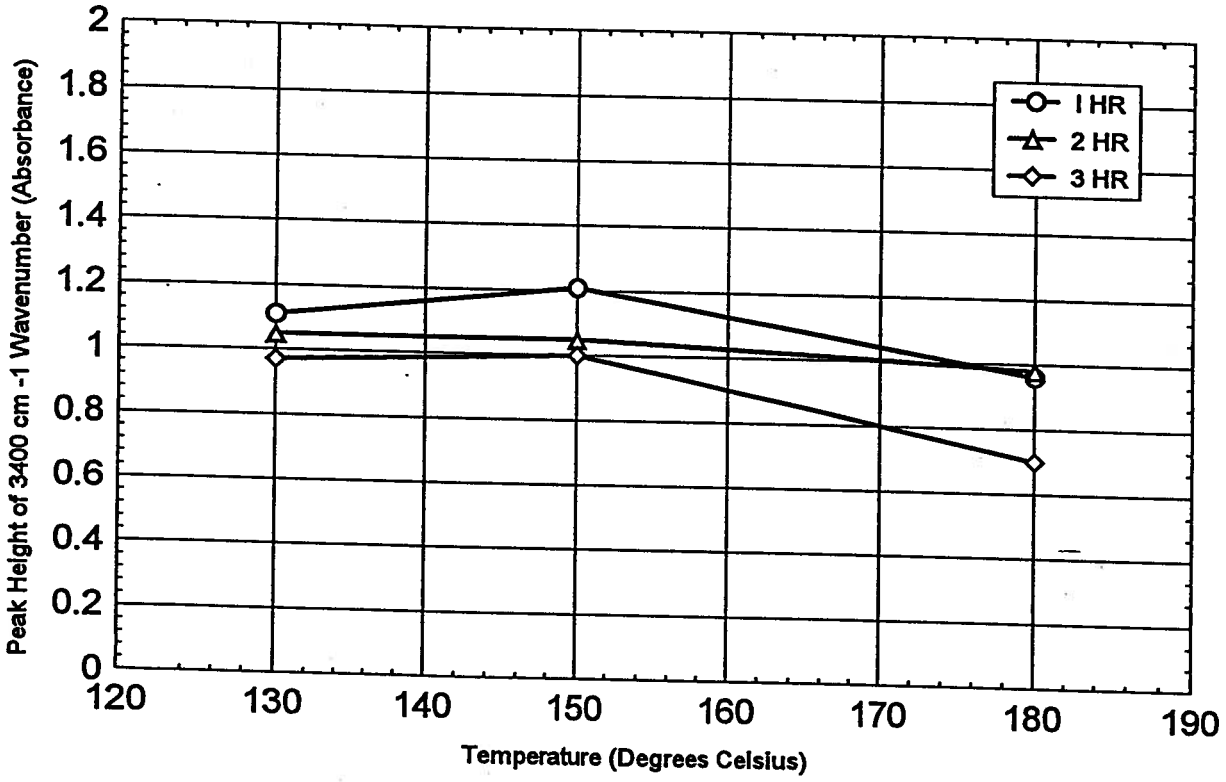


Figure 4.1.2.5. Effect of temperature on hydrogen bonding of cotton residues during solvent purification treatment (acetone:water: 90:10; liquor/solid ratio: 10/1; 0.16 N HCl).

In turn, this treatment is expected to offer cellulose with stronger hydrogen bonding, however, the outcome of the hydrogen bonding as shown in Fig. 4.1.2.5 is unremarkable and diverse. This is likely be due to the multilateral interactions of various solvents and complexes (i.e., $(CH_3)_2CO$, H_2O, HCl, $(CH_3)_2CO.H_2O$, $(CH_3)_2CO.HCl$, $H_2O.HCl$, $(CH_3)_2CO.H_2O.HCl$) available in the system in conjuction with the presence of weak hydrogen bond acid catalyst. It was also noted (Mortimer, 1971) that these complexes have somewhat different properties than those of their pure compounds.

4.1.2.5.Effect of Residence Time on Hydrogen Bonding of Cotton Residues during Solvent Purification Treatment

The object of this part of the study on the solvent purification treatment has been to investigate the influence of reaction time on hydrogen bonding of the treated cotton materials. The reason for this interest is because hydrogen bonds are usually involved in solvation and acid catalysis processes. In this respect, the time factor has an effect on them.

Fig. 4.1.2.6 shows different behaviour of hydrogen bonding within the cellulosic materials treated at different temperatures with TFA as the catalyst. The results shown in Fig. 4.1.2.6 indicate that the hydrogen bond strength for cotton treated at 130 ^oC appears to change with time (i.e.,

1.41 - 1 hr, 1.52 - 2 hr, and 1.17 - 3 hr). While the hydrogen bonding of the treated cotton at 150 ^{o}C increased steadily in absorbance with time (0.66 - 1 hr, 0.86 - 2 hr, 1.14 - 3 hr) indicating that the hydrogen bond was getting weaker. At 180 ^{o}C the hydrogen bond strength is found to go in the opposite direction, i.e., getting stronger. This flip in hydrogen bonding behaviour of the two different temperature treatments (150 and 180 ^{o}C) within a comparable reaction times (1 to 3hr) may be due to the fact that 150 ^{o}C provides suitable conditions for TFA to be involved with the reactants in side reactions. In turn, this situation may offer better chances for acetone as a major volume fraction in the solvent composition to develop weaker H-bonds within the cellulose. In other words, 150 ^{o}C is not high enough for TFA to bring about significant changes within the crystalline cellulose. The results of the weight loss for the two temperature treatments (150 ^{o}C, 180 ^{o}C, for 1, 2, and 3 hr) lend support to this assumption; 2.84%, 3.38%, 4.42%, and 7.11%, 12.02%, 18.07%, repectively.

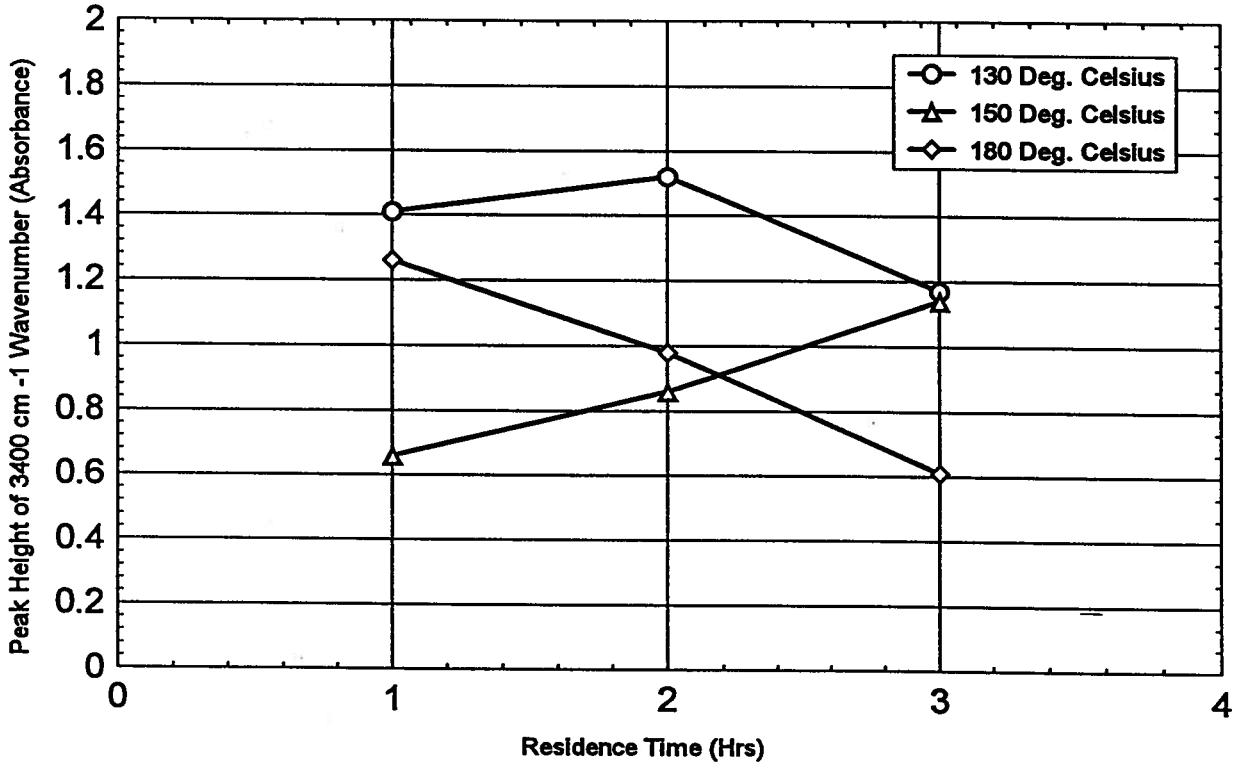


Figure 4.1.2.6 Effect of residence time on hydrogen bonding of cotton residues during solvent purification treatment (acetone:water: 90:10; liquor/solid ratio: 10/1; 1.5 N TFA).

These results explicitly indicate the removal of carbohydrate at 180 ^{o}C treatment with different reaction times. These results, also, demonstrate that the temperature is a more critical factor than the reaction time when other parameters were kept constant in the solvent purification treatment. In addition, the statistical analysis shows that the treatments of cotton for hydrogen bonding at different reaction times (Figs. 4.1.2.6 and 4.1.2.7) are not significantly different (except 3 hr treatment, HCl) for both acid catalysts (Duncan's multiple range test).

Fig. 4.1.2.7 shows the effect of residence time on hydrogen bonding of residual cotton when HCl was used as a catalyst in solvent purification treatment. The results shown in this figure demonstrate that the hydrogen bond gets slightly stronger with increase in the reaction time. This may be explained by the fact that chances for better solvation conditions increase with time due to changes in the environment of already solvated molecules (i.e., isopropylidenated sugars). Another most possible explanation may be that the residue which remains after such hydrolysis treatment is microcrystalline cellulose of higher crystallinity. This is consistent with the findings of Chang et al. (1977).

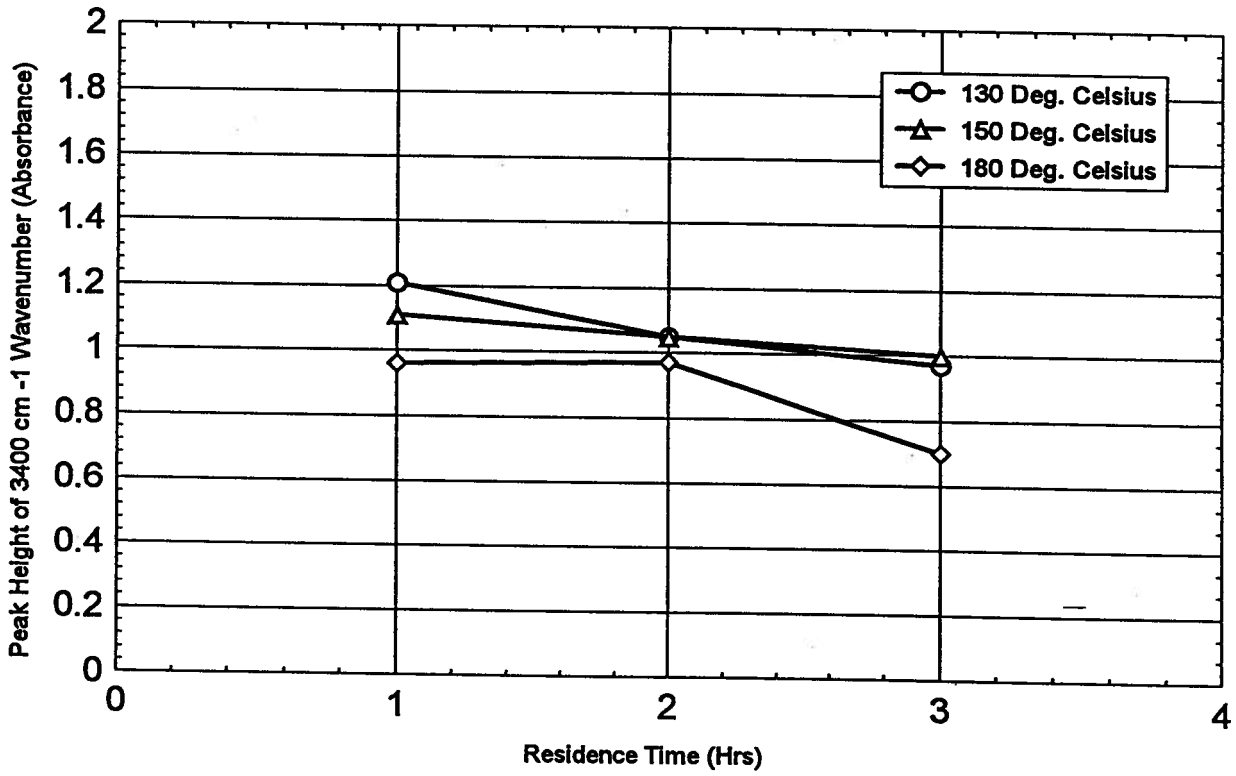


Figure 4.1.2.7. Effect of residence time on hydrogen bonding of cotton residues during solvent purification (acetone:water: 90:10; liquor/solid ratio: 10/1; 0.16 N HCl).

The results, which are shown in Figs. 4.1.2.2, 4.1.2.4 and 4.1.2.6, indicate that the use of TFA as a catalyst in the presence of acetone has led to much complexity in hydrogen bonding behaviour. However, the results shown in Figs. 4.1.2.3, 4.1.2.5 and 4.1.2.7 show that the hydrogen bond changes, in the case of hydrochloric acid, appear to be relatively simple and progressive.

It was emphasized in the literature that the nature of the solvent, more or less, has the some effect on the position of equilibria between conformations and hence the molecular rotation of a compound (Brewster, 1959; Stoddart, 1971; Lemieux et al., 1968). Also, changes in molecular rotation brought about by the solvent effect were noted (Brewster, 1959) to be sensitive to changes in temperature. Thus, involvement of TFA in the formation of hydrogen bonding, with more complexity than that resulting from the use of HCl as a catalyst, can have the following justifications. Trifluoroacetic acid (TFA) is classified as a polar protic (HBD) solvent with high ionizing power and fairly low nucleophilicity. Further, the TFA molecule has a resonance effect (Amis, 1966; Tchoubar, 1966; March, 1985; Reichardt, 1988). Besides, it was noted (Nissan, 1977; Jeffrey et al., 1991) that the strength of hydrogen bond is fairly dependent on the molecular structure of the hydrogen bond donor solvent, i.e., the strong hydrogen bond of TFA arises due to the presence of the highly electronegative F atom in the TFA molecule. Apparently, such properties make

TFA a strong carboxylic acid with a very strong hydrogen bond. Based on these facts TFA can develop a strong hydrogen bond with cellulose and form addition products with water, ketones, ethers and amines (Geddes, 1956; March, 1985). Now, it seems to be that TFA, most probably, is involved through hydrogen bonding with cellulose, acetone, and water. In turn, these reactions, in conjuction with other parameters, have different implications on the hydrogen bond strength of cotton that would take place during the solvent purification treatment. However, the major reaction that brings about irreversible structural changes (i.e., isopropylidene derivatives of sugars) within the cellulosic material, is the acetonation. This has been confirmed, in this work, by GC, HPLC, and C-13 CP/MAS solid state NMR.

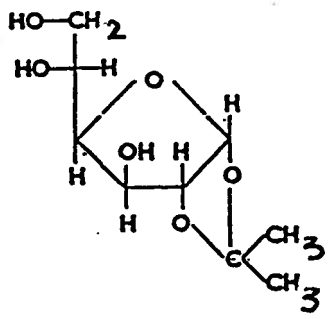
4.1.3 Cotton Hydrolysis during Solvent Purification Treatment

4.1.3.1. Gas Charomatographic (GC) Investigation - Isopropylidene Derivatives of Sugars, Identification during Solvent Purification Treatment

Hydrolysis of cellulose in acid catalyzed aqueous acetone is a novel technique. In anhydrous acidified acetone, isopropylidene groups are formed involving cis-hydroxyls on polyols of mono- and disaccharides (Kiso et al., 1976; Hasegawa et al., 1973; Hasegawa et al., 1973; Excoffier et al., 1984; Glushka et al., 1983; Khan et al., 1975; Ueno et al., 1981). Hydrolysis of substituted saccharide residues under these conditions has not been reported in the literature. On the other hand, in acid catalyzed aqueous acetone, rapid hydrolysis of cellulose to monomeric sugars, at high temperature, has been observed (Paszner et al., 1988). Their work indicated that the hydrolysis of cellulose in the presence of acetone was up to 700 times faster than in conventional aqueous acid hydrolysis.

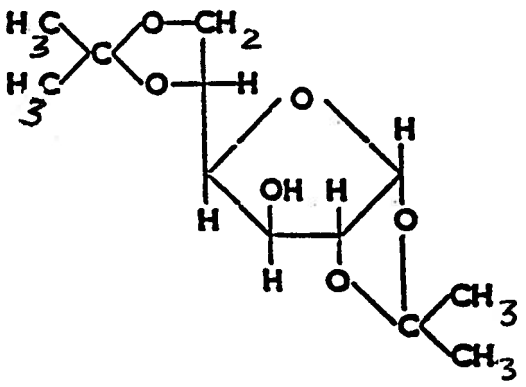
In order to separate and identify isopropylidene derivatives in the hydrolysate (nonreducing and reducing sugars) obtained on solvent purification of cotton, authentic solutions of 1,2-mono-acetal glucofuranose (Fig. 4.1.3.1), 1,2:5,6-diacetal glucofuranose (Fig. 4.1.3.2), 2,3:5,6-diacetal mannofuranose (Fig. 4.1.3.3) and 1,2:3,4-

diacetal galactopyranose (Fig. 4.1.3.4) were prepared with commercially available model compounds.



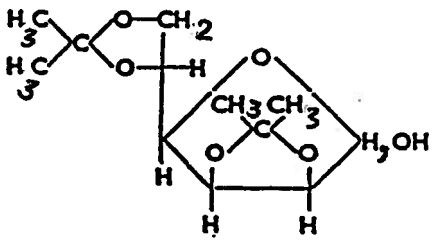
r.t. = 21.649 min

Figure 4.1.3.1. 1,2-O-isopropylidene-α-D-glucofuranose.



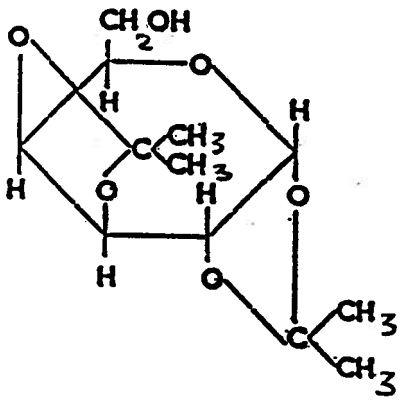
r.t. = 22.006 min

Figure 4.1.3.2 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose.



r.t. = 32.647 min

Figure 4.1.2.3. 2,3:5,6-di-O-isopropylidene-D-mannofuranose.



r.t. = 19.850 min

Figure 4.1.2.4. 1,2:3,4-di-O-isopropylidene-α-D-galactopyranose.

The structures of the cotton hydrolysate compounds (Figs. 4.1.3.5 and 4.1.3.6) have been established in a similar manner suggested by Tomori et al. (1984) by comparison of retention times with those of authentic ones. The nonreducing sugars in the hydrolysate (Fig. 4.1.3.5) appear to have two major isomers; one of them at the retention time 20.57 min is unknown, while the other at the retention time 21.91 min is 1,2:5,6-diacetal glucofuranose. Reducing sugars isolated from the hydrolysate on acetonation (Fig. 4.1.3.6) were found to have more than five major isomers; two of them have been identified 1,2:3,4-diacetal galactopyranose (r.t. 19.69 min.) and 1,2:5,6-diacetal glucofuranose (r.t. 22.02 min). It is noteworthy to mention that due to the fact that there are limited number of model compounds of isopropylidene derivatives of sugars available from commercial sources, it was not possible to identify all the major isomers developed in the hydrolysate. Neither is it logical to assume that all derivatized sugars are stable under these conditions and would survive the high temperature treatment. Nonetheless, isomers such as acetals of allose, altrose, gulose, idose, etc. could be anticipated to exist in the reaction mixture of the acetonation of cellulose.

Both Fig. 4.1.3.5 and 4.1.3.6 suggest that acetonation of cotton provides for a remarkable stereochemical versatility. In other words, much is characterized by isomerisation and interconversion reactions of glucose units

of cotton cellulose. The two figures also indicate that isomerization has led to the establishment of an equilibrium. It must be conceded that cyclic and acyclic carbohydrate residues react readily with aldehydes and ketones in the presence of acid catalyst to form cyclic acetals (Stoddart, 1971). Thus, after suitable reaction conditions, an equilibrium is eventually established in which the composition of the reaction mixture is determined by the relative free enegies of the cyclic acetals. However, from the stereochemical point of view, equilibrium is often complex. In other words, when an equilibrium exists between cyclic acetals of different ring sizes, acetal ring isomerization has to be taken into account in conjuction with configurational and/or conformational isomerizations (Stoddart, 1971). In addition, the two figures on cotton acetonation illustrate explicitly that isomerization does occur in three forms all together, i.e., constitutional, conformational and configurational.

Fig. 4.1.3.5 shows fewer isomers than that of Fig. 4.1.3.6. Further the amount and number of major isomers appears to be different. This could be attributable to the difference in stability of the various isomers, i.e., the unknown isomer at 20.57 min. retention time (Fig. 4.1.3.5) is more stable than the other major isomer - 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose. In this respect, a number of factors are involved in the stability and flexibility of isopropylidene derivatives. These are: the dioxolane and

dioxane ring system, sugar ring (pyranoid vs. furanoid), the electronic interactions between the functional groups and the molecular size of the derivatives (DeJong et al., 1964; Tomori et al., 1984; Tomori et al., 1984; Stoddart, 1971). Thus, when equilibrium is reached in solution by isomerization, the proportions of the different isomers are determined by their relative free energies (Stoddart, 1971).

It is significant and unexpected, however, that isopropylidene derivatives of glucose have survived the high temperature hydrolysis conditions of cellulose even in the presence of water.

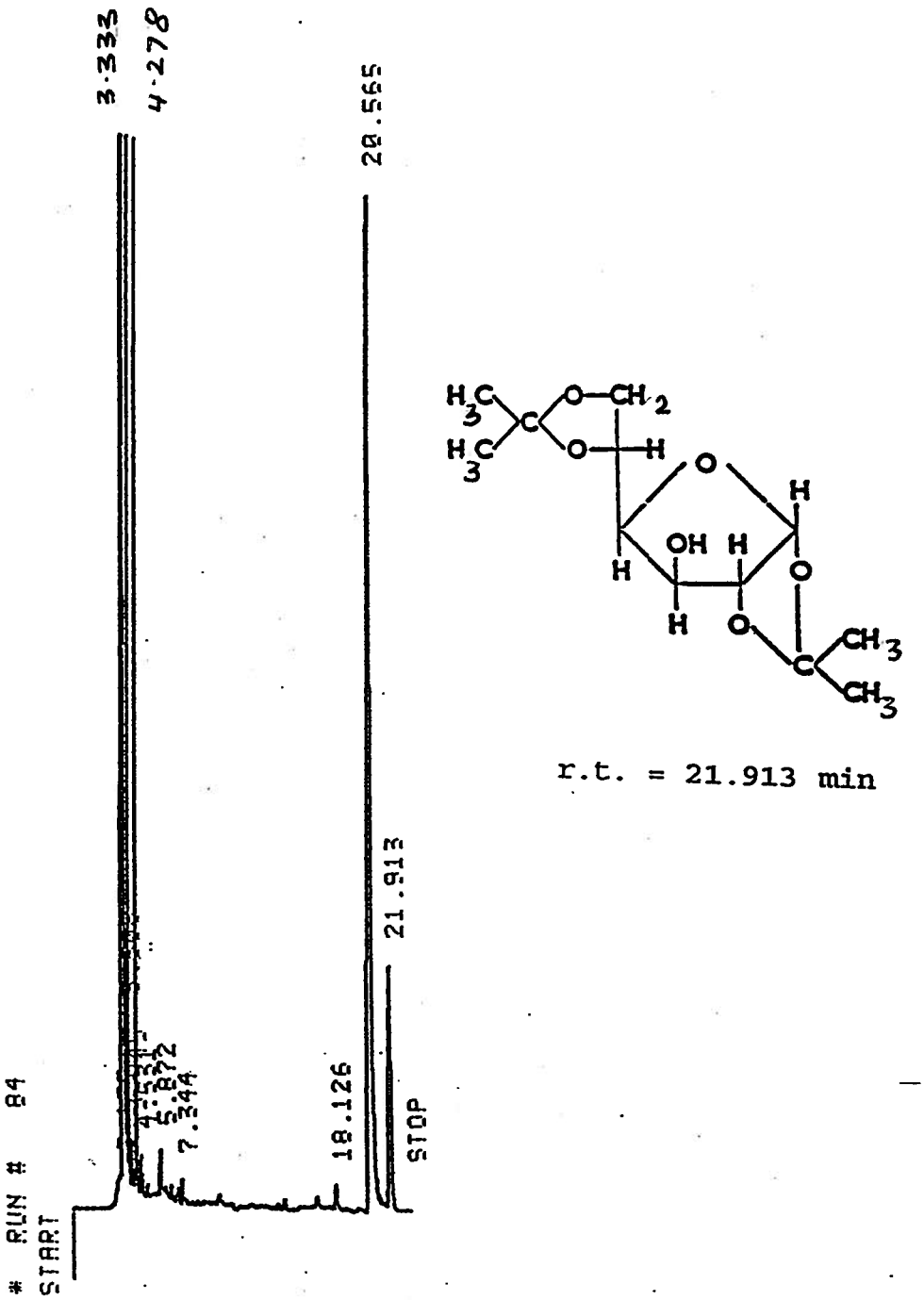
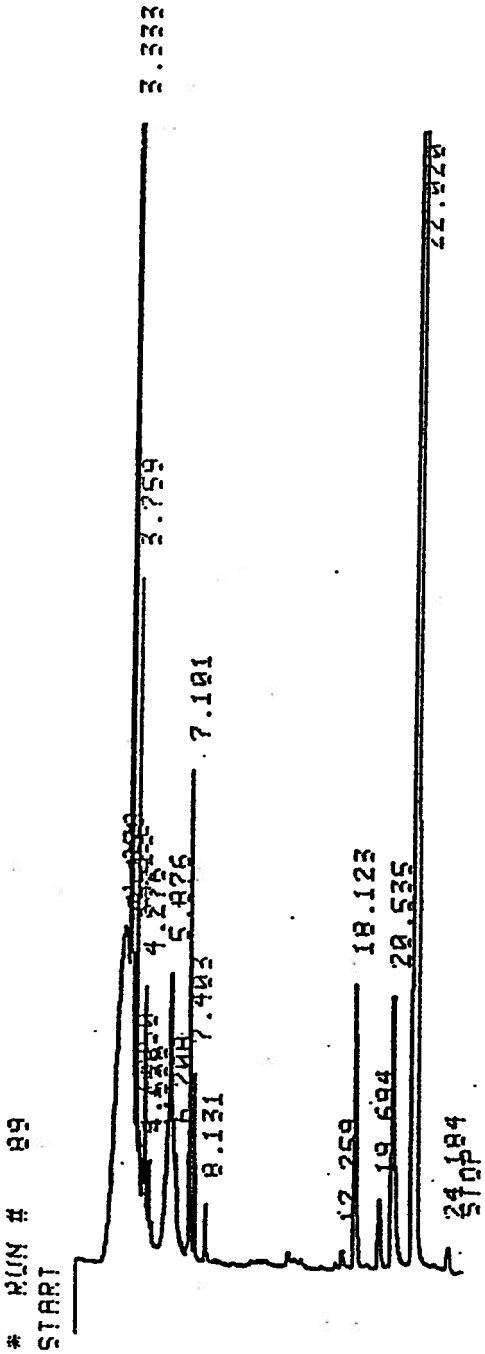
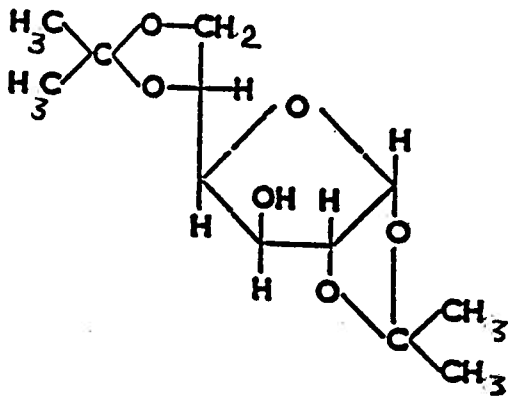
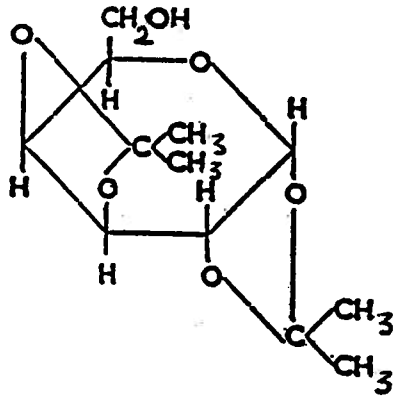


Figure 4.1.3.5. GC chromatogram of nonreducing sugars of the cotton hydrolysate of solvent purification treatment (acetone:water: 90:10; liquor/solid ratio; 10/1; 2 hr; 150 ^{o}C; 0.16 N HCl).





r.t. = 22.02 min



r.t. = 19.69 min

Figure 4.1.3.6. GC chromatogram of acetonated reducing sugars of cotton hydrolysate of solvent purification treatment (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C; 0.16 N HCl).

4.1.3.2 HPLC Analysis

The purpose of qualitative sugar analysis is to find out which sugars are extracted from the cotton, i.e., to know whether isomerization (epimerization) has taken place in the removal of acetone from isopropylidene derivatives of sugars. On the other hand, the quantitative sugar analysis is to assist in the determination of the predominance of the isopropylidenation reaction as the major mechanism (derivatives formation) responsible for the rapid hydrolysis and preventing the monomeric sugars from undergoing acid catalyzed dehydration.

Factors affecting the solvent purification treatment of cotton such as acetone concentration, type of acid, residence time, temperature, and acid concentration vs weight loss have also been studied (section 4.1.3.2.3).

4.1.3.2.1- Deacetonation - Epimerization

Not altogether unexpectedly Figs. 4.1.3.2.1, 2, 3, 4, 5, 6, 7, show the presence of different sugar isomers (epimers) in the hydrolysate. These resulted from various ketals as the result of the removal of isopropylidene groups by hydrolysis and deacetonation under different treatment conditions, i.e., type of acid catalyst, temperature, and reaction time. The results also indicate that glucose remained the major reducing sugar among the other epimers

resulting from the removal of acetone. In addition, the results also demonstrate the presence of minor by-products in small quantities such as 1,6-anhydroglucose (Fig. 4.1.3.2.8), furfural, and hydroxymethylfurfural. The appearance of small peak of furfural in all chromatograms of cotton hydrolysate could be attributed to the presence of small amounts of pectic substances in cotton cellulose. Although, cotton is considered as a pure cellulose (i.e., consists of glucose units only), however, it was reported in the literature (Hudson et al., 1948) that the constituents of mature cotton are as follows:

Constituent	% of dry weight
Cellulose	94.0
Protein (N x 6.25)	1.3
Pectic substances	1.2
Ash	1.2
Wax	0.6
Total sugars	0.3
Pigment	Trace
Other	1.4

These pectic substances are defined (Pigman et al., 1948) as a group of polysaccharides that consists of arabinans, galactans and largely polygalacturonide chains. Furthermore, it was noted (Frey-Wyssling, 1953) that the polygalacturonic acids are water-solube and when their sixth C atom (i.e., acid group) is replaced by H, we obtain the xylans or polyarabinans.

On the other hand, the unlabeled peaks of the reducing sugars indicated in the HPLC chromatograms are other isomers of glucose (i.e., not galactose and mannose). Isomers such

as allose, altrose, gulose, idose etc. could be expected to exist under those conditions in the reaction mixture. Unfortunately, due to the fact that there are limited number of model compounds of reducing sugars available from commercial sources, it was not possible to identify all the isomers produced in the hydrolysate. It is also noteworthy to mention that the reducing sugars (e.g., glucose, galactose) have experienced a shift of the retention time in different chromatograms. This may be explained by the fact that the column used for the separation of reducing sugars was an anion exchange resin one and these type of columns are known to be sensitive to the pH of the sample under investigation. In other words, the lower the pH of the sugar sample the shorter the retention time is.

The presence of 1,6-anhydroglucose in the cotton hydrolysate has been investigated by running an aqueous model compound of this sugar on HPLC. This is illustrated in Fig. 4.1.2.2.8.

The difference in the proportions of the various epimers in the hydrolysate is due to the fact that the accessibility of isopropylidene groups to hydrolysis was found to be different (Stanek et al., 1963). For example, in the hydrolysis of 1,2:5,6-di-O-isoproplidene-D-glucofuranose the 5,6-O-isopropylidene group is more sensitive to hydrolysis than the O-isopropylidene group in the 1,2 position. In other words, steric factors and electronic

interactions affect consideration (Stoddart, 1971) of the type of decomposition product formed.

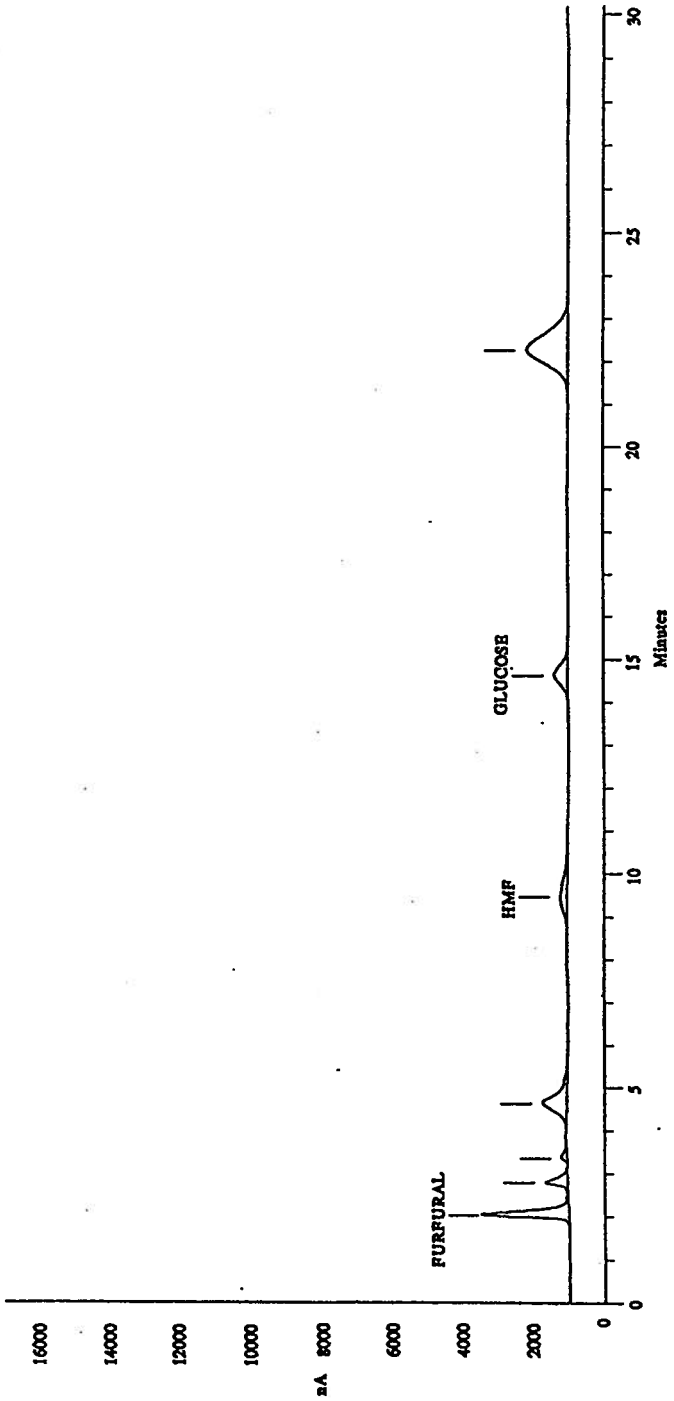


Figure 4.1.3.2.1. HPLC sugar chromatogram of cotton hydrolysate obtained at 150 °C (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; no acid catalyst added).

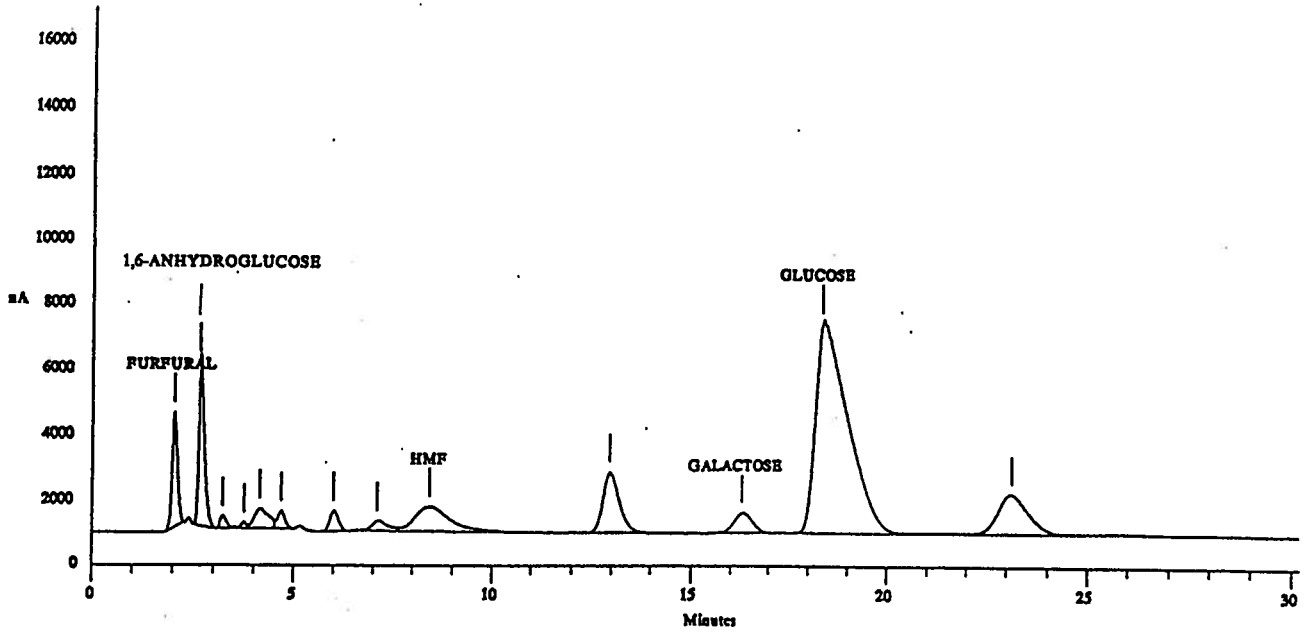


Figure 4.1.3.2.2. HPLC sugar chromatogram of cotton hydrolysate obtained at 130 ^{o}C (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 1.5 N TFA).

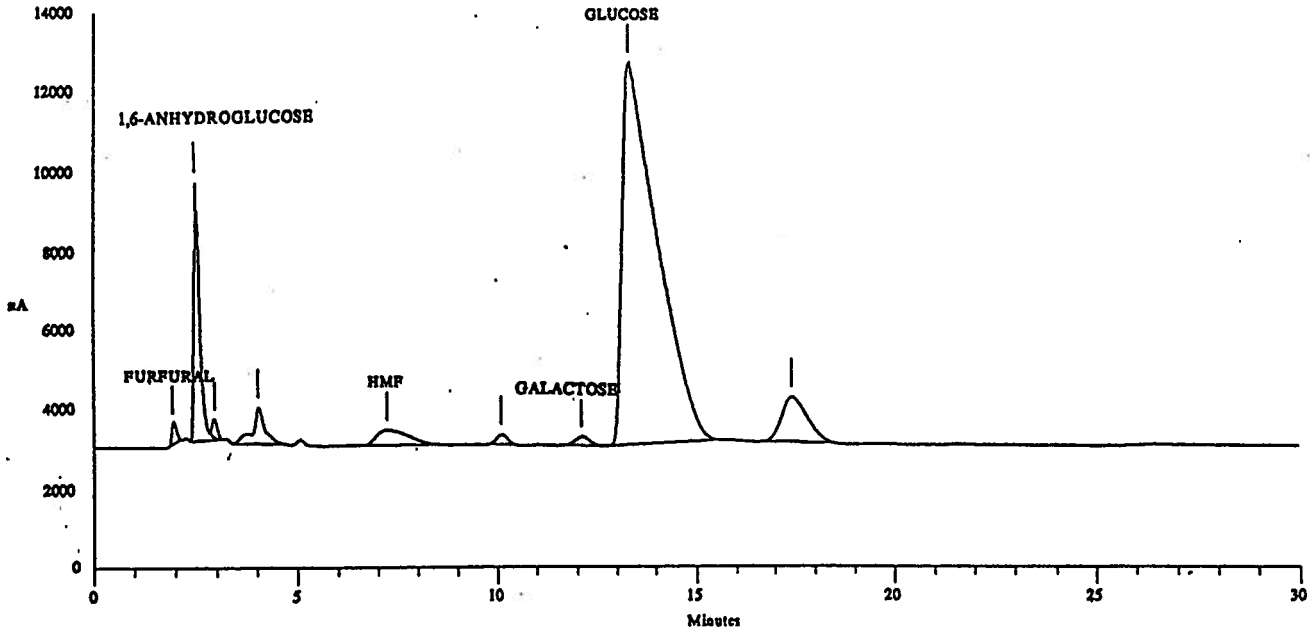


Figure 4.1.3.2.3. HPLC sugar chromatogram of cotton hydrolysate obtained at 130 °C (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 0.16 N HCl).

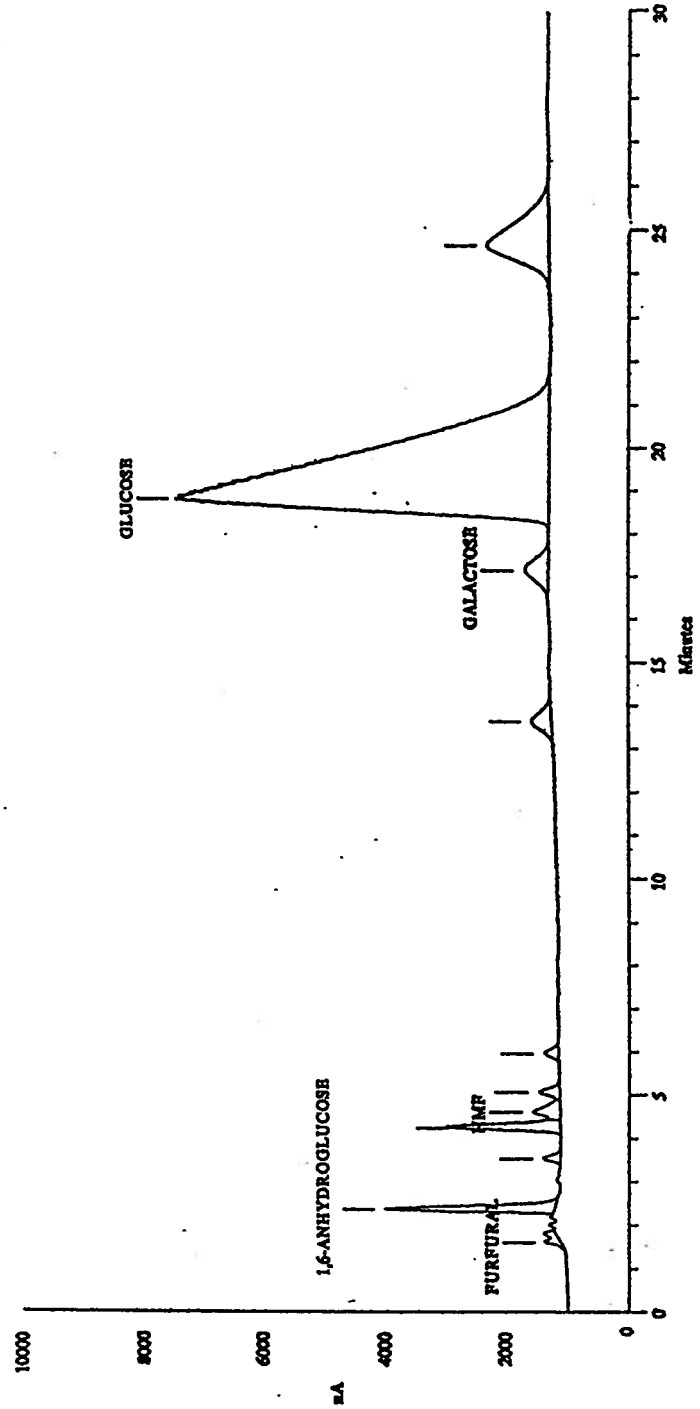


Figure 4.1.3.2.4. HPLC sugar chromatogram of cotton hydrolysate obtained at 150 °C (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 1.5 N TFA).

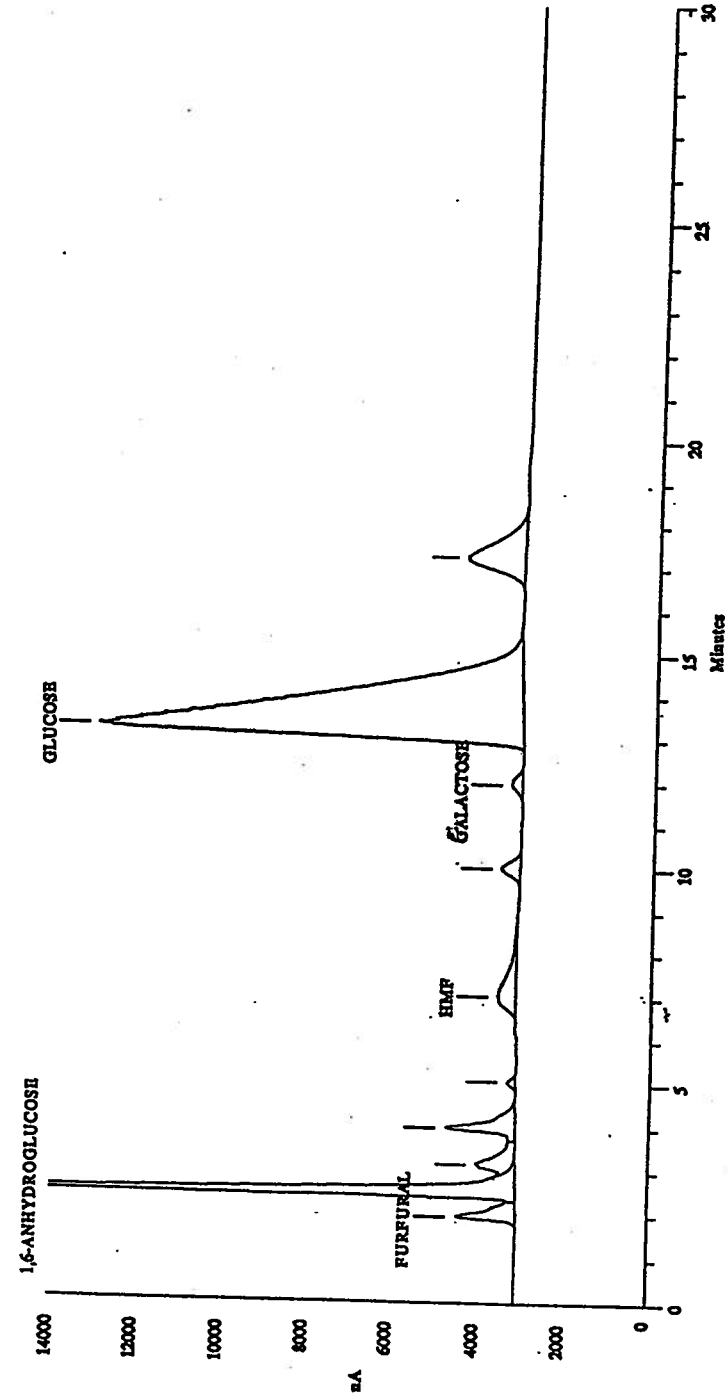


Figure 4.1.3.2.5. HPLC sugar chromatogram of cotton hydrolysate obtained at 150 °C (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 0.16 N HCl).

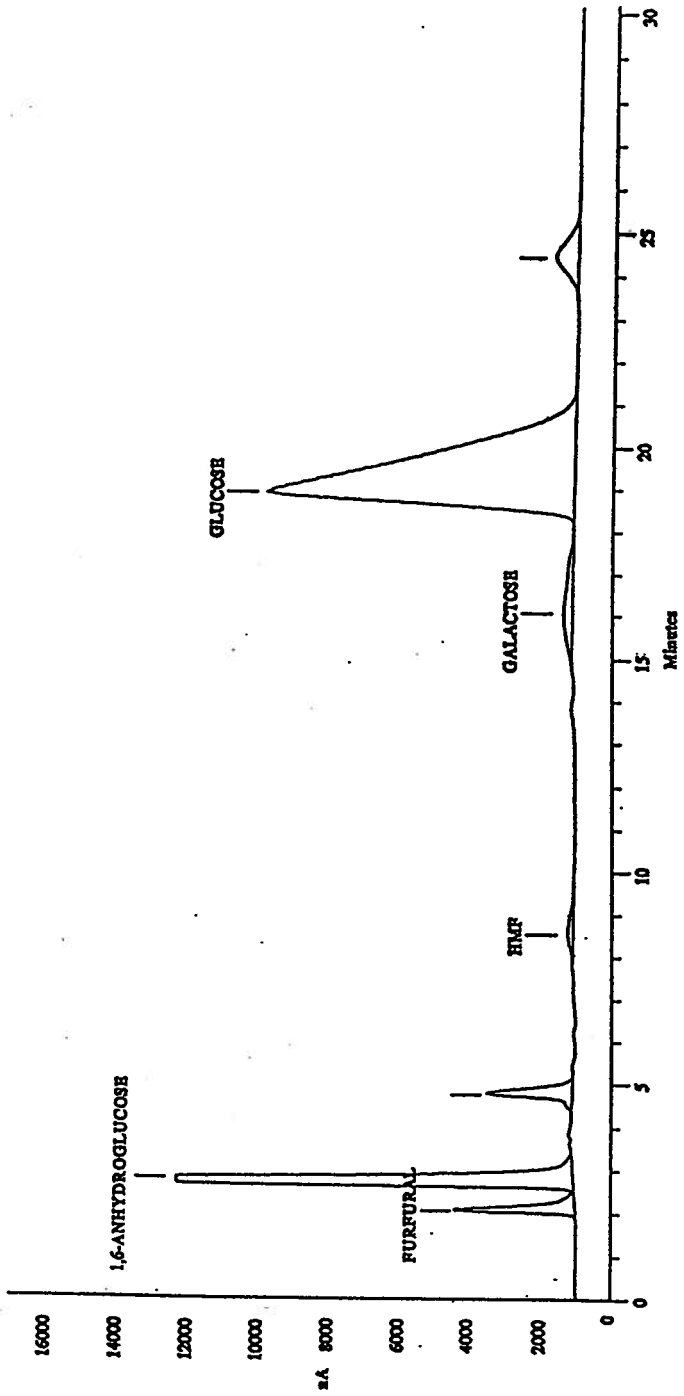


Figure 4.1.3.2.6. HPLC sugar chromatogram of cotton hydrolysate obtained at 180 °C (acetone:water: 90:10; liquor/solid ratio: 10/1; 1 hr; 1.5 N TFA).

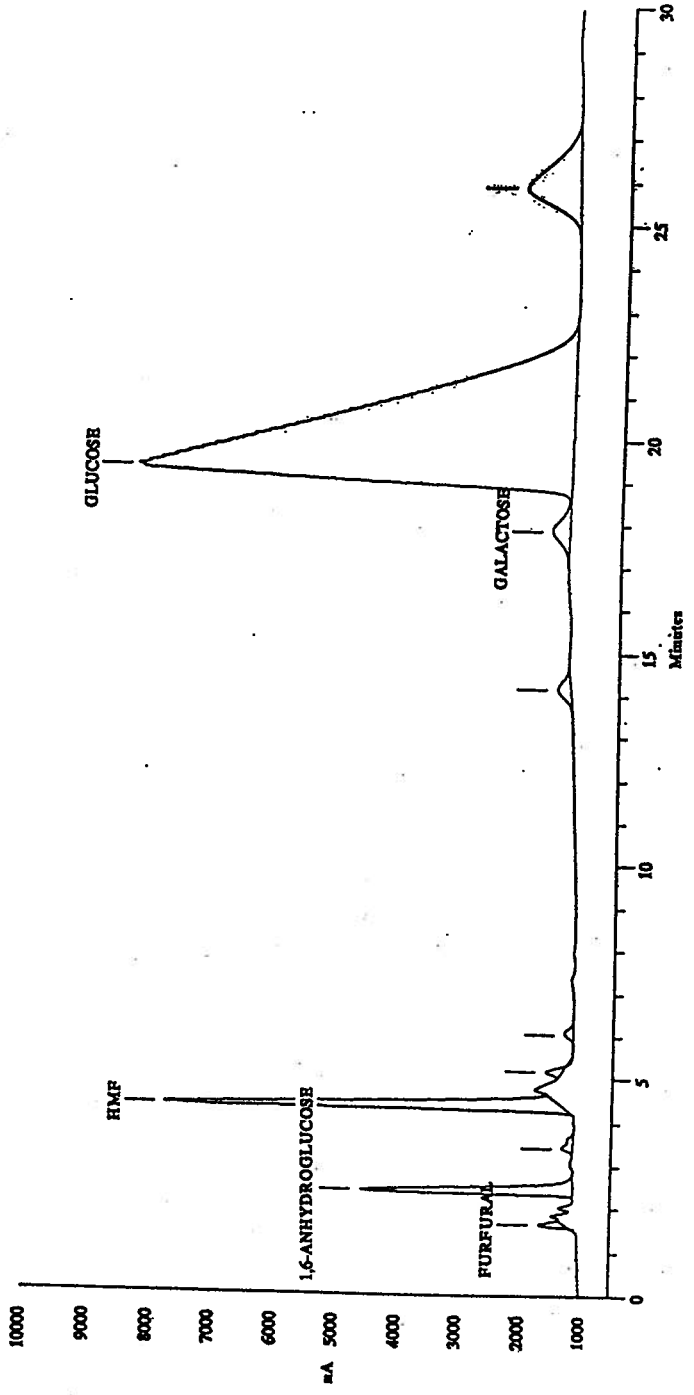


Figure 4.1.3.2.7. HPLC sugar chromatogram of cotton hydrolysate obtained at 180 °C (acetone:water: 90:10; liquor/solid ratio: 10/1; 1 hr; 0.16 N HCl).

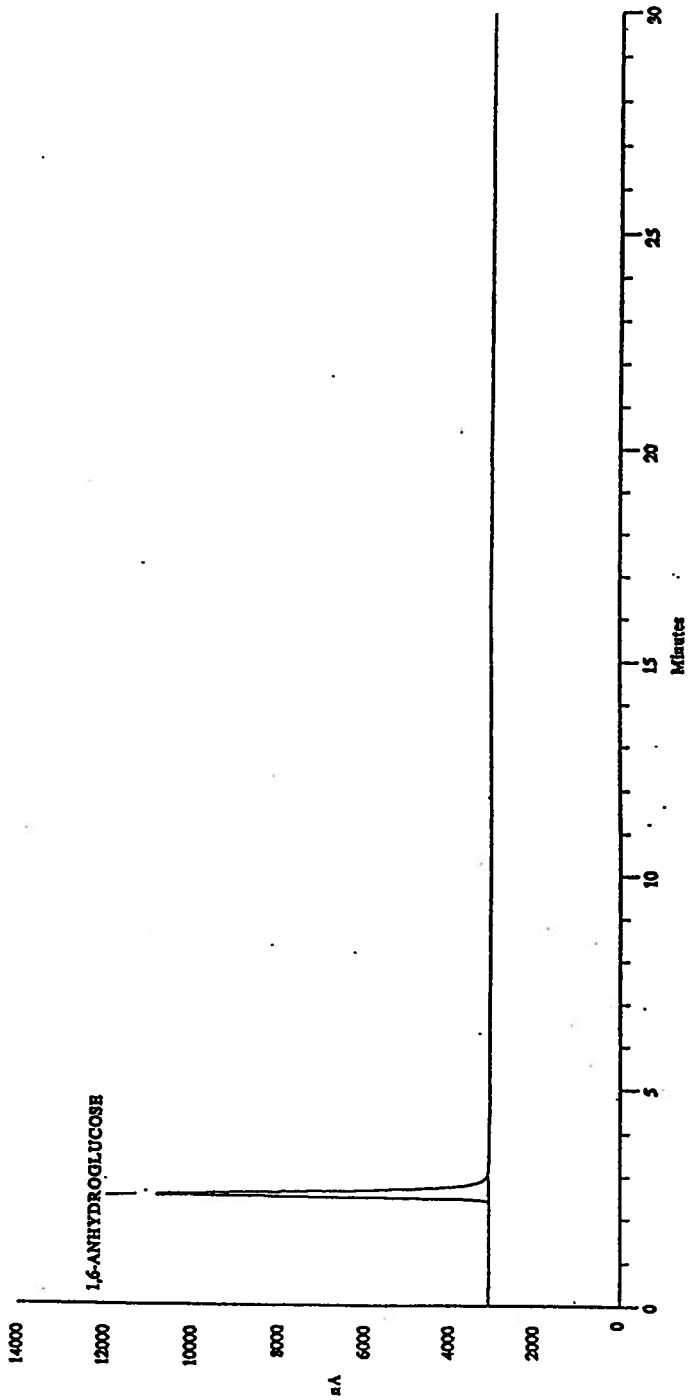


Figure 4.1.3.2.8. HPLC sugar chromatogram of 1,6-anhydroglucose.

With HCl as the catalyst the treatment at high temperature (180 ^{o}C) and for longer reaction times (3 hr) has given rise to a considerable increase in the amount of hydroxymethylfurfural (HMF) as dehydration product, at the expense of other epimers. This is well illustrated in Figs. 4.1.3.2.9 and 10. The results also suggest that the high acid concentration of hydrochloric acid (HCl) even at a moderate temperature (150 ^{o}C) has led to a remarkable increase of hydroxymethylfurfural (see Fig. 4.1.3.2.11). However, higher acid concentrations of trifluoroacetic acid (TFA) in the presence of acetone appear to have little effect on the formation of hydroxymethylfurfural (Fig. 4.1.3.2.12).

Although the results confirm that the sugar ring has enough protection by isopropylidene groups formed during solvent purification treatment, however, high temperature exposure for prolonged reaction times is likely to increase the chances of profound stereochemical changes. In turn, this would bring about, to a greater extent, sugar structures more accessible to degradation and dehydration reactions.

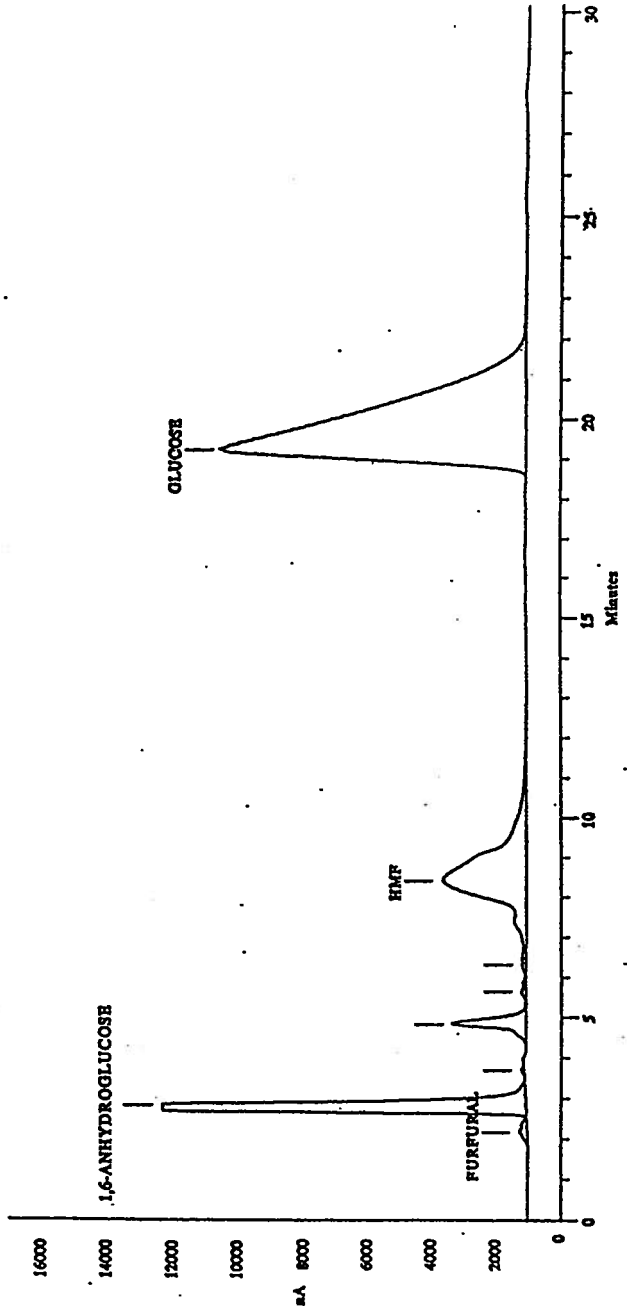


Figure 4.1.3.2.9. HPLC sugar chromatogram of cotton hydrolysate obtained at 180 °C (acetone:water: 90:10; liquor/solid ratio: 10/1; 3 hr; 1.5 N TFA).

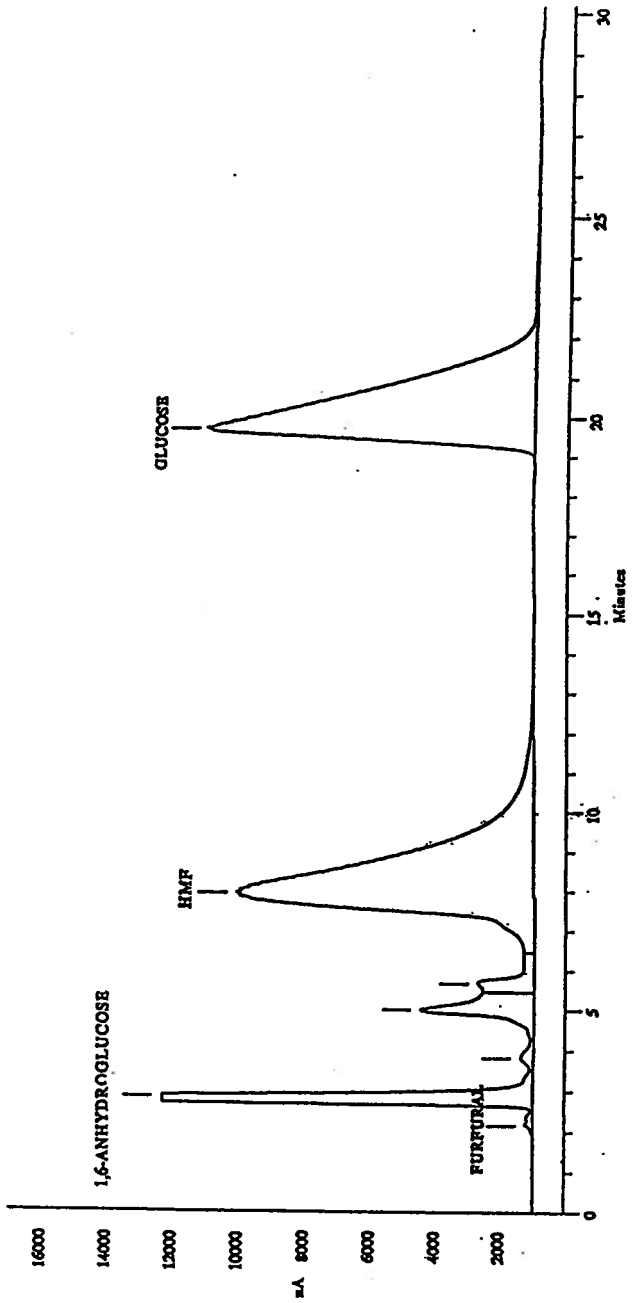


Figure 4.1.3.2.10. HPLC sugar chromatogram of cotton hydrolysate obtained at 180 °C (acetone:water: 90:10; liquor/solid ratio: 10/1; 3 hr; 0.16 N HCl).

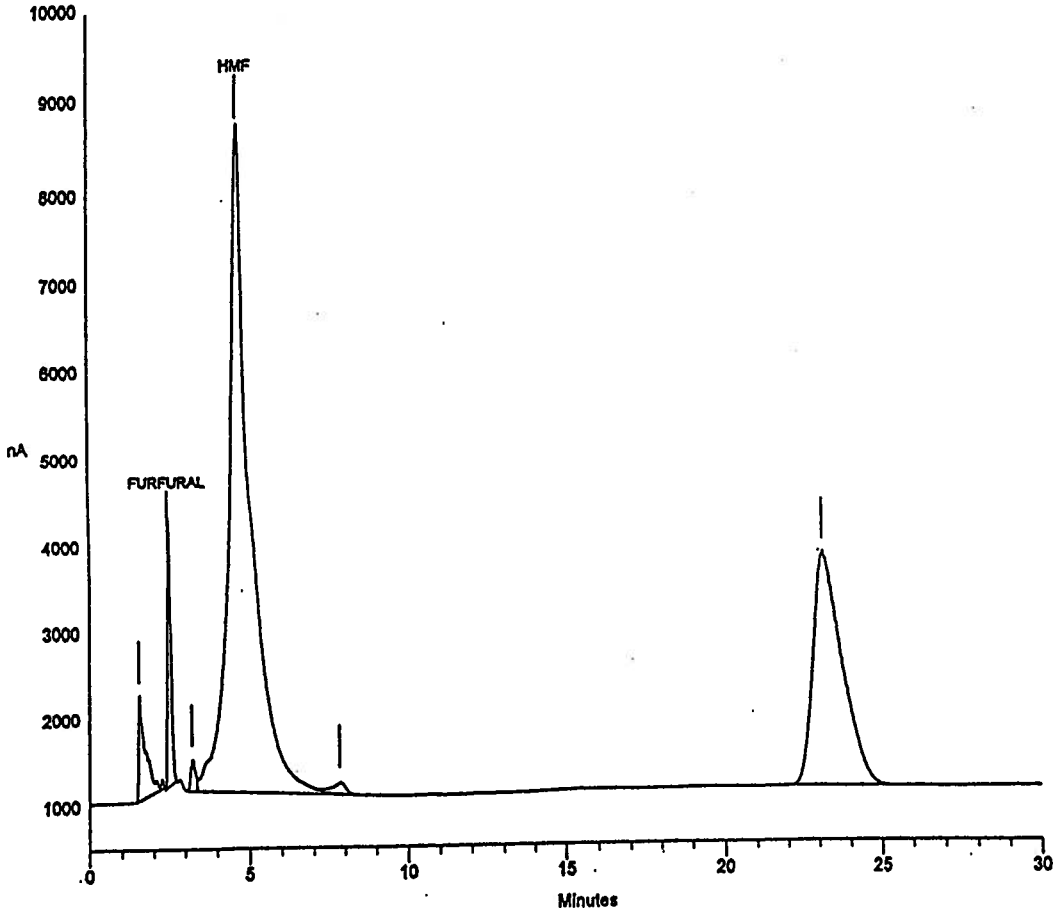


Fig. 4.1.3.2.11. HPLC sugar chromatogram of cotton hydrolysate obtained at 150 ^{o}C (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 0.8 N HCl).

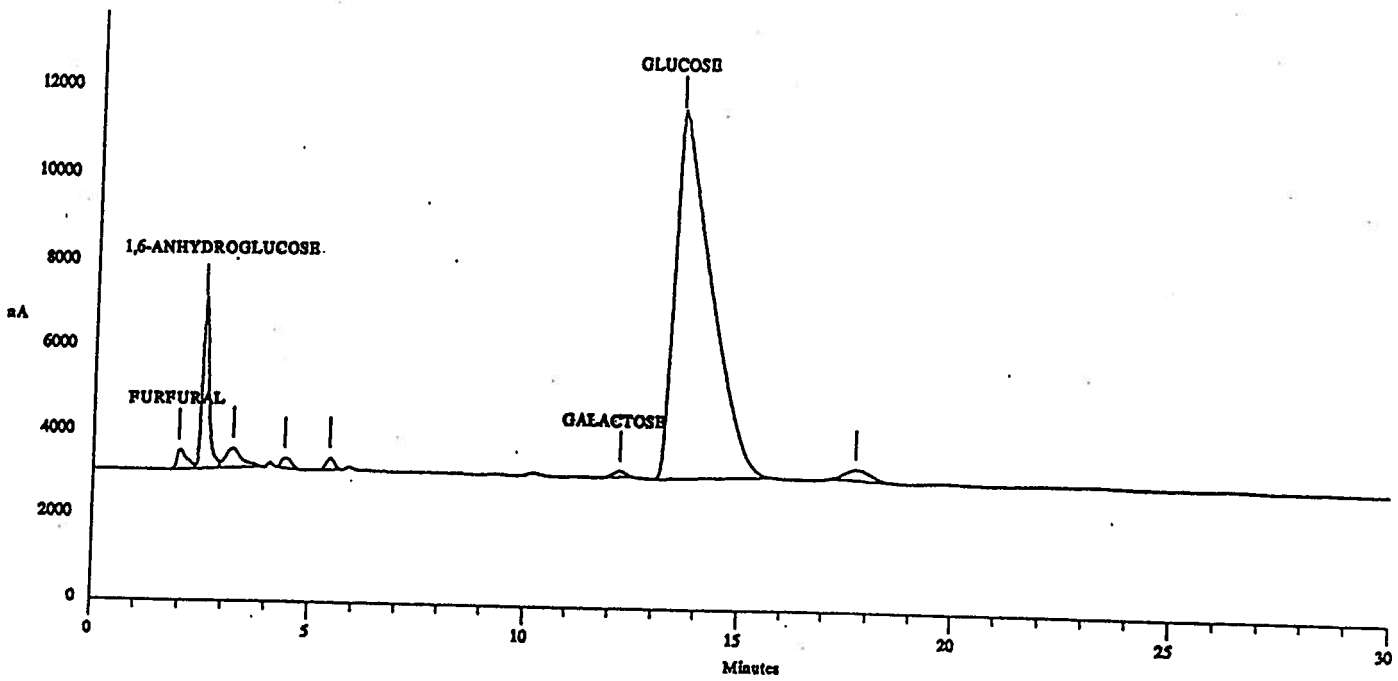


Figure 4.1.3.2.12. HPLC sugar chromatogram of cotton hydrolysate obtained at 150 °C (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 3 N TFA).

From these experiments it is apparent that TFA would be an effective but milder acid catalyst in the purification of cellulose that could altogether avoid dehydration of the dissolved sugars (Fig. 4.1.3.2.9, 4.1.3.2.12).

4.1.3.2.2. Quantitation - the Predominance of Acetonation Sugar Product Formation during the Solvent Purification Treatment

Using a sugar analyzer (HPLC), the different reducing sugars (identifiable and unidentifiable) resulting from both primary and secondary hydrolyses have been considered as of glucose origin. Their concentration in the hydrolysate was determined by the programmed HPLC system. The yield of acetonation sugar products was calculated based on the weight loss. Table 4.1.3.2.2.1 shows the sugar yields, for a set of solvent purification treatments conducted under the following conditions: acetone:water 90:10; 2 hr; 0.16 N HCl; 150 ^{o}C. The total sugar recovered was 86.33%. From this result about 40% of the potential sugar yield is found to be in reducing form, i.e., the primary hydrolysate. However, the remaining amounts of the acetonation sugar yield (around 46%) were nonreducing sugars and their conversion into reducing form is attained through secondary hydrolysis as illustrated in Table 4.1.3.2.2.1. Thus, the sugar yield result shows that the acetonation sugar products are the predominant part of the soluble hydrolyzed cellulose. It is

worth noting that the quantitative total sugar yield is in agreement with that stated by previous workers (Paszner et al., 1983; Ward et al., 1988). Also, the results indicate that the sugar yield resulting after the secondary hydrolysis increased with the extent of the reaction time.

It is important to mention that the results (GC analysis, deacetonation, and quantitation) obtained by the treatment of cotton with acidified aqueous acetone (acetone:water: 90:10) are in accord with that reported in the literature. It has been confirmed for many decades that cyclic and acyclic carbohydrate derivatives react readily with acetone in the presence of an acid catalyst to form cyclic acetals (Stanek et al., 1963; Stoddart, 1971). On the other hand the results (subsection 4.1.3.1, 4.1.3.2.1 and 4.1.3.2.2) are not in agreement with the Ward and Grethlein's interpretation. It was noted (Ward et al., 1988) that the formation of 1,6-anhydroglucose is the dominant mechanism responsible for the enhancement of the sugar yield in acidified aqueous acetone hydrolysis. However, that is not the case, because the formation of 1,6-anhydroglucose is expected to dominate in aqueous acidic solutions where high energies are applied (Stoddart, 1971). In addition, the formation of 1,6-anhydroglucose on cellulose units does not explain the high hydrolysis rates of cellulose in acetonation process. In conclusion, the possibility of isopropylidene groups on the cellulose units might significantly weaken the glycosidic linkages in cellulose.

In turn, this could lead to a rapid depolymerization of cellulose to isopropylidenated sugars.

Now it is evident that the yield of reducing sugars obtained during solvent purification treatment of cotton is fairly high. This high degree of sugar survival can only be explained by the formation of protecting groups (i.e., isopropylidenes) on the sugar rings.

The undetermined losses in quantitative analysis (around 13%), most probably, contain small quantities of isopropylidenated oligomers, 1,6-anhydroglucose and fairly stable isopropylidene derivatives of sugars such as monoacetals of endo dioxolane ring (e.g. 2,3-O-isopropylidene-mannofuranose) or/and monoacetals of pyranoid ring form (e.g. 1,2-O-isopropylidene-α-D-glucopyranose).

Table 4.1.3.2.2.1. Reducing sugar (primary + secondary hydrolysis) yield in cotton hydrolysate following the treatment with: acetone:water: 90:10; 2 hr; 0.16 N HCl; 150 °C.

Type of Hydrolysis	Amount	Yield	Total Sugars Prim. + Sec. Hyd. Amount	Yield
	mg	%	mg	%
Primary Hydrolysis	108	40.45	---	---
Second. Hydrolysis 1/2 hr treatment	90	33.71	198	74.16
Second. Hydrolysis 1 hr treatment	122.5	45.88	230.5	86.33

4.1.3.2.3 Changes in Weight Loss during Solvent Purification Treatment

The obvious measure of the extent of cellulose hydrolysis is the weight loss arising from the production of soluble sugars. Hence, in this work, weight loss is taken as a measure to examine the effect of each factor on the solvent purification treatment. Factors such as acetone concentration (with and without acid catalyst), temperature, residence time, acid concentration and type of acid catalyst have been investigated.

The result given in Fig. 4.1.3.2.3.1 shows that the successive increase in acetone concentration has been found to give rise to a systematic increase in weight loss. This result is consistent with those obtained in the investigation of reaction rates in stationary hydrolysis of cotton linters as a function of acetone concentration (Paszner et al., 1988). This result is also consistent with that obtained for the effect of acetone on hydrogen bonding of the cellulose (Fig. 4.1.2.1). In other words, the more accessible the cellulose, the much easier the hydrolysis reactions take place. In addition, the statistical analysis shows that the treatments of cotton with various acetone concentrations for the weight loss are significantly different (except 2 treatments), see Fig. 4.1.3.2.3.1 (Duncan's multiple range test).

In regards to the hydrolysis of cotton which occurred during solvent purification treatment in the presence of just acetone and water (i.e., no acid catalyst was added) this can be attributed to the protonation of glucosidic linkages with acetone/water mixture and the acids of pectic substances precent in the cotton cellulose. However, although cotton is considered a homogeneous cellulosic polymer (i.e., consists of glucose units only), it was recorded (Hudson et al., 1948) in the literature that cotton has the following constituents; cellulose 94.0%, protein (N x 6.25) 1.3%, pectic substances 1.2%, ash 1.2%, wax 0.6%, total sugars 0.3%, pigment traces, and other 1.4%. Those pectic substances were defined (Pigman et al., 1948) as a group of polysaccharides that consists of arabinose, galactose units and largely polygalacturonic acids. Furthermore, it was stated (Frey-Wyssling, 1953) that these galacturonic acids are water-soluble. In addition, the formation of acetic acid and methyl alcohol was ascertained by Ehrlich et al. (1929). On the other hand, the presence of small quantities of water in the solvent composition at relatively high temperatures appears to give rise to the formation of a complex from the reaction of acetone with the water molecules. This interpretation has been reached, in the present work, due to the drop in pH of the solvent treatment buffer (acetone:water: 90:10; 2 hr; 150 ^{o}C) from 7.46 to 5.77. This assumption is given due to the fact that the pH of cotton hydrolysate dropped from 7.46

to 4.59 within identical treatment conditions. On the other hand, the acidity of the acetone/water complex was also noted by Fong et al. (1969) and Waggoner et al. (1982). However, the explanation, given earlier by Zarubin et al. (1989) when they used acetone and water for their pulping study, was due to the hydrolysis of polysaccharides by the acid (acetic acid) formed during the pulping process. In addition, the increase in weight loss (from around 0.5 to 1.0%) maintained with the increasing acetone concentration (50 to 90%) is likely to occur from the better solvent-solute solvation that could take place in both amorphous and crystalline zones. This process of solvation will apparently lead to the opening up of hydrogen bonding and provision of strained glycosidic linkages on isopropylidenated sugars. Thus, the formation of isopropylidene groups between the adjacent sugar residues (Khan et al., 1975) could offer a reasonable explanation for the ease of breakage of glycosidic linkages in the cellulose chains.

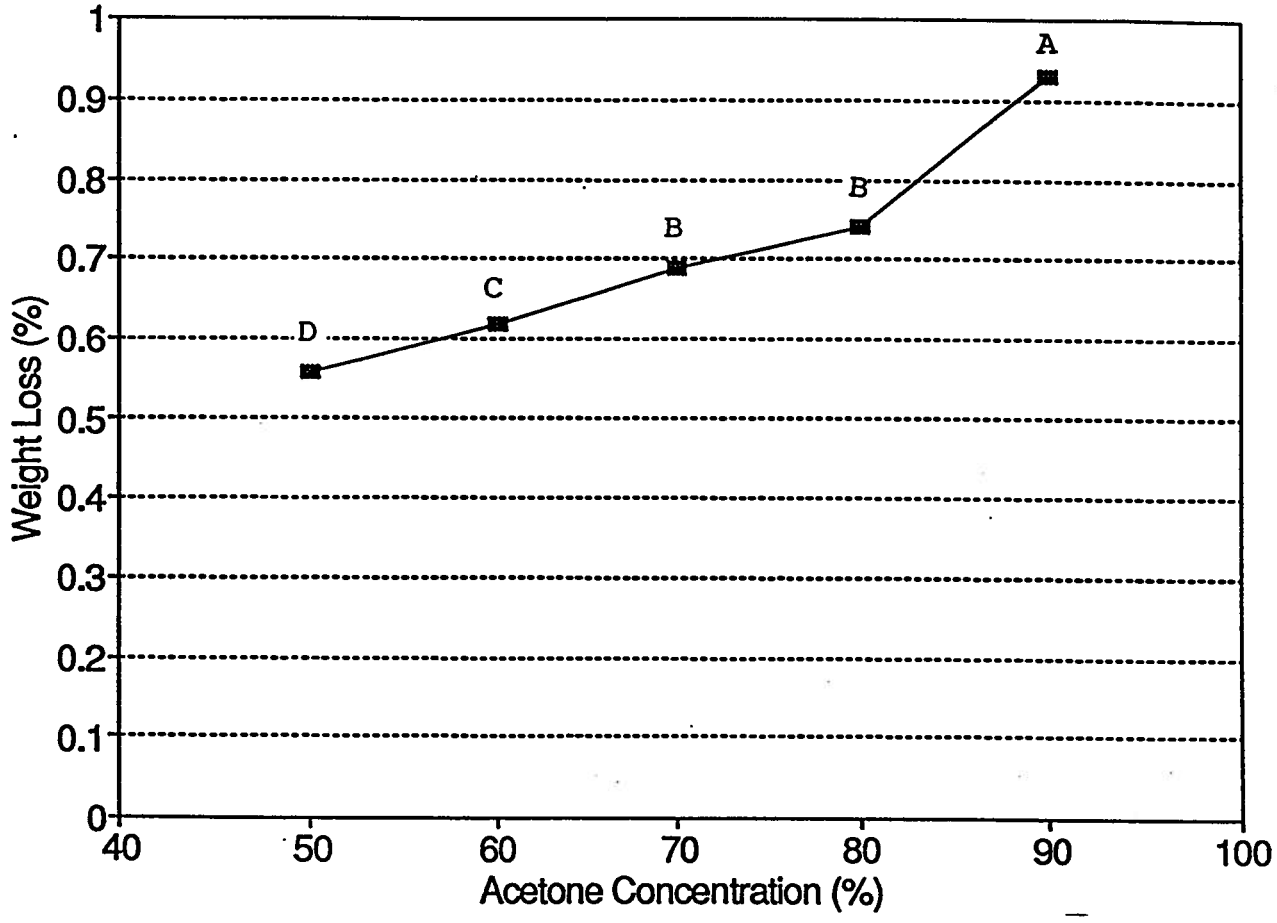


Figure 4.1.3.2.3.1. Effect of acetone concentration on the weight loss of solvent purified cotton (liquor/solid ratio: 10/1; 150 ^{o}C; 2 hr; no acid catalyst was added).

* Means with the same letter are not significantly different.

** Significance at 95% confidence level.

Figs. 4.1.3.2.3.2 and 3 illustrate the remarkable increase in the weight loss of solvent purified cotton due to the increase in temperature to (180 ^{o}C). The increase of temperature from 130 ^{o}C to 150 ^{o}C is shown to have slight effect on the weight loss of treated cotton. It is also important to mention that the temperatue increase from 150 ^{o}C to 180 ^{o}C caused a nonlinear increase in the dissolution of cellulose, increasing disproportionately at the higher temperature. However, the statistical analysis indicates that the treatments of cotton at different temperatures for the weight loss, in the case of the two acid catalysts, are significantly different (Duncan's multiple range test).

These results are consistent with those of Chang et al. (1976, 1977) and Paszner et al. (1988) on wood. It was noted that low temperarure hydrolytic dissolution of wood in acid catalyzed aqueous acetone occurred in two stages, i.e., bulk and main hydrolysis, while at high temperature the hydrolysis became first order all the way to complete dissolution.

Higher temperature increases the reaction rate of the system. In turn, this would lead to further stereochemical changes that can bring about, to a greater extent, more H-bond disruption in the cellulosic material. Consequently, more active sites (i.e., H-bond-free hydroxyl groups) will be available to undergo isopropylidenation. Besides, the reactivity of both acetone and acid catalyst increases with increased temperature as does the system pressure. This

would also speed up the isopropylidenation process by the involvement of more acetone molecules and hydrogen ions with the glucose units to yield isopropylidene groups along the cellulose chains. On the other hand, dissociation of both water and acid catalyst molecules into ions increases with the increase in temperature and this will, eventually, lead to a considerable participation of hydronium and hydrogen ions in the cleavage of glycosidic linkages.

This process, most probably, will have a significant impact on stereochemical alterations and formation of isopropylidene groups (i.e., the destruction of intramolecular H-bond between C6 and glycosidic O + configurational isomerism - from β to α). However, the best explanation for the effect of temperature on the rate of chemical reactions is given in the classical Arrhenius equation.

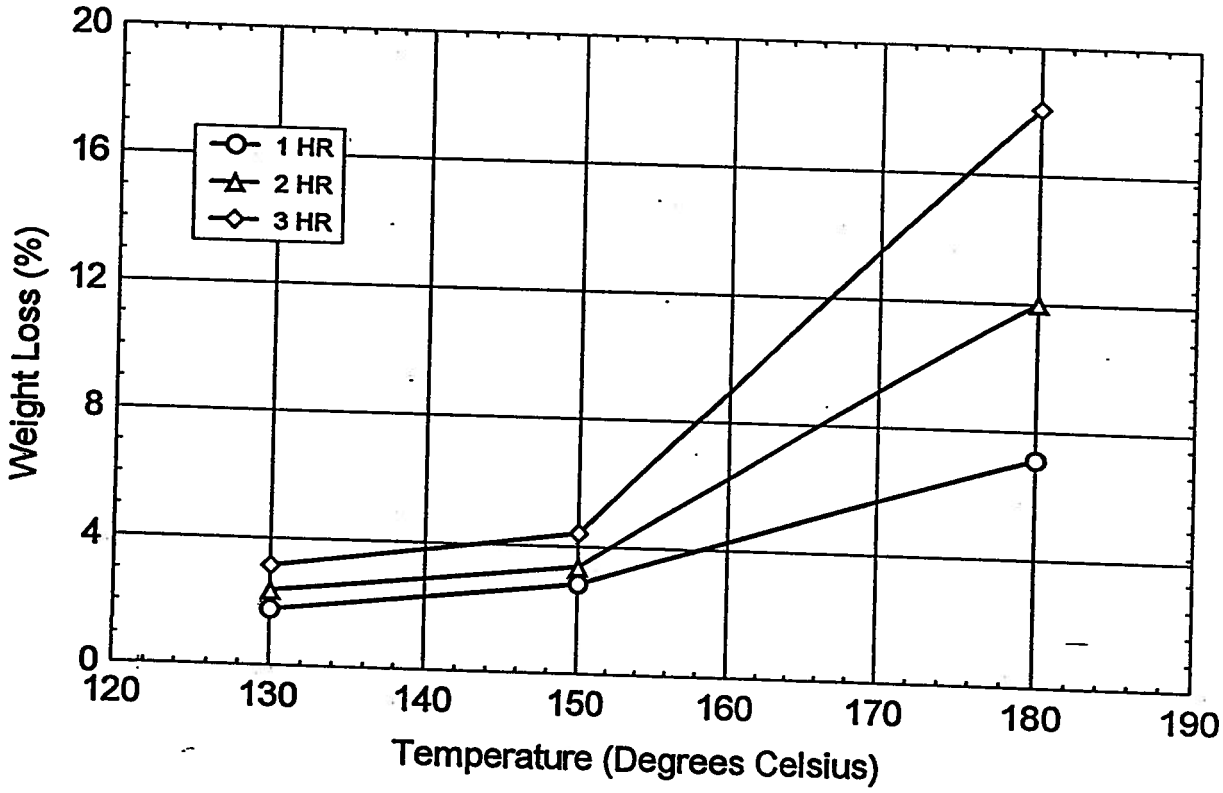


Figure 4.1.3.2.3.2. Effect of temperature on the weight loss of solvent purified cotton (acetone:water: 90:10; liquor/solid ratio: 10/1; 1.5 N TFA).

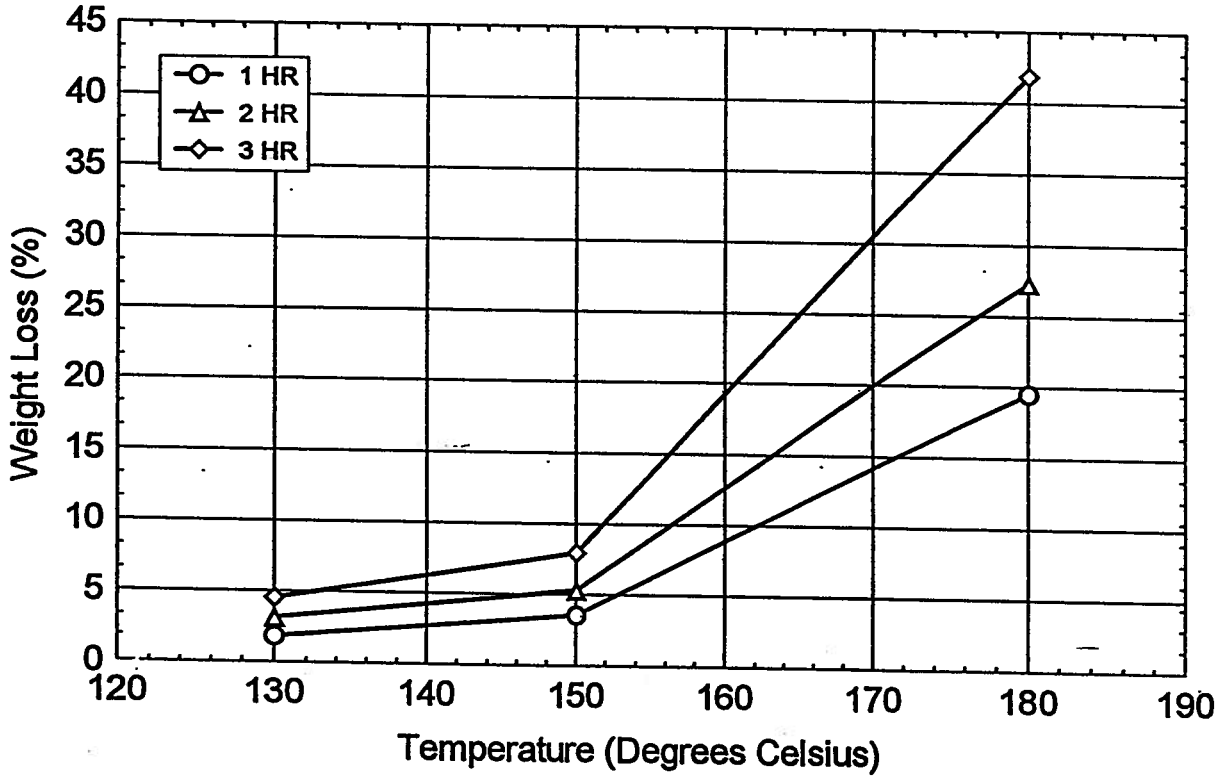


Figure 4.1.3.2.3.3. Effect of temperature on the weight loss of solvent purified cotton (acetone:water: 90:10; liquor/solid ratio: 10/1; 0.16 N HCl).

Figs. 4.1.3.2.3.4 and 5 show that the increased reaction time from 1 to 3 hr at lower temperatures (130 ^{o}C and 150 ^{o}C) resulted only in a slight increase in weight loss (from 1.76 to 3.15% at 130 ^{o}C, and from 2.84 to 4.42% at 150 ^{o}C, in the case of TFA as catalyst, for HCl the weight loss is between 1.88 and 4.58% at 130 ^{o}C, 3.56 to 7.96% at 150 ^{o}C) of solvent treated cotton. On the other hand, longer residence time (3 hr) coupled with higher temperatures (180 ^{o}C) appear to have a marked effect on the weight loss (18.07% and 41.9% for TFA and HCl, respectively) of solvent purified cotton. However, the statisical analysis demonstrates that the treatments of cotton at different reaction times for the weight loss, for different type of acid catalysts (TFA and HCl), are not significantly different (Duncan's multiple range test).

The time factor is found to have a lesser effect on carbohydrate (weight) loss after the initial solvent purification treatment when other parameters are kept constant. The reduced removal of carbohydrates in such a case can be explained by the fact that the stereochemistry of isopropylidinated units may bring about more or less the some effect on the adjacent molecules . This has implications on more H-bond disruption allowing the more accessible cellulose units to undergo rapid isopropylidenation and hydrolysis reactions.

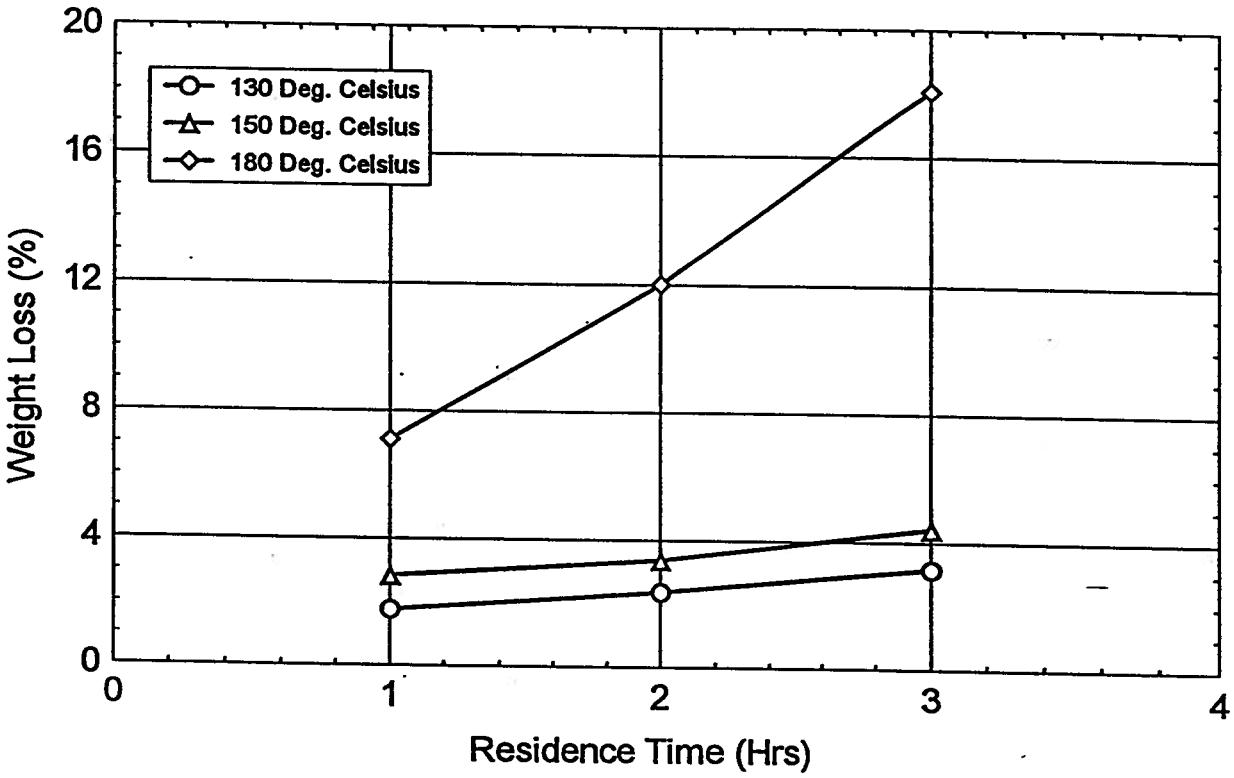


Figure 4.1.3.2.3.4. Effect of residence time on the weight loss of solvent purified cotton (acetone:water: 90:10; liquor/solid ratio: 10/1; 1.5 N TFA).

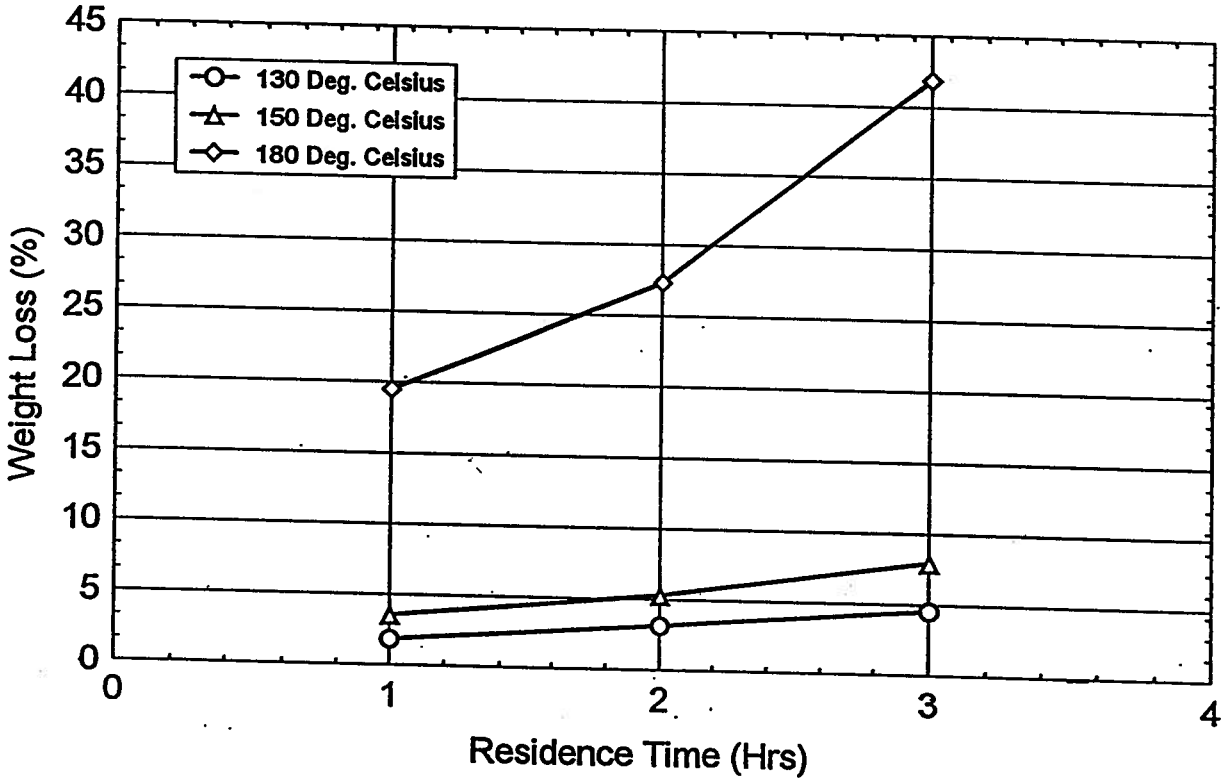


Figure 4.1.3.2.3.5. Effect of residence time on the weight loss of solvent purified cotton (acetone:water: 90:10; liquor/solid ratio: 10/1; 0.16 N HCl).

The effect of acid concentration for both hydrochloric acid (HCl) and trifluoroacetic acid (TFA) on weight loss has also been investigated. Both Figs. 4.1.3.2.3.6 and 7 show that weight loss has increased with the increase of acid concentration of different type of acid catalysts. However, the results also indicate that greater increase (4.9% vs 33.5%) in the weight loss of solvent purified cellulose (cotton) has been attained by the use of HCl than with TFA. The results also are in agreement with those found for mineral acids in the previous work with wood by Paszner et al., (1988). Nonetheless, the statistical analysis shows that the treatments of cotton with different acid concentrations for the weight loss, for the two acid catalysts (TFA and HCl), are significantly different, see Figs. 4.1.3.2.3.6 and 7 (Duncan's multiple range test).

The increase of weight loss with the increase in acid concentration regardless of the acid catalyst can be attributed to higher concentration of hydrogen ions for protonation of glycosidic linkages.

The inefficiency of trifluoroacetic acid (TFA) in the presence of acetone in the hydrolysis of cellulose (lower weight loss) is due to the fact that the two solvents have fairly different properties that probably lead them to react with each other as it was noted before by Geddes (1956), Harris (1965), Isaacs (1974), March (1985). This reaction between catalyst and acetone is most likely to retard the hydrolysis of cellulose (i.e., competing reactions). In

addition, the active centres of cellulose molecules which take part in the hydrolysis reaction may have also been blocked by hydrogen bonding due to the interaction of trifluoroacetic acid with cellulose. However, this factor can not be ruled out since TFA has unique properties for developing strong hydrogen bonds with other compounds (Isaacs, 1974; Nissan, 1977; March, 1985; Jeffrey et al., 1991). Thus, in this respect the break up of hydrogen bonding between TFA and cellulose requires more energy to be applied in order to attain faster hydrolysis reactions to occur. Nonetheless, trifluoroacetic acid is classified as a polar protic solvent (i.e. hydroxylic) (Reichardt, 1988), with a high ionizing power and particularly low nucleophilicity (Isaacs, 1974; March, 1985). On the other hand, acetone is a dipolar aprotic (i.e., nonhydroxylic) hydrophylic solvent (Frey-Wyssling, 1953: Bax et al., 1972; Isaacs, 1974) with a high nucleophilicity (Reichardt, 1988) and with a very reactive carbonyl group (Tchoubar, 1966). However, both of them have a molecular resonance effect (Tchoubar, 1966; Reichardt, 1988). Suggestions of similar reactions between acetone and TFA were also noted elsewhere (Geddes, 1956; Harris, 1965; March, 1985).

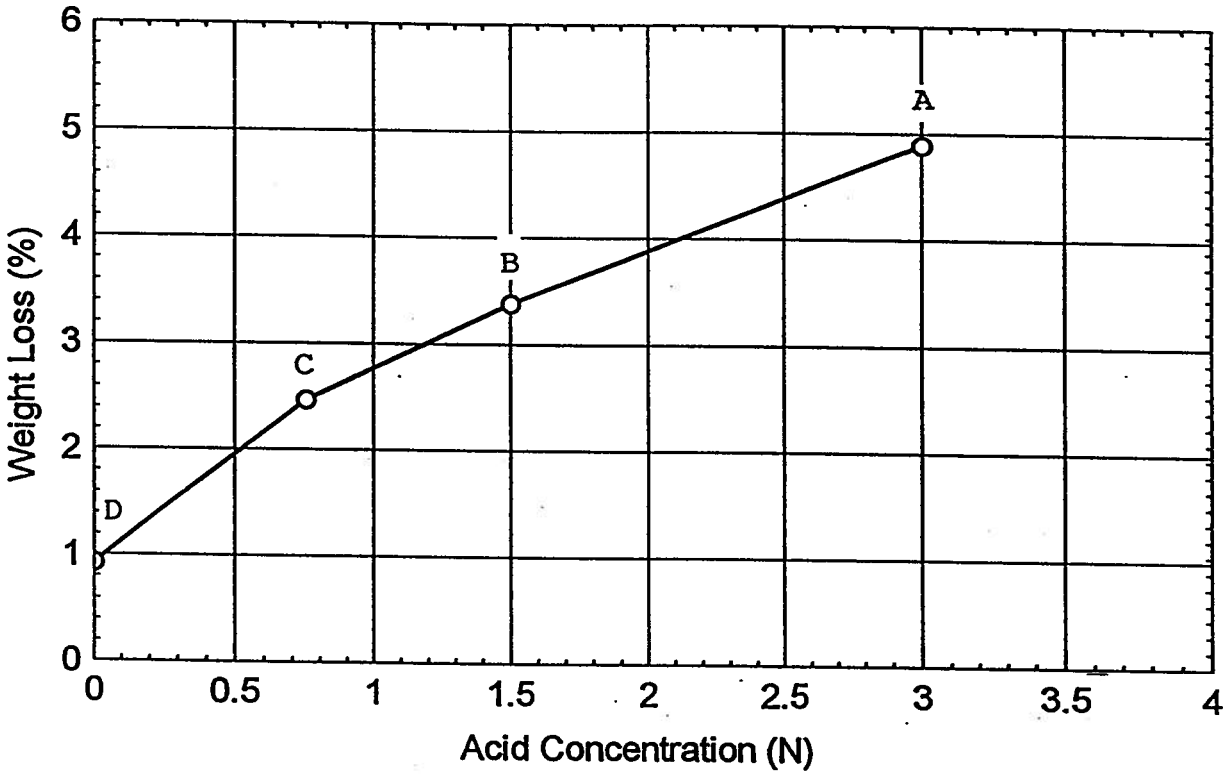


Figure 4.1.3.2.3.6. Effect of acid concentration on the weight loss of solvent purified cotton (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C; TFA).

* Means with the same letter are not significantly different.

** Significance at 95% confidence level.

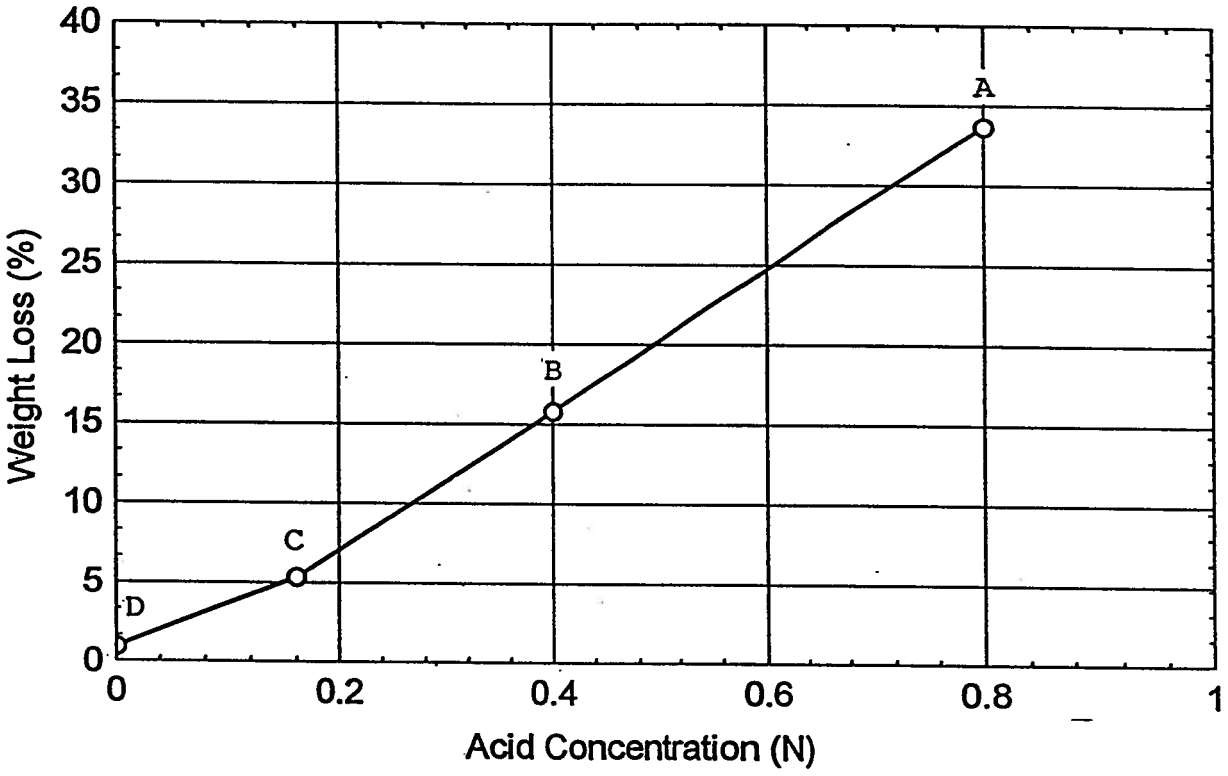


Figure 4.1.3.2.3.7. Effect of acid concentration on the weight loss of solvent purified cotton (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C; HCl).

* Means with the same letter are not significantly different.

** Significance at 95% confidence level.

4.1.4 C-13 CP/MAS solid state NMR Investigation - Isopropylidene Intermediates in Residual Cotton during Solvent Purification Treatment

High-resolution C-13 NMR spectroscopy has gained much interest in the last decades as a powerful tool for the structural elucidation of natural polysaccharides. However, native and modified celluloses have not been assessed extensively by this technique because of such intrinsic properties as insolubility in solvents and fairly high solution-viscosities in the case of their dissolution. Nonetheless, it has been clear for some time that C-13 solid state NMR spectroscopy, with magic-angle spinning and cross polarization has been found (Saito, et al., 1981; Saito et al., 1981; Attalla, 1985; Hoshino et al., 1989) to provide useful information about celluloses. In this work, C-13 CP/MAS NMR has been employed for clarification of whether acetone molecules react covalently with the cellulose in the solid state (i.e., formation of isopropylidene intermediates on the cellulose molecules as a first step in the hydrolytic breakdown) during the solvent purification treatment. In addition, the effect of isopropylidenation on decrystallization of residual cotton has also been investigated.

Fig. 4.1.4.1 shows the C-13 CP/MAS NMR spectrum of the residual cotton treated with normal acetone (i.e., C-13 natural abundance is 1.11%), and the spectrum resembles that of untreated one (Fig. 4.1.4.2). However, no signals

appeared in the methyl group region. Fig. 4.1.4.3a shows the C-13 CP/MAS NMR spectrum of the residual cotton treated with C-13 labeled acetone. The results illustrated in Fig. 4.1.4.3a show that the acetonated cotton residue has given two peaks at 26.5 and 31.8 ppm, respectively. Those peaks can be assigned to be methyl groups since they do not disappear in the non quaternary suppresion spectrum (see Fig. 4.1.4.3b).

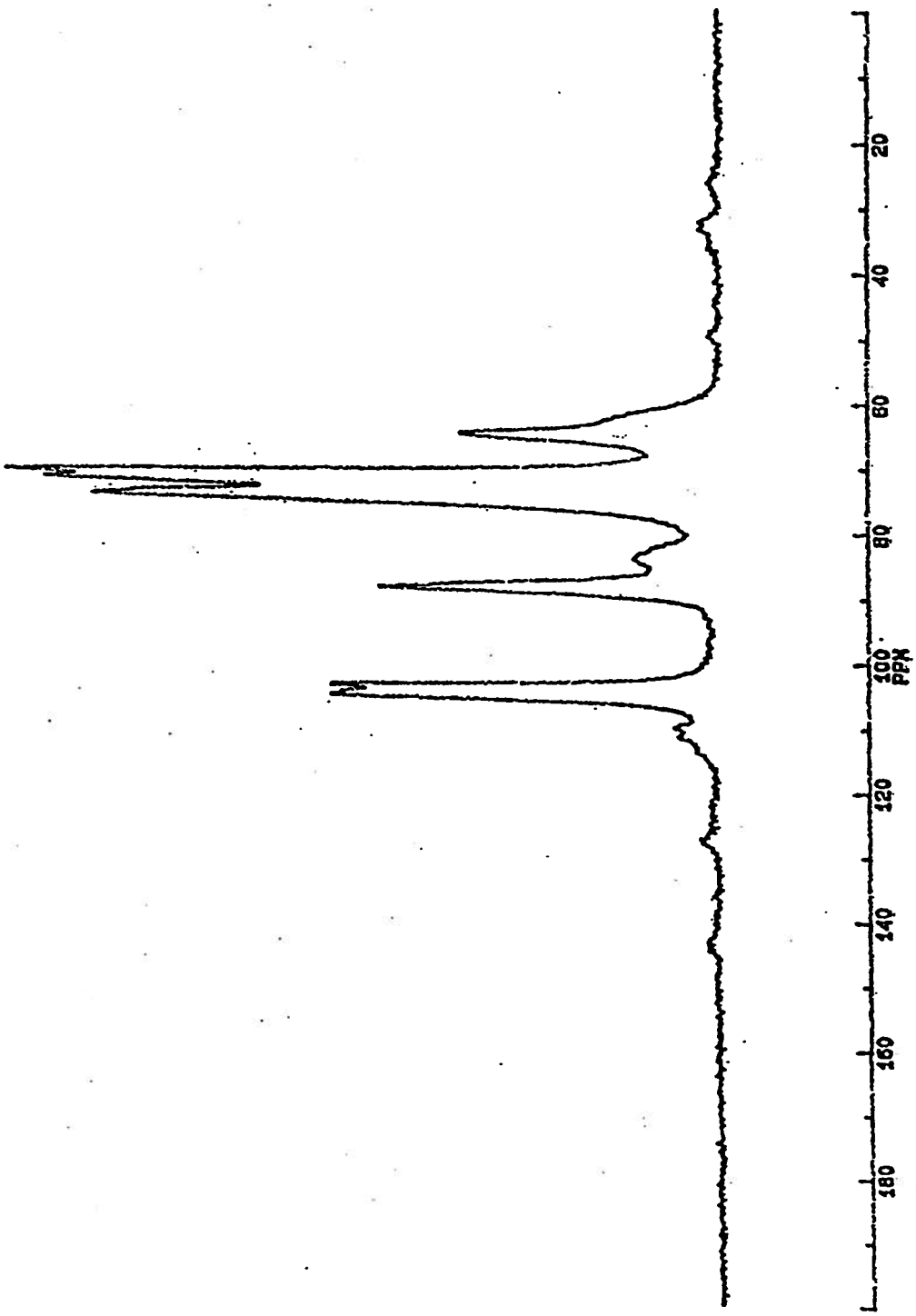


Figure 4.1.4.4.1. C-13 CP/MAS NMR spectrum of the residual cotton treated with normal acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 °C; 0.16 N HCl).

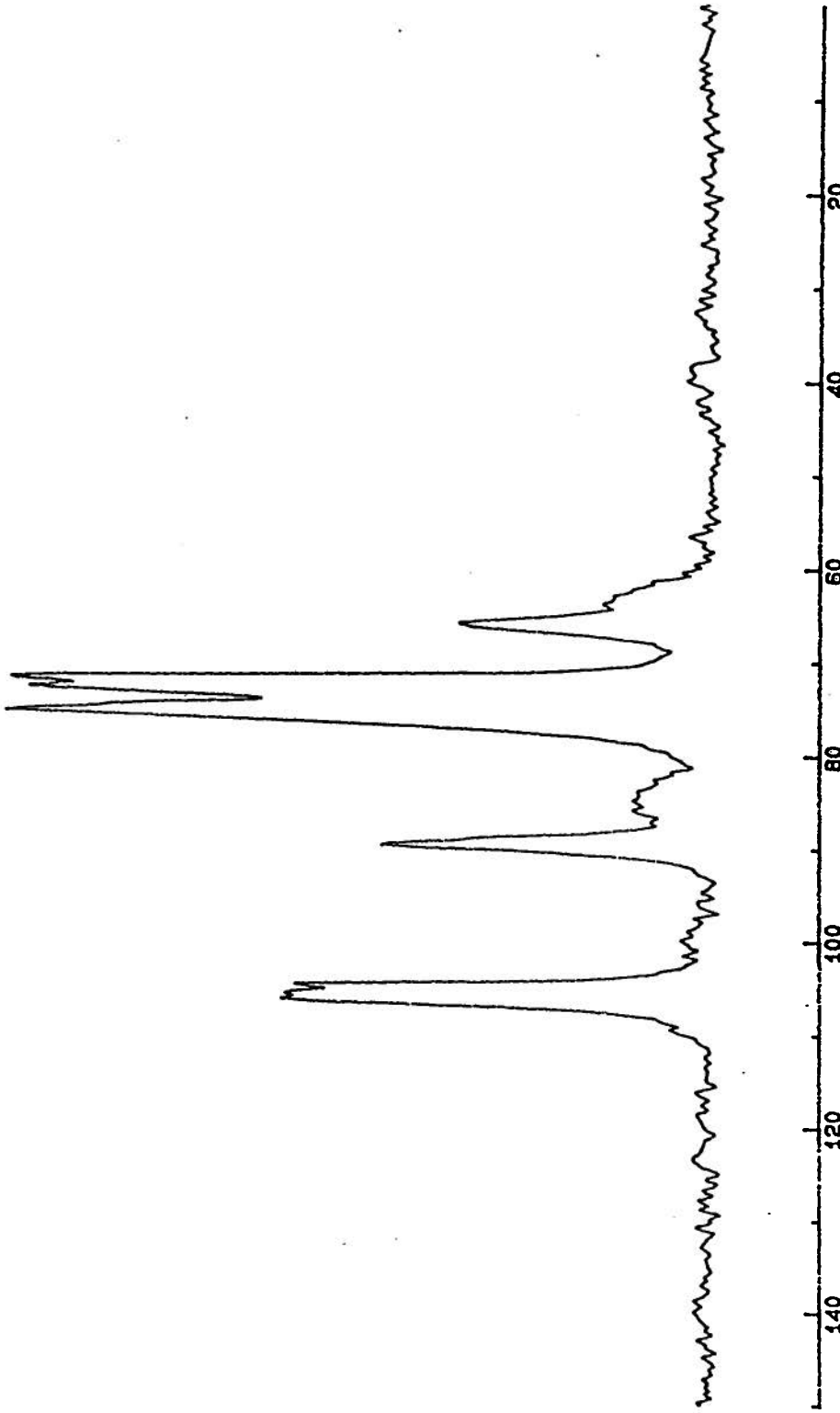


Figure 4.1.4.2. CP/MAS C-13 NMR spectrum of untreated cotton (control).

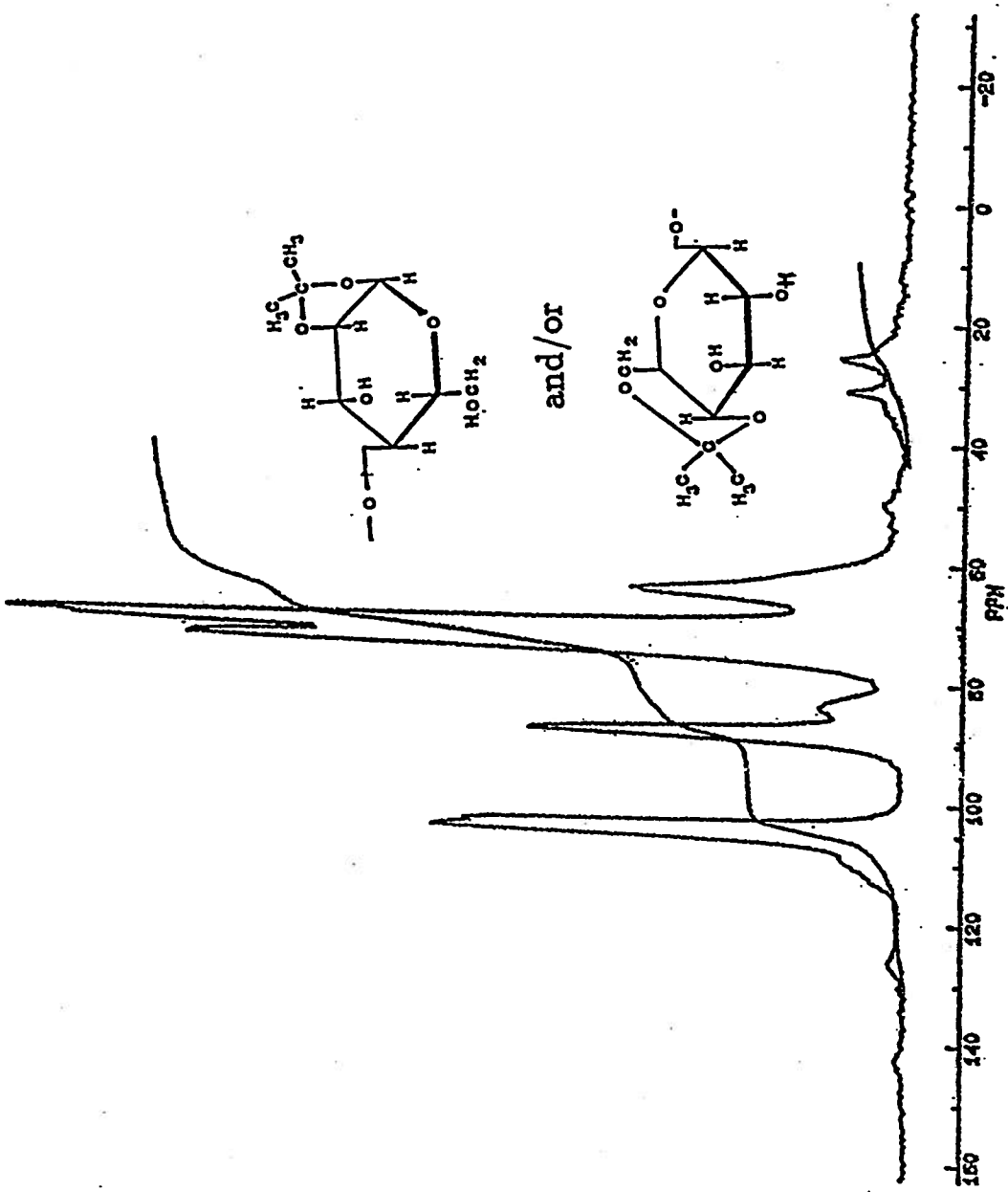


Figure 4.1.4.3a. C-13 CP/MAS NMR spectrum of the residual cotton treated with C-13 labeled acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 oC; 0.16 N HCl).

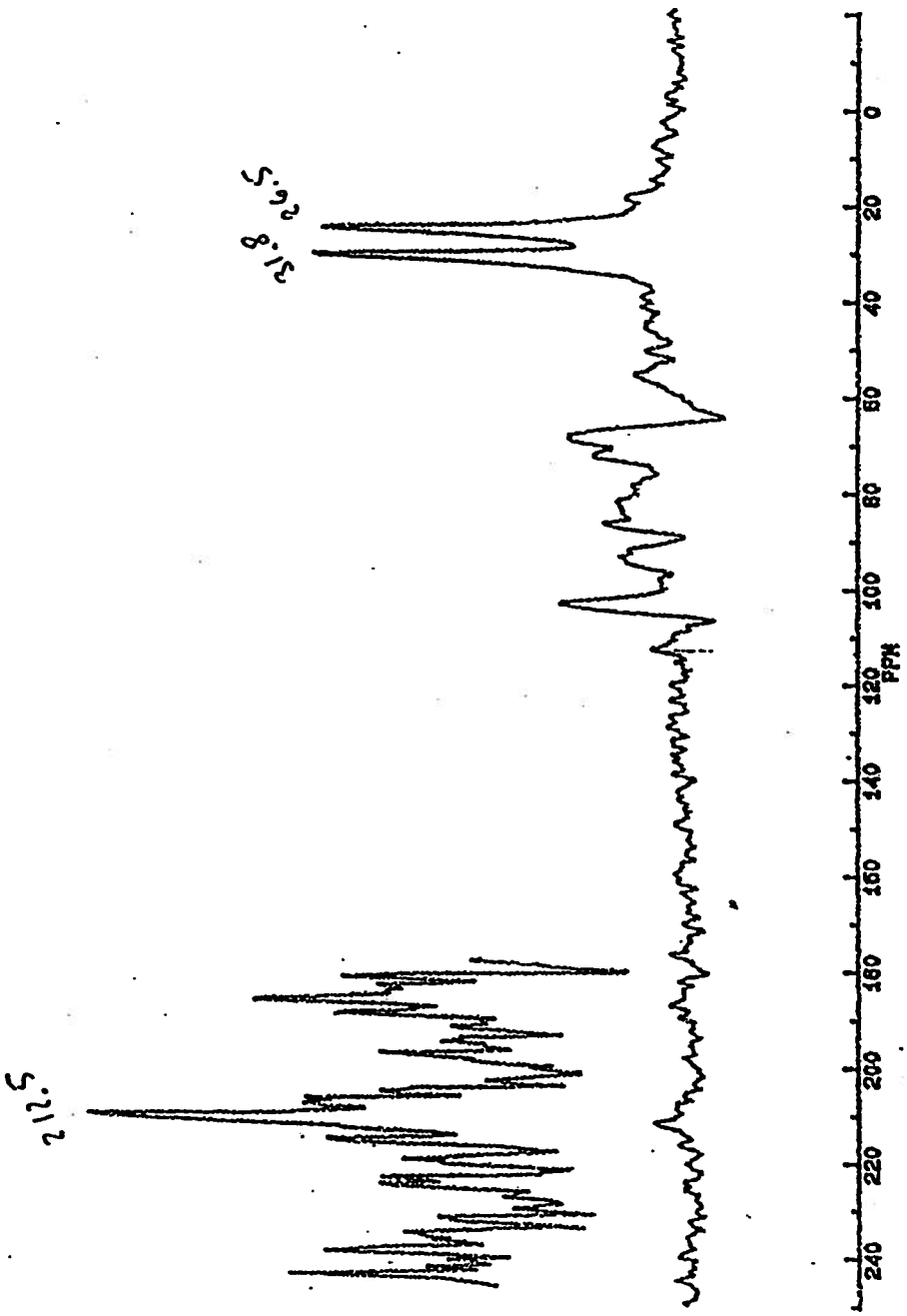


Figure 4.1.4.3b. Non quaternary carbon NMR spectrum of the residual cotton treated with C-13 labeled acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 °C; 0.16 N HCl).

Furthermore, these methyl signals cannot be due to physically adsorbed acetone because triply labeled acetone was used. Therefore, additional to methyl signals at around 30 ppm, a carboxyl signal at around 210 ppm should be found. Even though there might be a small amount present in the residue, (see Fig. 4.1.4.3b, very weak signal at 212 ppm) , the methyl signals are too large to originate from adsorbed acetone. Therefore, the evidence is that the acetone must have reacted with the cellulose to form an isopropylidene. The possible form of such an intermediate has been shown in Fig. 4.1.4.3a.

In general the integral in C-13 CP/MAS spectroscopy is a much more reliable measure for the relative numbers of spins than that in solution C-13 NMR. In other words, it allows us to estimate how many of the cellulose units are involved in this reaction. There are 6 carbons per glucose unit. The natural abundance of C-13 is 1.11%.

Per acetone molecule, there are 2 methyl groups with an isotope abundance of 99%, and

1 carbonyl carbon with 99% abundance covered within the cellulose carbon peaks (between 80 and 90 ppm), hence

$I_1 = [(6 \times 1.11) + (n \times 99)]I_o = 10.4$ (from the spectrum)

$I_2 = (2 \times n \times 99)I_o = 0.7$ (from the spectrum)

$I_1/I_2 = (6 \times 1.11) + (n \times 99)/(2 \times n \times 99) = 10.4/0.7$

$(6 \times 1.11) + (99 \times n) = 10.4/(0.7(2 \times 99 \times n)$

$(6 \times 1.11) = [10.4/(0.7 \times 2 \times 99 \times n)] - 99 \times n$

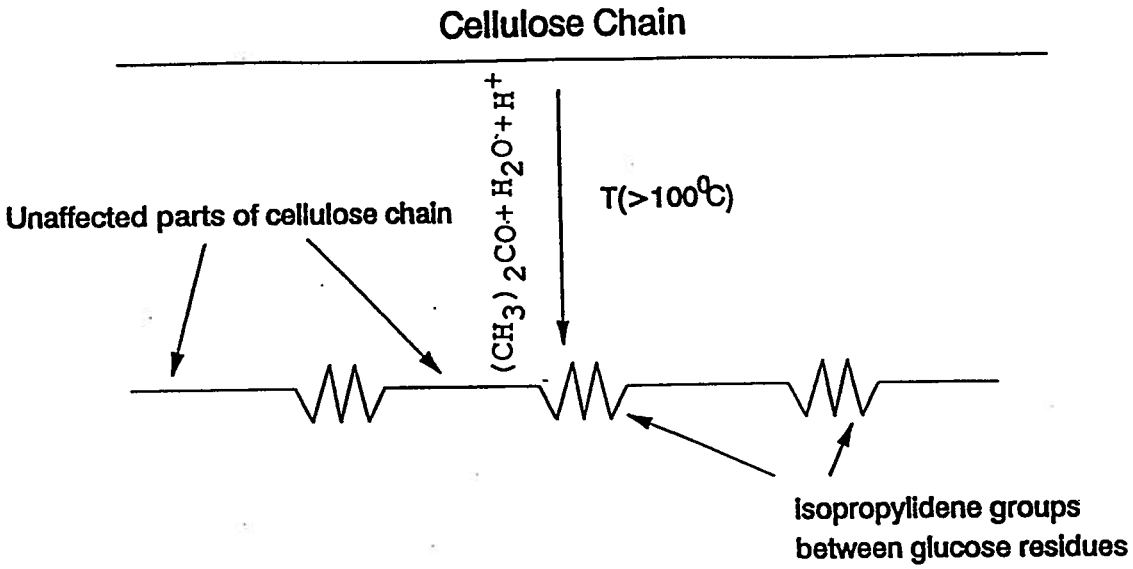
$6.66 = (n \times 99)\ [2(10.4/0.7) - 1]$

$n = \sim 1/430$

where I_1, I_2, and I_o are the intensities of carbon 13 for glucose unit, two methyl groups, and 1 carbon atom, respectively.

This means there is only one isopropylidene group per every 400-500 glucose units of solvent purified cotton treated at 150 ^oC (acetone:water; 90:10, liquor/solid; 10/1, 2 hr, 0.16 N HCl). In other words, around 400-500 glucose units have remained unaffected by isopropylidenation at this designated treatment condition. This calculation is in accord with the viscosity value (about 3.5 CP, see Fig. 4.1.7.4.) at this treatment condition and is just slightly higher than the limiting DP of 300 (Rydholm, 1965). Also, it has already been determined, in this work, that the weight loss under these treatment conditions is equal to 5.34% and the deacetonation sugar product yield is 86.33% (Table 4.1.3.2.1). Hence, this suggests that the major isopropylidenated fraction of cellulose has been removed into the solution (hydrolysate). In addition, by using acid catalyzed aqueous acetone in solvent purification of cotton the viscosity has dramatically dropped as shown in Fig. 4.1.7.3 (viscosity analysis section). This could also be attributed to the formation of isopropylidene groups at a uniform interval pattern between the glucose residues along the cellulose chains as it is proposed in Fig. 4.1.4.4. It is also noteworthy to mention that the formation of isopropylidene groups between the adjacent sugar units has

already been established by Khan et al. in 1975 in their study on sucrose (a comprehensive review is given in chapter 2). On the other hand, the possibility of the reaction of acetone molecules with C6 and the hemiacetal oxygen can not be ruled out, although neither the previous works, nor the present one, were able to substantiate this possibility as the number of isopropylidene substituents would be expected to be much larger than found in this work. However, the drop in CuEn viscosity is substantially increased in the presence of acid catalyst with the increase of temperature as illustrated in Figs. 4.1.7.4 and 4.1.7.5 (from 28.5 CP to 2.7 CP). This indicates very rapid penetration of the acid throughout the entire cellulose matrix but not necessarily involving also the crystalline regions, the destruction of which is possible only with concentrated acids, but not with dilute solutions. The weight loss has also shown similar trend (from 0.93 to 42.3%). All these results would be interpreted as follows:



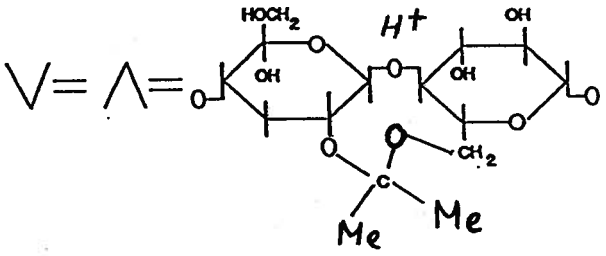


Figure 4.1.4.4. Proposed formation of isopropylidene groups along the cellulose chain.

a- higher temperature increases the reaction rate of the system. In turn, this would lead to further stereochemical changes that can bring about, to a greater extent, more H-bond disruption/destruction in the cellulosic material. Consequently, more active sites (H-bond free hydroxyl groups) will be available to undergo isopropylidenation. Besides, the reactivity of acetone molecules increases with increased temperature as does the system pressure. This would also speed up the isopropylidenation process by the involvement of more acetone molecules with glucose units to yield isopropylidene groups along the cellulose chain. This can be illustrated in Fig. 4.1.4.5.

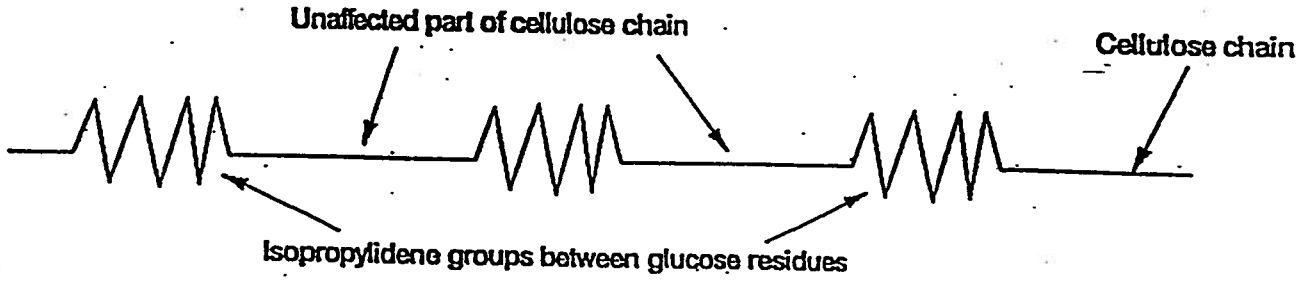


Figure 4.1.4.5. Proposed formation of isopropylidene groups along the cellulose chain at higher temperatures.

b- dissociation of both water and acid catalyst molecules into ions increases with increase in temperature (Bernal et al., 1933) and this will, eventually, lead to considerable participation of hydrogen ions in the cleavage of glycosidic linkages. This process, most probably, will also have a remarkable impact on stereochemical alterations and formation of isopropylidene groups, i.e., the destruction of intramolecular H-bond between C6 and glycosidic oxygen + configurational isomerism - from β to α.

In consequence, the removal of isopropylidene derivatives of sugars in the solution during the hydrolysis reactions would lead to disproportionation of the cellulose chain. Apparently, the disproportionation offers residual cellulose with short chains isopropylidenated at the reducing and/or non-reducing sugar terminals, however, the most likely one can be shown in Fig. 4.1.4.6.

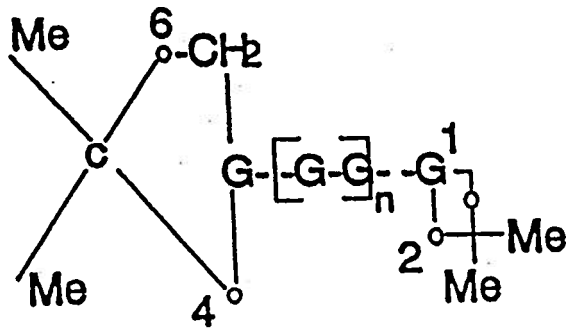


Figure 4.1.4.6. Solvent purified cellulose chain of residual cotton.

Concerning the formation of isopropylidene intermediates during solvent purification treatment, the appearance of the methyl signals in the solid state NMR spectrum given in Fig. 4.1.4.3a , is a strong indication that acetone as a major volume fraction in the solvent (acetone/water) is capable to react covalently with the cellulose molecules as also shown by HPLC traces Fig. 4.1.3.2.1. It is evident that the two methyl signals shown in Fig. 4.1.4.3a illustrate explicitly the formation of monoketal in the residual (solid) cotton. The small difference, in chemical shift for the carbon atoms of the methyl groups (5.3 ppm) suggests the formation of the dioxolane ring on the cellulose unit. However, the probability of a skewed form of 1,3-dioxane ring would not be ruled out. It was stated (Buchanan et al., 1980; Buchanan et al., 1982; Grindley et al., 1985) that the acetal carbon of such cyclic rings resonates in the range of 100.6-101.1 ppm. Nonetheless, it is possible a mixture of both acetal rings (i.e., 1,3-dioxolane and 1,3-dioxane) is present in the solvent treated cotton residues.

In conclusion, one may suggest that the monoacetal structure of interest is 1,2-O-isopropylidene-α-D-glucopyranose - reducing sugar, however a 4,6-monoacetal glucopyranose could also be possible (but less likely) as indicated in Fig. 4.1.4.6.

4.1.5 X-ray Diffraction Analysis - Changes in Crystallinity and Crystallite Breadth of Cotton Residues during Solvent Purification Treatment

The main purpose of this work is to study the effect of solvent purification treatment on the crystalline structure of cotton residues. Also, it is of interest to follow the progressive crystalline changes that have taken place in the cellulose when factors such as acetone concentration, temperature, and acid concentration are tested.

4.1.5.1 Acetone Effect on Crystallinity and Crystallite Breadth of Cotton Residues during Solvent Purification Treatment

The acetone effect on the crytalline structure of cellulose, in this work, was tested by using different acetone concentrations in the treatment without adding acid catalyst. Figs. 4.1.5.1, 4.1.5.2 and 4.1.5.3 show that the successive increase in acetone concentration has resulted in hightening the intensities of 101, $10\bar{1}$, and 002 planes. The increase in peak heights of 101 and $10\bar{1}$ can be attributed to reorientation of hydrogen bonding (spacing) as result of the effect of acetone on the cellulosic material. The increase in peak height observed at the 002 plane demonstrates the enhancement of crystallinity. A similar trend of a slight increase in crystallinity index of treated cotton in 50% of acetone is illustrated in Table 4.1.5.1. Also, results given in Table 4.1.5.1 show that the crystallite breadth, i.e.,

full width at half maximum height, FWHM ($10\bar{1}$) is slightly increased. In other words, this indicates that the crystallite size is slightly decreased since crystallite breadth is inversely proportional to crystallite size (Ahtee et al., 1983).

The results illustrated in Figs. 4.1.5.1, 2, and shown in Table 4.1.5.1 correlate well with those of the hydrogen bonding (Fig. 4.1.2.1). This can be explained by the fact that the successive decrease in the strength of the hydrogen bond of the cellulosic material with the increase of acetone content has led to a progressive decrease in the crystallite size. In other words, presumably, the new orientation of the hydroxyl groups (i.e., weak H-bonds) of cellulose molecules does not provide suitable conditions for the crystallites to pack tighter together and coalesce in stronger lateral order. They also correlate well with the weight loss obtained at different acetone concentrations (Fig. 4.1.3.2.3.1). This can be interpreted by the fact that the successive increase in weight loss of the treated cottons was associated with systematic increase in crystallinity index as the acetone concentration was consecutively increased in the solvent composition. On the other hand, the systematic increase in crystallinity index of the residual cotton (Table 4.1.5.1) as the acetone content was successively increased in the treatment correlates well with the progressive loss of the hydrogen bond strength of the cellulose (Fig. 4.1.2.1). This explicitly means that within

the prevalence of selective removal of amorphous cellulose higher degree of crystallinity can be attained in an accessible cellulose .The results given in Table 4.1.5.1 for crystallite breadth agree well with those for hydrogen bonds obtained at different acetone concentrations (Fig. 4.1.2.1). The higher the acetone concentration, the weaker the hydrogen bond, the bigger the crystallite breadth (i.e., reduced crystallite size). Thus, these results strengthen our belief that acetone solvent, in this process, penetrates the cellulose fibres (amorphous and crystalline zones), swells them, and brings about structural changes. In other words, the changes in crystallinity index and the crystallite breadth (i.e., crystallite size) indicate that an intramicellar swelling has taken place during the acetonation of cellulose. It was noted (Frey-Wyssling, 1953) that in intramicellar swelling there is a stronger affinity between the swelling agent and chain molecules than the binding forces in the chain lattice. Usually, in this type of swelling the solvent penetrates into the crystal lattice and widens it. This widening is accompanied by structural changes that can be followed by means of the X-ray diffraction technique (Frey-Wyssling, 1953). It seems most likely that the enhancement of crystallinity was attained in the solvent purification treatment by the selective removal of amorphous cellulose in conjuction with the greater accessibility (i.e., weaker hydrogen bonding at both inter- and intramolecular levels) of cellulose. However, the

selective removal of the amorphous cellulose by the solvent treatment could be considered as the main reason for the enhancement of crystallinity. With regards to the correlation held among accessibility, weight loss, and enhancement of crystallinity, this is strongly indicative of the superiority of the solvent purification treatment over the current purification processes. Hence, the ability of the solvent technique to ensure advantages such as increased accessibility (reactivity) of cellulose, and high degree of specificity in the removal of amorphous cellulose (i.e., enhancement of crystallinity) is a practical answer to the problems encountered with the current processes.

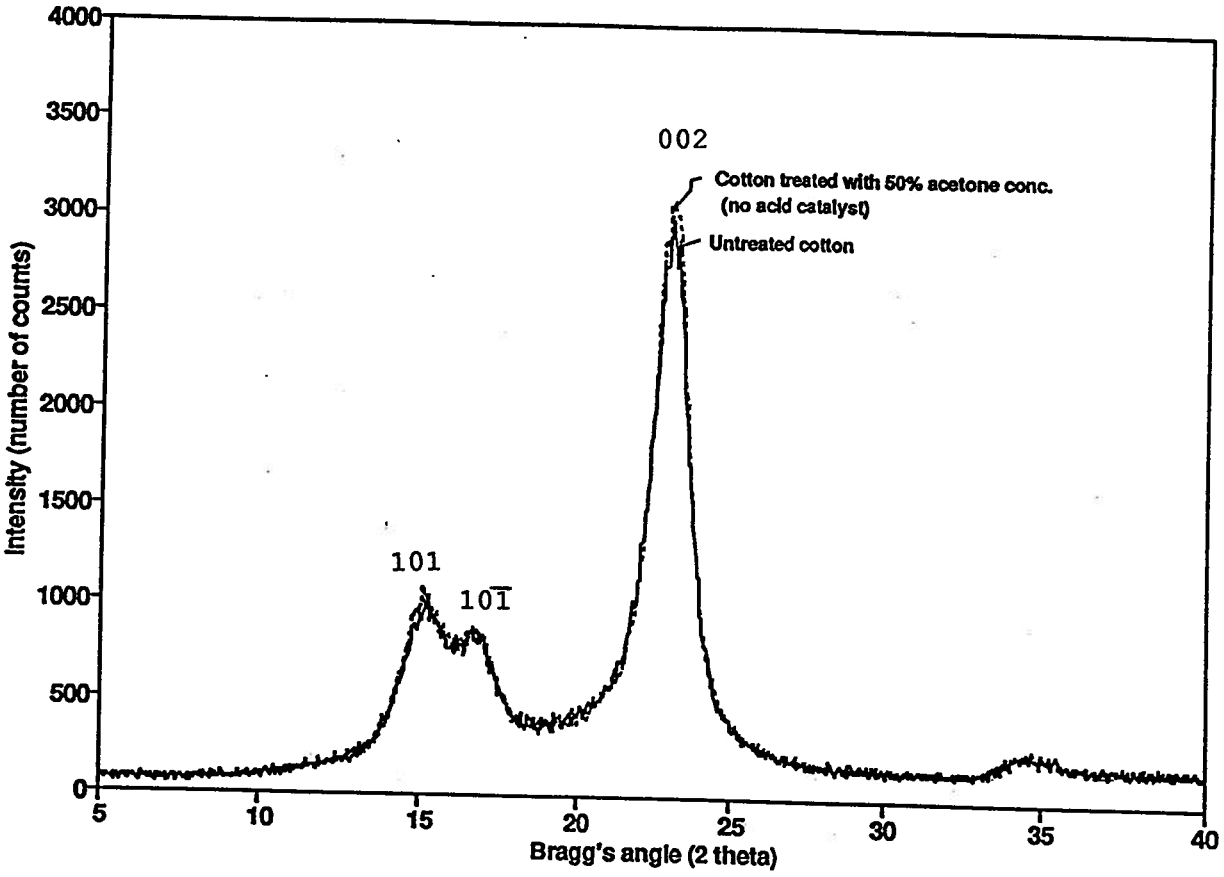


Figure 4.1.5.1. Comparison of diffraction patterns of treated (acetone:water: 50:50; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C) with untreated cotton (control).

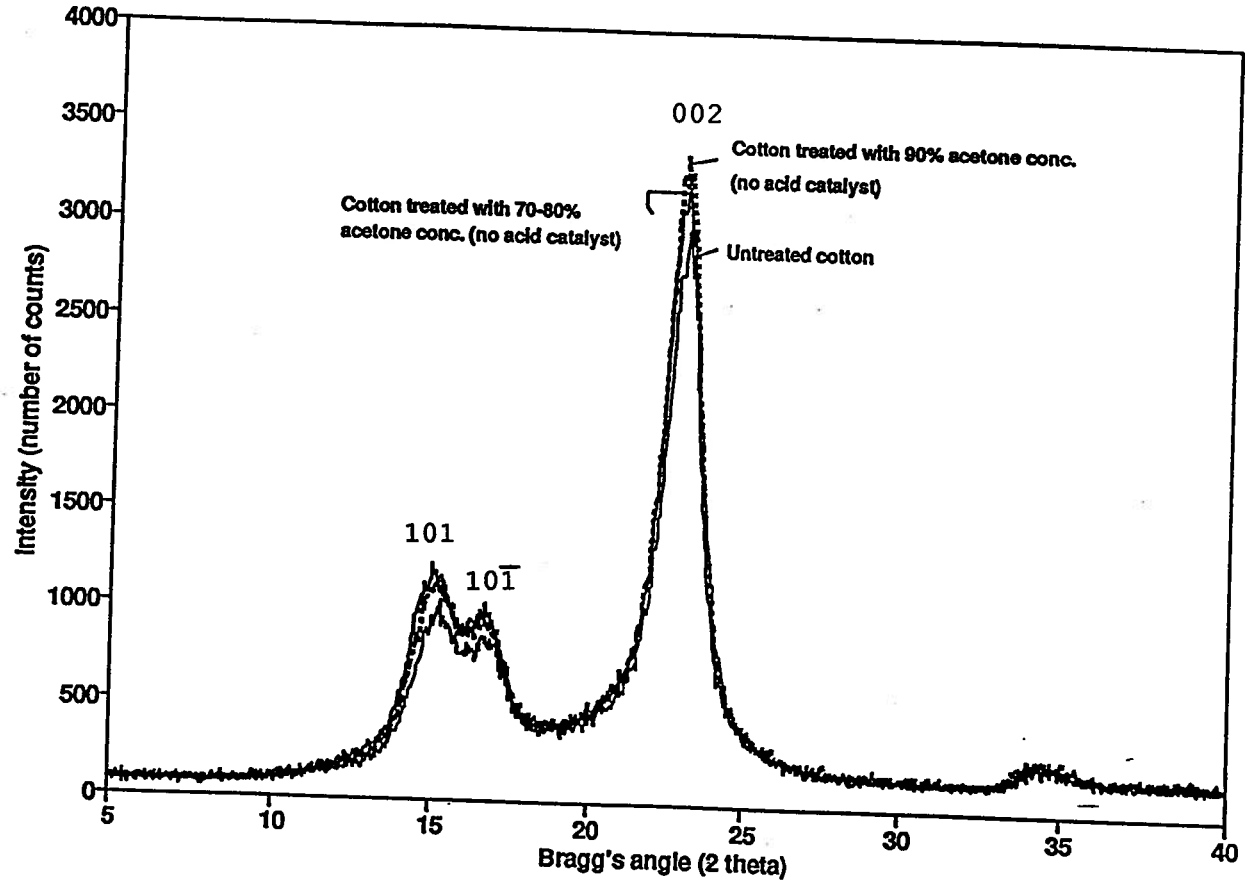


Figure 4.1.5.2. Comparison of diffraction patterns of treated (acetone:water: 70:30, 80:20, and 90:10; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C) with untreated cotton (control).

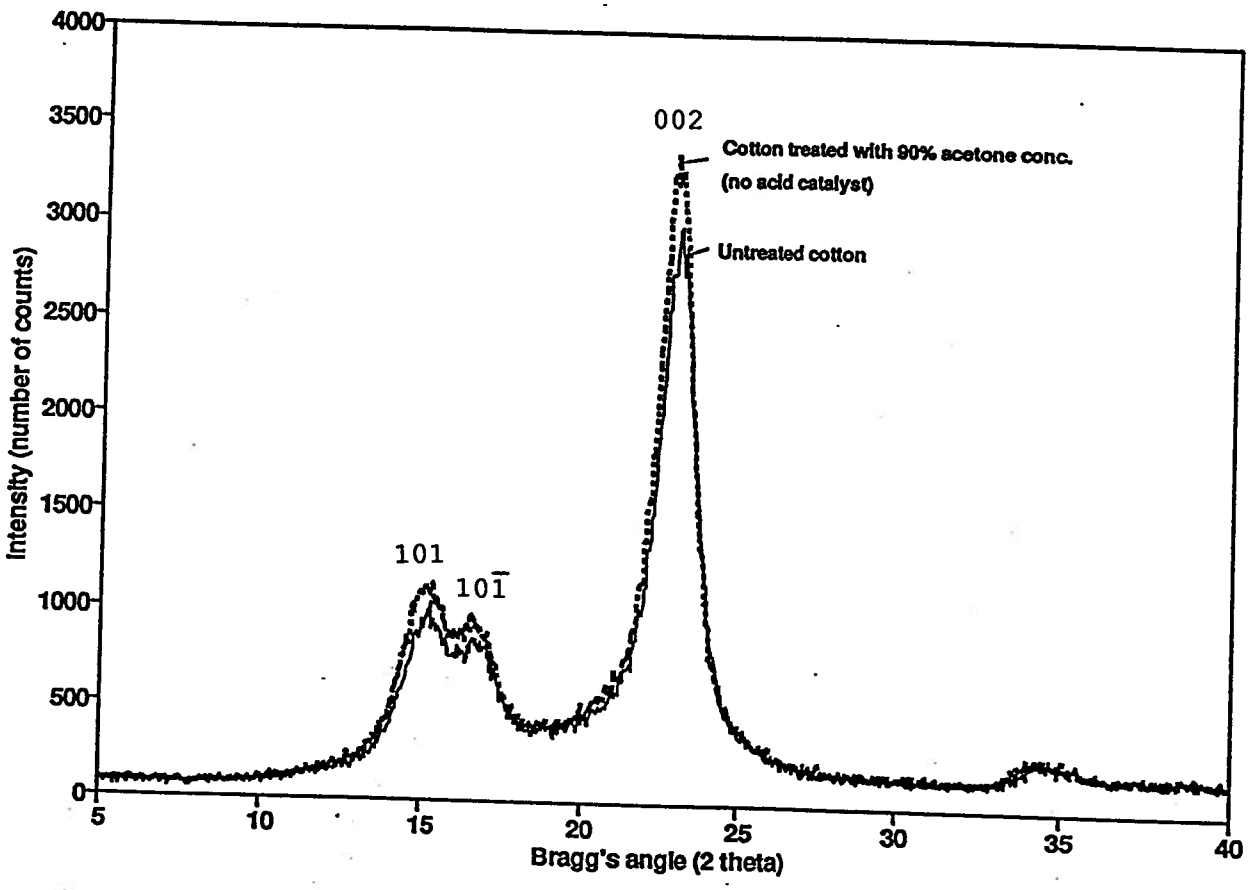


Figure 4.1.5.3. Comparison of diffraction patterns of treated (acetone:water, 90:10: liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C) with untreated cotton (control).

Table 4.1.5.1. Acetone effect on crystallinity index and crystallite breadth of cotton residues treated with different concentrations of acetone, while other variables were kept constant (liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C; no acid catalyst added).

Acetone Concentration %	CI %	S.D.	$FWHM_{002}$ (Degree)
Untreat. cotton	74.37	0.21	2.01
50	74.38	0.24	2.14
60	74.34	0.32	2.16
70	74.62	0.10	2.15
80	74.74	0.22	2.17
90	75.44	0.34	2.16

Usually aqueous acid hydrolysis brings about considerable broadening of the reflection peaks of 101, $10\bar{1}$, and 002 planes. Besides, the peak heights of these planes have been noticed to experience appreciable decrease (Kulshreshtha et al., 1973). Those changes in acid hydrolysis indicate that decrystallization is the result of a decrease in crystallite size and an increase in lattice disorder.

It was stated by Nishimura et al. (1987) that similar stereotype decrystallization and reduction of crytallite size also takes place in the mercerization of cellulosic material. For instance, the formation of alkali Cellulose I is achieved by lowering the crystallinity of the original

cellulose. In this respect, Cellulose II is less crystalline than Cellulose I (Nishimura et al., 1987).

However, the interesting features of enhancement of crystallinity, with the slight decrease in crystallite size, and increase of peak heights of 101 and $10\bar{1}$ planes by acetone, can be considered as one of the many major advantages of the solvent purification treatment. From the results presented here, important conclusions can be drawn as follows:

It appears that there is a reconciliation between decrystallization and crystallization, "they go hand in hand" in solvent purification treatment. Apparently, the decrystallization can be achieved by the interaction of acetone, as swelling agent, with the hydroxyl groups of the cellulose molecules through their hydrogen atoms and provision of certain types of H-bonds (i.e., weak or nonlinear) (Scheiner et al., 1985). This also gives us some insight into how acetone disrupts hydrogen bonding (i.e., accessibility) in the cellulosic material, i.e., hydrogen bond disruption (1st hypothesis). In addition, the protophylicity of acetone is explicitly demonstrated, in this work, in Figs. 4.1.2.1 and 4.1.3.2.3.1, i.e., the higher acetone content, the greater extent of accessibility, the higher degree of removal of amorphous cellulose. Furthermore, it was also emphasized (Bax et al., 1972; Isaacs, 1974) earlier that acetone could be classified as a dipolar aprotic protophylic solvent. On the other hand, the

enhancement of crystallinity can be attained by selective removal of the derivatized sugars. They appear to be more susceptible to hydrolysis reactions than the free sugars. On the other hand, it is interesting that the results given in Table 4.1.5.1 indicate that the strength of the hydrogen bonds has no effect on the crystallinity index. The major impact on crystallinity index is likely to result from the packing order of the crystal lattice and selective removal of the amorphous cellulose.

However, from the results shown in Fig. 4.1.2.1, 4.1.5.1, 4.1.5.2, 4.1.5.3 and Table 4.1.5.1 it is fairly clear that the rearrangement of hydrogen bonding has a considerable impact on the crystallite size. This has been reflected by the changes that have taken place on 101, $10\bar{1}$ planes and the slight systematic increase in crystallite breadth.

4.1.5.2. Effect of Type of Acid Catalyst and Acid Concentration on Cristallinity and Crytallite Breadth of Cotton Residues during Solvent Purification Treatment

In the present work, results have shown that the solvent purification process is, more or less, affected by the type of acid catalyst. This is well demonstrated by the selective removal of sugars (i.e., weight loss) under conditions which provide maintenance of an accessible cellulose (i.e., hydrogen bonding). Similar investigations were carried out to examine the effect of type of acid

catalyst on the crystallinity and crystallite size of cotton during acetonation. This was accomplished by employing different acid concentrations for each type of acid catalyst (i.e., TFA and HCl, respectively).

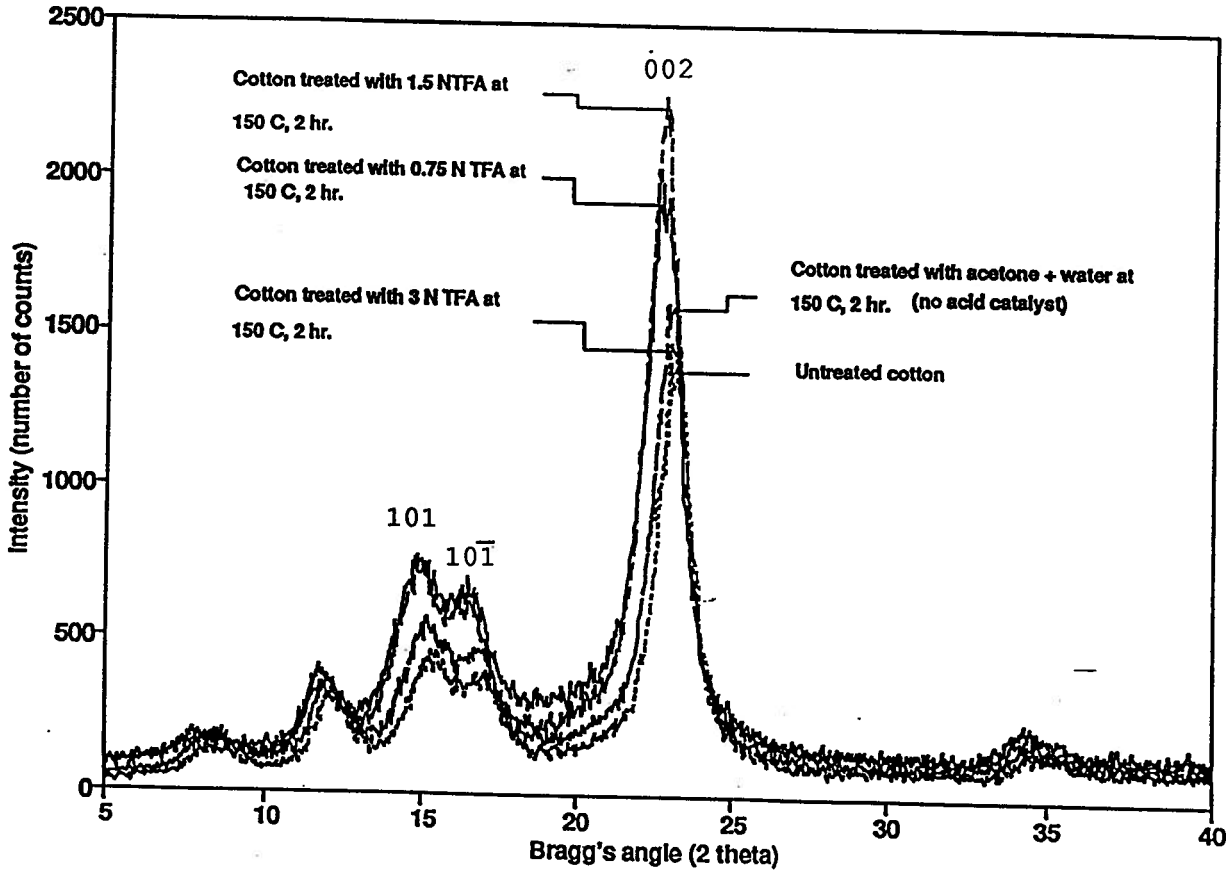


Figure 4.1.5.4. Comparison of diffraction patterns of treated cotton at different acid concentrations (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C, TFA).

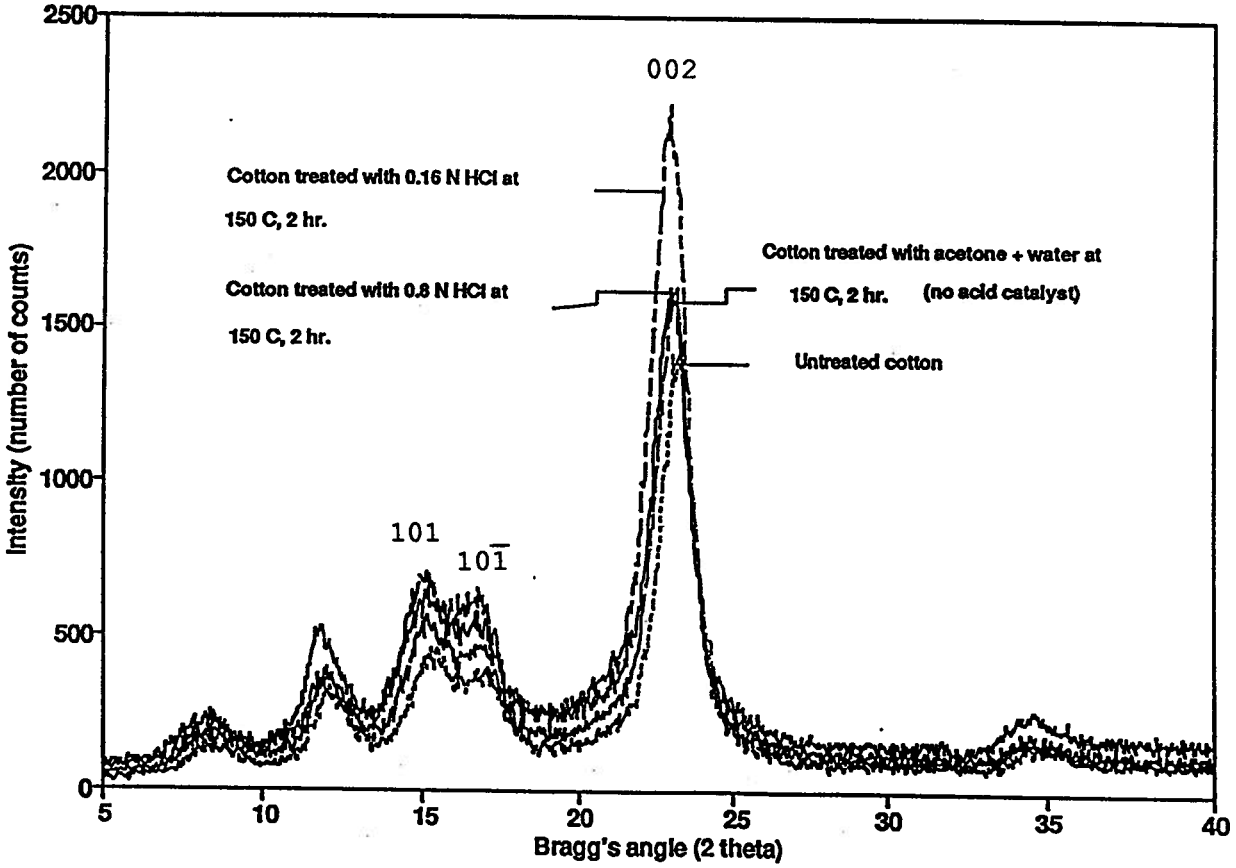


Figure 4.1.5.5. Comparison of diffraction patterns of treated cotton at different acid concentrations (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C, HCl).

Table 4.1.5.2. Effect of type of acid catalyst on crystallinity and crystallite breadth of cotton residues treated at different acid concentrations, while other variables were kept constant (acetone:water: 90:10; liquor/solid ratio: 10/1; 2hr; 150 ^{o}C; TFA).

Acid Concentration N	CI %	S.D.	$FWHM_{002}$ (Degree)
Untreat. cotton	74.37	0.21	2.01
0.75	74.87	0.19	2.04
1.5	75.15	0.27	2.23
3.0	71.50	0.15	2.31

Table 4.1.5.3. Effect of type of acid catalyst on crystallinity and crystallite breadth of cotton residues treated at different acid concentrations, while other variables were kept constant (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C; HCl).

Acid Concentration N	CI %	S.D.	$FWHM_{002}$ (Degree)
Untreat. cotton	74.37	0.21	2.01
Treted with acetone + water (no catalyst used)	75.44	0.24	2.16
0.16	74.48	0.15	2.23
0.8	71.82	0.27	2.35

Figs. 4.1.5.4 and 4.1.5.5 and Tables 4.1.5.2 and 4.1.5.3 show that there is a slight decrease in both crystallinity (i.e., 74.37% for untreated, 71.50% and 71.82%

for treated ones with TFA and HCl, respectively) and crystallite size (2.01 for untreated cotton, 2.31 and 2.35 for the treated ones with TFA and HCl, respectively), i.e., since crystallite breadth is inversely proportional to crytallite size. Usually, the influence of acid and alkaline solutions in conventional hydrolysis and mercerization is defined by the removal of hemicelluloses and amorphous cellulose. In turn, this offers a fairly low crystallinity index and reduced crystallite size. However, the small decrease in crystallinity and crystallite size shown in Tables 4.1.5.2 and 4.1.5.3 does not correspond to this criterion, in the case of the solvent purification process. For example, the weight loss obtained with 3 N TFA is 4.9%, while that with 0.8 N HCl is 33.7%, but their crystallinity indices and crystallite sizes (71.50%, 71.82%, and 2.31, 2.35 for TFA and HCl, respectively) are similar. From the results, one may draw the following conclusions:

1- acetonation ensures a high degree of selectivity in removing amorphous cellulose, i.e., it is likely that there is a simultaneous action of crystallization and decrystallization due to the stereochemical changes that take place during acetonation. These stereochemical alterations would prevail at both hydrogen bonding and derivatization levels, and

2- the solvent purification treatment offers irreversible structural transformations (i.e., weak nonlinear hydrogen bonds and isopropylidene groups) and they appear to have the

considerable effects on the crystallinity index and the crystallite size. In other words, these structural changes (new type of lattice) brought about on cellulose (cotton) by acetonation, are the primary factors responsible for shaping the crystal packing order.

The results shown in Figs. 4.1.5.4 and 4.1.5.5 and Tables 4.1.5.2 and 4.1.5.3 illustrate that acid concentration has only a slight effect on crystallinity and crystallite size although the hydrolysis rates may be quite different. This effect is determined by the extent of catalyst contribution to hydrogen bonding of the cellulosic material, because both crystallinity and crystallite size are influenced by hydrogen bonding rearrangements (Marchesault, 1962; O'Connor et al., 1958; Hurtubise et al., 1960; Sarko et al., 1973). These observations are consistent with those made in the preceding section (i.e., IR investigation) of this work.

4.1.5.3. Effect of Temperature on Crystallinity and Crystallite Breadth of Cotton Residues during Solvent Purification Treatment

In most physico-chemical processes, temperature is an important parameter. This fact explicitly appears in those reactions which take place when assisted with better solvent penetration. Thus, the crystalline structure of the

cellulose, under the solvent purification treatment, should be affected by temperature.

Fig. 4.1.5.6 shows the effect of temperature on cryctallinity index and crystallite size of cotton residues when different temperatures were applied during acetonation of cellulose. In general, the diffractograms following exposure to three levels temperature (130, 150, and 180 ^{o}C) show a slight increase in the peak heights of 101, $10\bar{1}$, and 002 reflections, however the three peaks which appear in the Fig. 4.1.5.6 overlap each other. The increase in peak heights of 101 and $10\bar{1}$ planes is strongly indicative of the changes that have taken place at inter- and intramolecular hydrogen bonding levels during the solvent purification treatment. Nonetheless, explicit information about the crystalline changes that have taken place during acetonation is given in Table 4.1.5.4. The results illustrated in Table 4.1.5.4 show a moderately increasing tendency in the crystallinity index, while the crystallite size has decreased slightly as the temperature was increased from 130 to 180 ^{o}C.

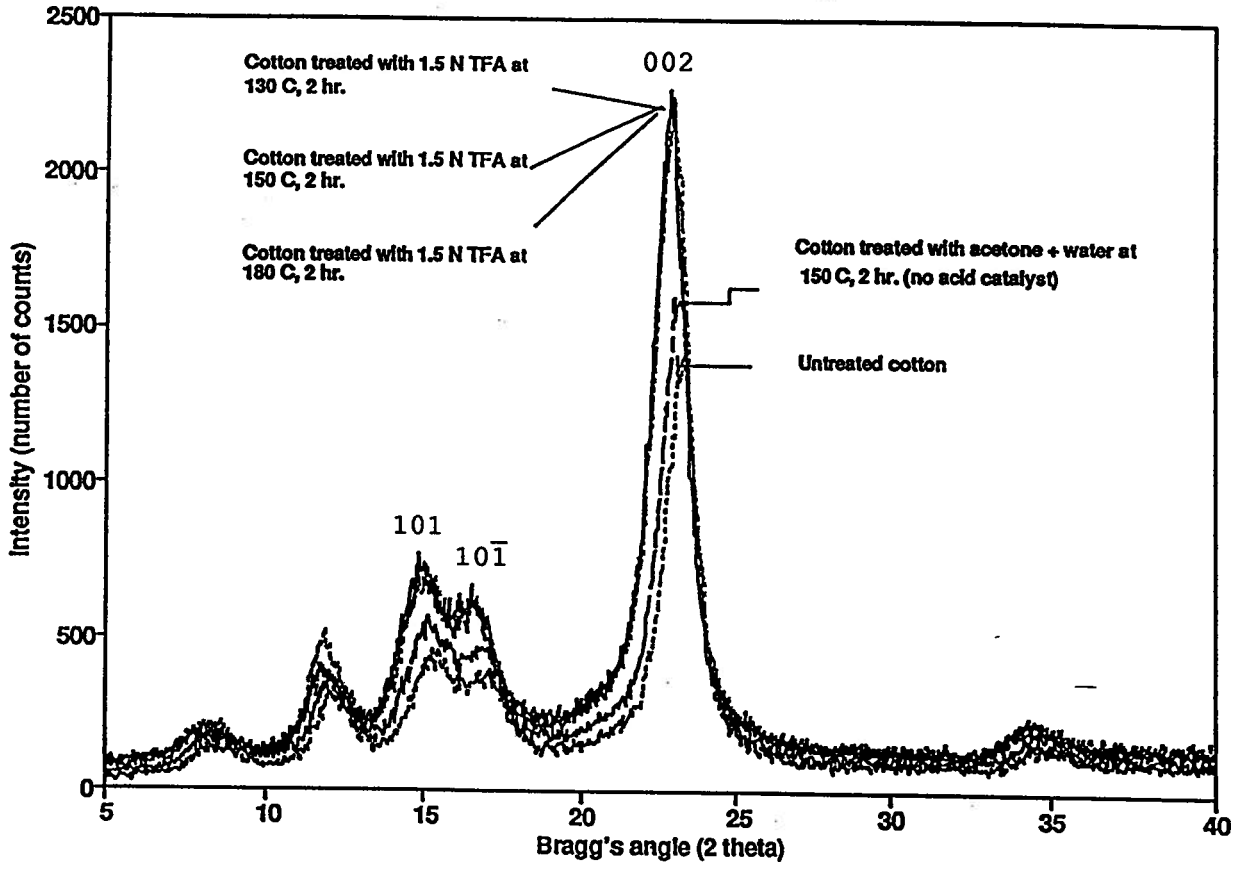


Figure 4.1.5.6. Comparison of diffraction patterns of cotton residues treated at different temperatures, while other variables were kept constant (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 1.5 N TFA).

Table 4.1.5.4. Effect of temperature on the crystallinity index and crystallite breadth of cotton residues treated at different temperatures, while other variables were kept constant (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 1.5 N TFA).

Temperature ^{o}C	CI %	S.D.	$FWHM_{002}$ (Degree)
Untreated cotton	74.37	0.21	2.01
130	74.48	0.17	2.18
150	75.00	0.26	2.20
180	75.05	0.23	2.11

Higher temperature increases the reaction rate of the system. In turn, this would lead to further stereochemical changes that can be brought about, and to a greater extent, more H-bond disruption/destruction in the cellulosic material is observed. Consequently, more active sites (i.e., H-bond free hydroxyl groups) will be available to undergo isopropylidenation. Besides, the reactivity of acetone molecules increases with increased temperature as does the system pressure. In this respect, it was also emphasized (Vinogradov et al., 1971) that the kinetic energy of the molecules increases by raising the temperature of the reaction system. In addition, with the increase of temperature the molecules of the solvent are believed (Bradley et al., 1993) to reorient much more freely and faster in the reaction medium due to the lowering of the density. This would also speed up the formation of weaker hydrogen bonding (i.e., accessibility) and

isopropylidenation processes by the involvement of more acetone molecules with glucose units to yield isopropylidene groups along the cellulose chain. Thus, from this point of view, such thermal changes brought about by temperature could considerably affect the crystalline structure and reactivity of the cellulose.

4.1.5.4 Effect of Residence Time on Crystallinity and Crystallite Breadth of Cotton Residues during Solvent Purification Treatment

Fig. 4.1.5.7 and 4.1.5.8 show the effect of residence time on crystalline structure of cotton residues during solvent purification treatment. The results in these two figures indicate that a slight increase in crystallinity index of treated cotton samples has been attained by the increase of reaction time. Also, Fig. 4.1.5.7 and 4.1.5.8 show that the peak heights of the 101, and $10\bar{1}$ planes have increased. The increase in intensities of both the 101 and $10\bar{1}$ planes strongly suggests that the solvent purification treatment has brought about structural transformations (new type of lattice), and hence these changes influenced both inter- and intramolecular H-bonding of the cellulose. In addition, similar results illustrating the increase of crystallinity index and increase in full width at half maximum height (FWHM), which is inversely proportional to crystallite width (i.e., crystallite size) are shown in

Tables 4.1.5.5 and 4.1.5.6. These results correlate well with those showing the effect of residence time on hydrogen bonding.

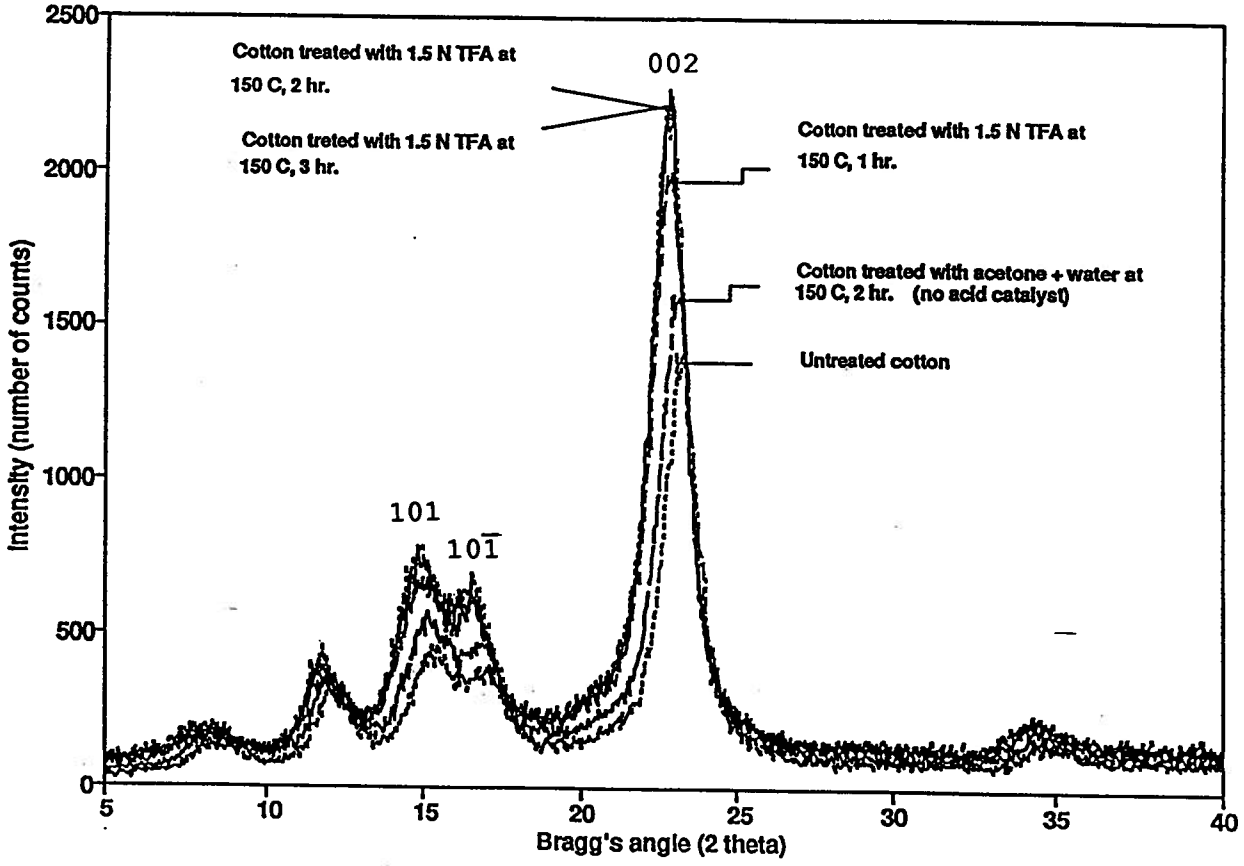


Figure 4.1.5.7. Comparison of diffraction patterns of cotton residues treated at different residence times, while other variables were kept constant (acetone:wate: 90:10; liquor/solid ratio: 10/1; 150 ^{o}C; 1.5 N TFA).

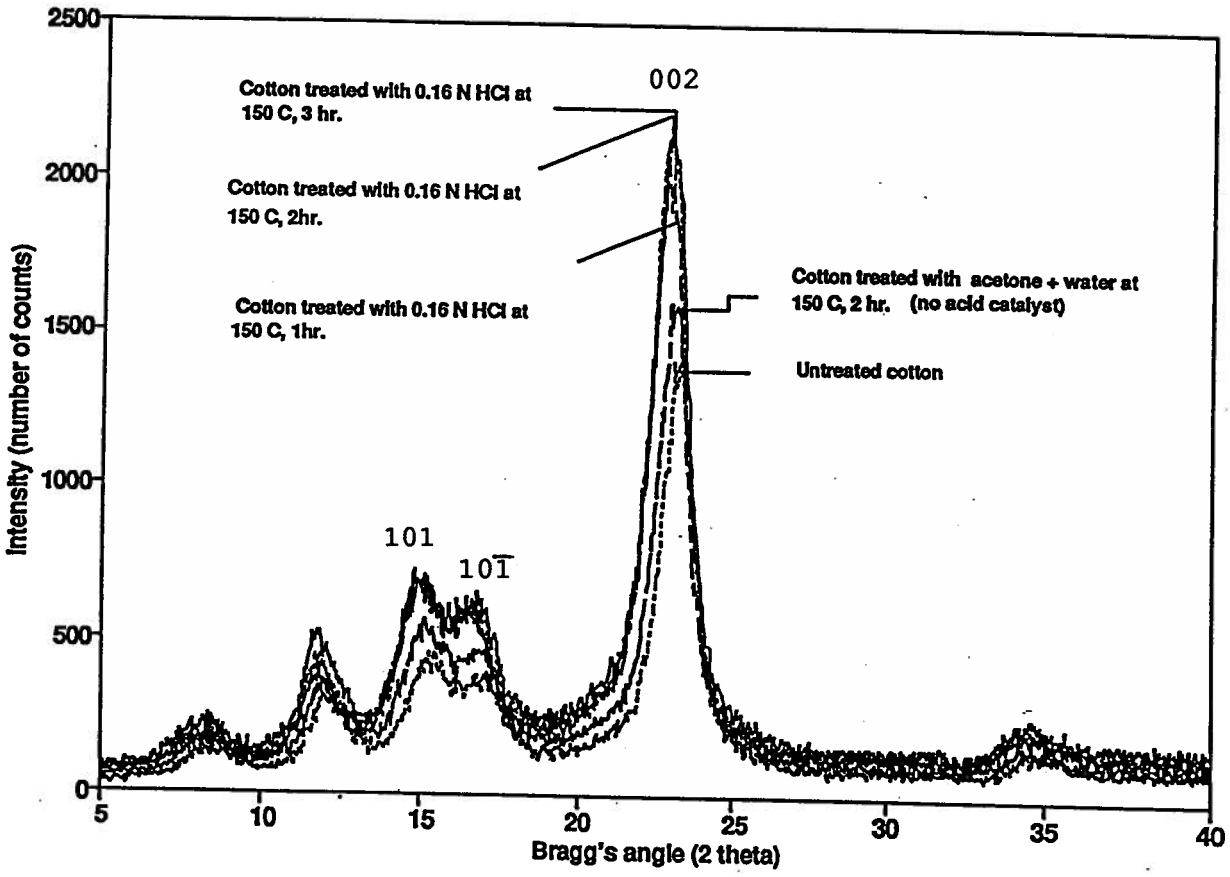


Figure 4.1.5.8. Comparison of diffraction patterns of cotton residues treated at different residence times, while other variables were kept constant (acetone:water: 90:10; liquor/solid ratio: 10/1; 150 ^{o}C; 0.16 N HCl).

Table 4.1.5.5. Effect of residence time on the crystallinity index and crystallite breadth of cotton residues treated at different residence times, while other variables were kept constant (acetone:water: 90:10; liquor/solid ratio: 10/1; 150 ^{o}C; 1.5 N TFA).

Residence Time hr	CI %	S.D.	$FWHM_{002}$ (Degree)
Untreated cotton	74.37	0.21	2.01
1	75.15	0.12	2.04
2	76.16	0.10	2.30
3	76.24	0.22	2.30

Table 4.1.5.6. Effect of residence time on the crystallinity index and crystallite breadth of cotton residues treated at different residence times, while other variables were kept constant (acetone:water: 90:10; liquor/solid ratio: 10/1; 150 ^{o}C; 0.16 N HCl).

Residence Time hr	CI %	S.D.	$FWHM_{002}$ (Degree)
Untreated cotton	74.37	0.21	2.01
1	74.48	0.11	2.23
2	74.72	0.21	2.33
3	75.65	0.18	2.33

The time factor was shown to have a lesser effect on crystallinity index after the initial solvent purification treatment when other parameters were kept constant (i.e.,

temperature, solvent composition, liquor to solid ratio and acidity, see Fig. 4.1.5.7 and 4.1.5.8 and Table 4.1.5.5 and 4.1.5.6). The slight increase in crystallinity index and reduced crystallite size can be explained by the fact that the interaction of acetone with more OH groups and stereochemistry of isopropylidenated sugar units may bring about, more or less, the some effect on the adjacent molecules. This has implications on more H-bond disruption/destruction indicating further structural changes within the cellulosic material.

4.1.6 Molecular Weight Distribution (MWD) Analysis - Changes in Molecular Weight Distribution (i.e., molecular uniformity) of Solvent Purified Cotton Residues

Depolymerization of cellulose may result from different degradative reactions such as aqueous acid or alkaline hydrolysis, enzymatic hydrolsis, oxidative, thermal and mechanical reactions, as well. Successful depolymerization can be assessed from the shape of molecular weight distribution curves and the polydispersity of the treated cellulose. In this respect, determination of molecular weight distribution (MWD) provides useful information for understanding the way in which degradation takes place in the solvent purification process. For getting a better insight into the depolymerization of cellulose in acetonation, the molecular weight distribution of solvent

purified cellulose was investigated under different reaction conditions. In this work, variables believed to influence molecular weight distribution, such as acid concentration, temperature and residence time, were investigated.

4.1.6.1 Effect of Acid Concentration on Molecular Weight Distribution of Solvent Purified Cotton Residues

Figs. 4.1.6.1 and 4.1.6.2 and Tables 4.1.6.1 and 4.1.6.2 show that the treatment of cotton with just acetone and water (90:10),i.e., no catalyst has caused depolymerizion of the cotton material. Apparently, depolymerization has taken place due to the action of buffer (acetone/water mixture) and the acids of pectic substances present in cotton cellulose on glycosidic linkages of the cellulose (cotton) molecules. This result is consistent with the previous observation (Zarubin et al., 1989) when acetone and water were used as a pulping liquor. However, the hydrolysis action was attributed (Zarubin et al., 1989) to acetic acid that resulted from the reaction of water molecules with the acetyl groups of the hemicelluloses present in the cellulose (wood pulp). Nonetheless, the results obtained, in the present work, on the change of the pH, i.e., before and after the treatment when no acid and raw material were used, indicate that the hydrolysis could possibly, in part, be achieved through the action of

acetone/water complex. This is because the pH was found to drop within differnt treatments. This has been observed when the control solution (acetone-water) was heated at reaction temperature (150 ^{o}C) for 2 hr the pH fell from 7.46 to 5.77, and the pH of cotton hydrolysate at identical conditions dropped from 7.46 to 4.59. Apparently, these experimental tests indicate the formation of an acetone-water complex, which appears to be weakly acidic. In turn, since the acetone-water complex possesses a weak acidic property (pH = 5.77), it can be expected to contribute to the hydrolysis of glycosidic linkages. On the other hand, the acidity of the acetone-water complex was also observed by other workers (Fong et al., 1969; Waggoner et al., 1982). In addition, the involvement of acids resulting from cotton in hydrolysis reactions may not be ruled out. The formation of acids from cotton during solvent purification treatment has earlier been discussed in subsection 4.1.3.2.3.

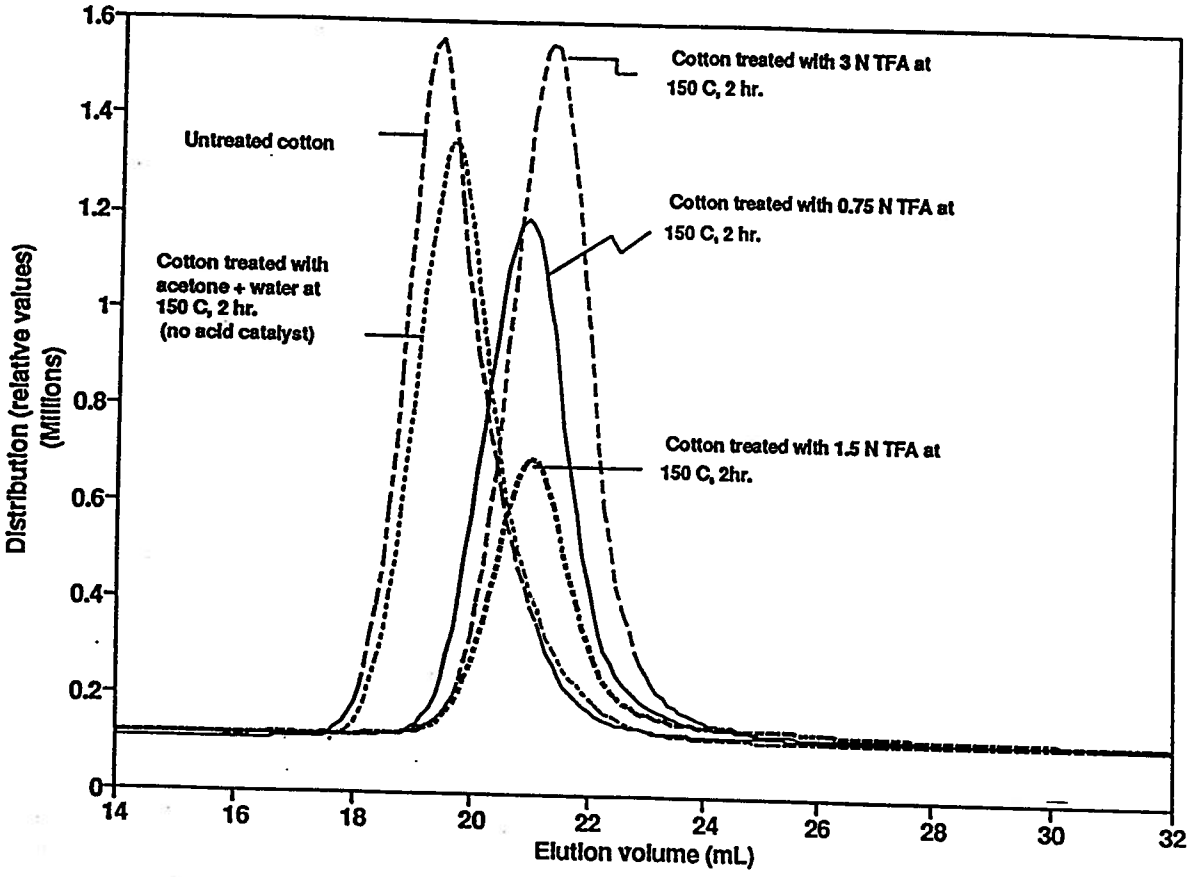


Figure 4.1.6.1. Effect of acid concentration on molecular weight distribution of cotton residues when TFA was used as catalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C).

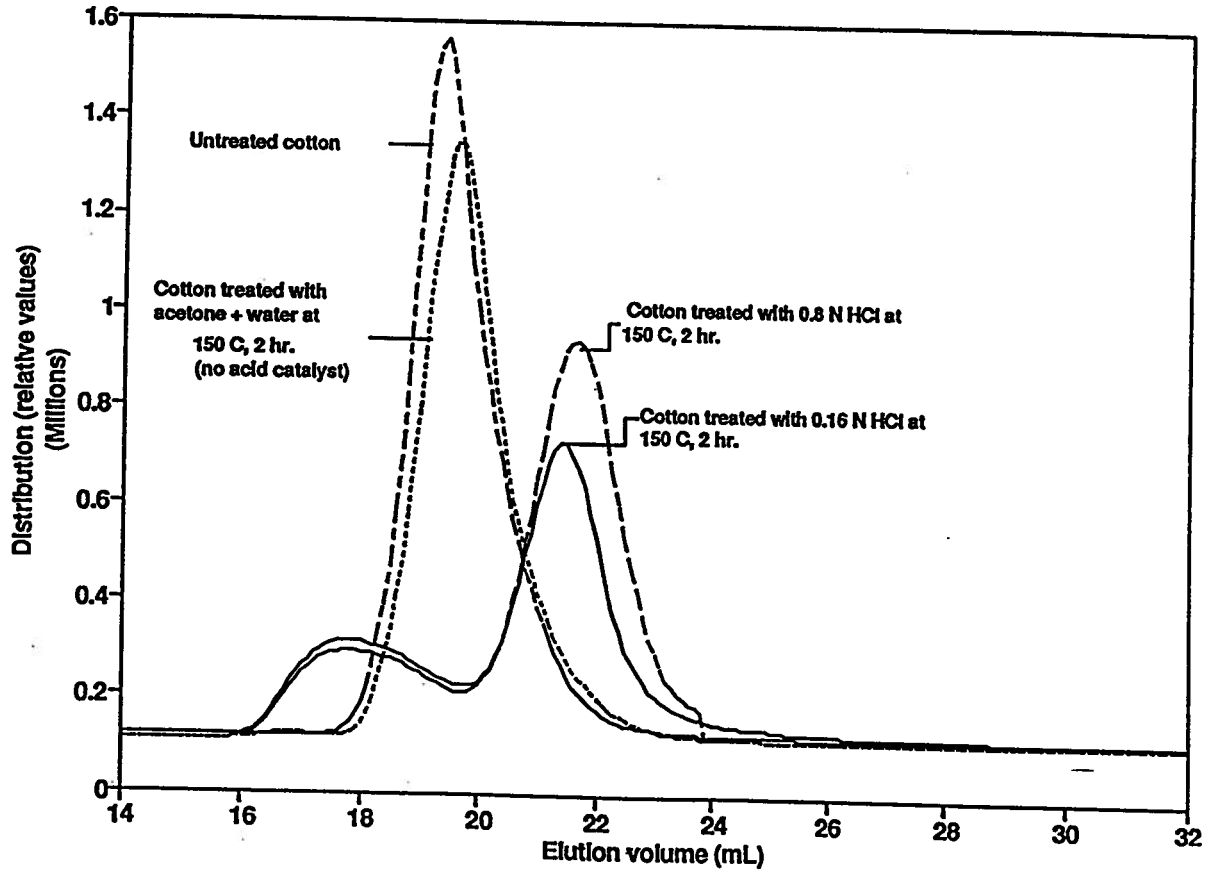


Figure 4.1.6.2. Effect of acid concentration on molecular weight distribution of cotton residues when HCl was used as catalyst in aqueous acetone (acetone:water: 90:10; solid/liquor ratio: 10/1; 2 hr; 150 ^{o}C).

Table 4.1.6.1. Effect of acid concentration on molecular weight distribution and polydispersity of cotton residues when TFA was used as catalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C; TFA).

Sample Acidity N	$\overline{M}_w$ ($x10^{-3}$)	$\overline{M}_n$ ($x10^{-3}$)	Polydispersity $\overline{M}_w/\overline{M}_n$
Untreated cotton (control)	902	296	3.05
0 N	450	67	6.72
0.75 N	188	103	1.82
1.50 N	158	83	1.89
3.00 N	145	54	2.70

Table 4.1.6.2. Effect of acid concentration on molecular weight distribution and polydispersity of cotton residues when HCl was used as catalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C).

Sample Acidity N	$\overline{M}_w$ ($x10^{-3}$)	$\overline{M}_n$ ($x10^{-3}$)	Polydispersity $\overline{M}_w/\overline{M}_n$
Untreated cotton (control)	902	296	3.05
0 N	450	67	6.72
0.08 N	175	93	1.88
0.16 N	1248	122	10.21
0.80 N	1452	82	17.64

Results shown in Figs 4.1.6.1 and 4.1.6.2 illustrate, as expected, that an increase in acid concentration

acetonation offers more low molecular weight fractions (i.e., the MWD curve shifts towards the low molecular region - greater elution volumes). The tables, also show that lower acid concentrations for both acid catalysts (TFA and HCl) provide more uniform molecular weight distribution (i.e., narrow polydispersity) than the higher ones. This may be explained by the fact that lower acid concentrations are more suitable for the protonation of the strained glycosidic linkages, i.e., under isopropylidenation reactions. However, differences between the two acid catalysts can also be observed. The results given in Fig. 4.1.6.1 and 4.1.6.2 and Table 4.1.6.1 and 4.1.6.2 show explicitly that TFA at different acid concentrations has offered more symmetrical and uniform molecular weight distributions (i.e., narrow polydispersity), while molecular weight distributions produced by HCl at higher acid concentrations are become broader and bimodal as compared to those of the original untreated sample. This may appear a physical impossibility. It was noted by Rantanen et al. (1986) that the nonuniformity of molecular weight distribution accompanied with the appearance of a shoulder in the high molecular range of the MWD curve is due to the presence of long molecule clusters and aggregates remaining in sample solution during the GPC analysis. The explanation for the presence of molecule aggregates, in this case, is probably due to the nonequivalence in steric effects and electronic interactions among the cellulosic units, resulting from the

acetonation reactions with cellulose in conjuction with the abundance of an effective acid catalyst (HCl). This is because it would be inappropriate if the large-sized ion (Cl^-) is taken into account as the main reason for impaired penetrability of a solvent. In spite of a large number of publications on the swelling, the available literature on the penetration process is scanty. However, penetration and swelling can be considered in some degree as two phenomena that resemble and complement each other. The influence of ions on the swelling phenomena was earlier explained on the basis of the diameter and hydration layers. It was noted (Frey-Wyssling, 1953) that the lesser degree of swelling can be attained the stronger hydration layer of the ion, i.e., small ions have thicker hydration layers. This can be explained by the fact that the water dipoles are attracted more strongly as the distance between the centre of gravity and the surface of the ion decreases. Thus, the ion size for hydrochloric acid in penetration and swelling aspects does not seem to be a problem, i.e., thin hydration layer. In addition, the performance of HCl in hydrolysis reactions (depolymerization) other than these two incidents with broader MWD, appears to resemble that of TFA - offering low molecular weight fractions with narrow polydispersity. On the other hand, TFA was claimed (Fengel et al., 1979; Fanta et al., 1984) to be selective in hydrolysis reactions of cellulose. However, that is not the case, because TFA with its loose hydrogen atom (Tchoubar, 1966; Amis, 1966; March,

1985) might form different complexes with various compounds. Reactions such as involvement of TFA with acetone in addition reactions (Geddes, 1956; Harris, 1965; March, 1985), TFA with water (Geddes, 1956) and with cellulose molecules in strong hydrogen bonding (section 4.1.2, Fig. 4.1.2.2 and 4.1.2.4) may undermine the activity of TFA, as well. In addition, in support of our belief that the efficiency of TFA is likely retarded due to these reactions, it was usually used for longer periods in hydrolysis reactions in order to obtain a reasonable amount of soluble sugars. The treatment (Fanta et al., 1984) of wheat straw with 1 N TFA for 7 hr at 100 ^{o}C yielded around 23% xylose based upon initial straw weight. On the other hand, the stability of sugars in response to hydrolysis reactions was found to be different (Harris, 1975), and the hemicellulose sugars were most accessible to hydrolysis.

Furthermore, penetration of these acids and solvents into the cellulosic materials is usually accompanied by different reactions. These reactions can be such as hydrogen bonding reorientation, protonation, derivatization (acetonation), and in some cases redistribution of substrate components (Wong et. al., 1988). Thus, with regards to the complexity of the whole process of penetration, other factors such as molecular structure (Bax et al., 1972; Isaacs, 1974), reactivity of the molecules (Tchoubar, 1966; March, 1985), chemical environment (Lindstrom et al., 1980), and apparently electronic properties of the molecules (i.e.,

dipole moment, dielectric constant) would have to be taken into account. However, further investigations in the significance of these factors in conjuction with the molecular size of reagents to the penetration process are needed.

4.1.6.2 Effect of Temperature on Molecular Weight Distribution of Solvent Purified Cotton Residues

Figs. 4.1.6.3 and 4.1.6.4 show that the MWD curves of cotton residues shift towards a lower molecular weight distribution region with the increase in temperature. This suggests that more cleavage of glycosidic bonds has taken place at different sites of isopropylidenated molecules along the cellulose chain. In other words, the effect explicitly suggests that the increase of temperature leads to production of shorter cellulose chains on acetonation of cellulose. This has not been observed in the literature for acetonation of oligomeric sugar residues (Glushka et._al., 1983; Aamlid, 1983) in the past. The two figures also illustrate that the shift of the cellulose MWD curve for the residues, treated with the HCl catalyst, is more extensive towards the low molecular weight distribution region than that for the samples treated with TFA. The results shown in Fig. 4.1.6.4 illustrate that the molecular weight distribution curves for the treatments at 150 ^{o}C and 180 ^{o}C temperature apparently coincide with each other, however,

the results shown in Table 4.1.6.4 indicate that the weight-average and number-average molecular weight distributions for the two treatments are in fact different and hence their polydispersity must differ. Minor GPC graphical deviations recently were shown to be highly significant due to the excellent reproducibility of the method (Schwantes et al., 1994).

Furthermore, the 2 hr results illustrated in Fig. 4.1.6.5 and Table 4.1.6.5 provide further evidence that an increase in temperature (with the exception of 150 ^{o}C treatment) of the solvent treatment offers residual cellulose with lower molecular weights (weight-average and number-average molecular weights). The results given in Table 4.1.6.5 show that an increase of temperature acossiated with longer reaction time (2 hr) has resulted in production of shorter cellulose chains than that with lesser residence time (1 hr), see Table 4.1.6.4. The results shown in Table 4.1.6.5, also, indicate that the polydispersity of the treated cellulose (except 150 ^{o}C treatment) has narrowed with the increase of temperature. The results given in Tables 4.1.6.3, 4.1.6.4 and 4.1.6.5 are consistent with those shown in section 4.1.3, i.e., weight loss results. In other words, the higher the temperature of the treatment, the greater the weight loss, and the shorter the cellulose chain of the treated sample.

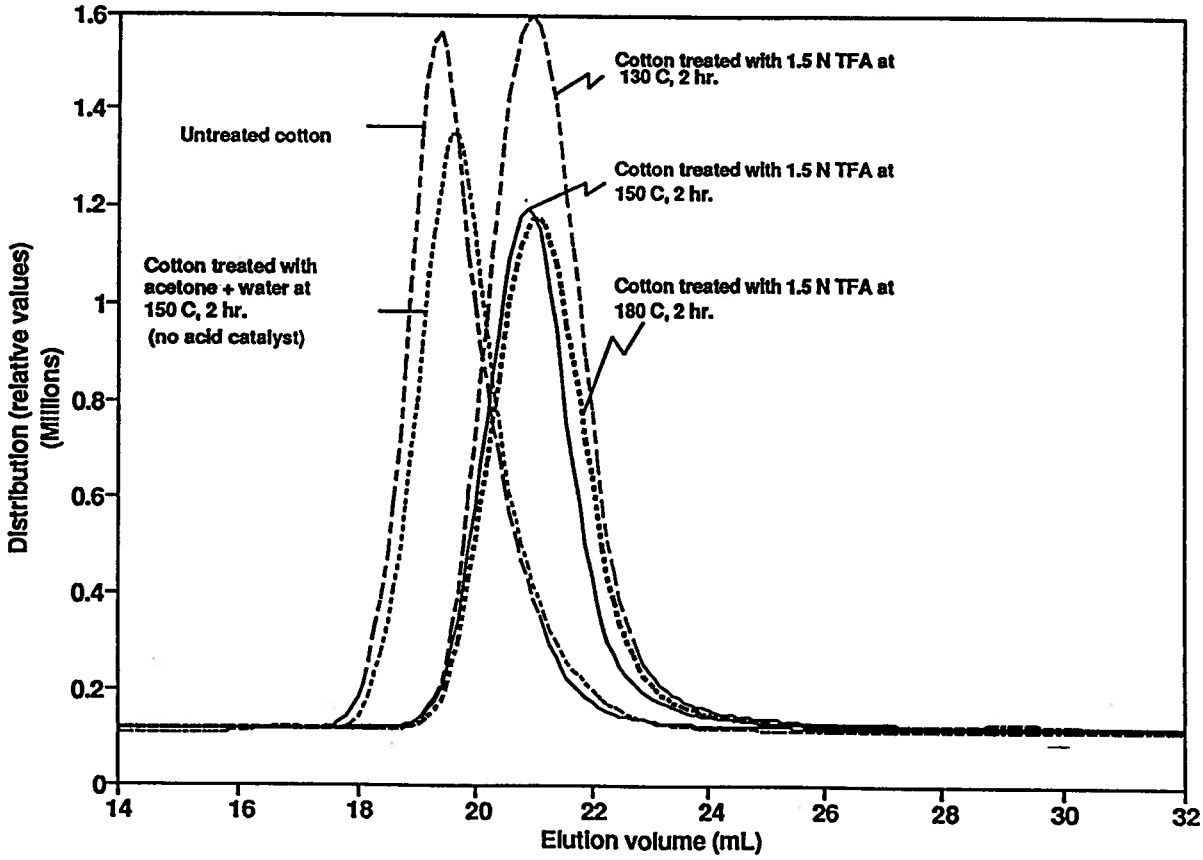


Figure 4.1.6.3. Effect of temperature on molecular weight distribution of cotton residues when TFA was used as catalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 1.5 N TFA).

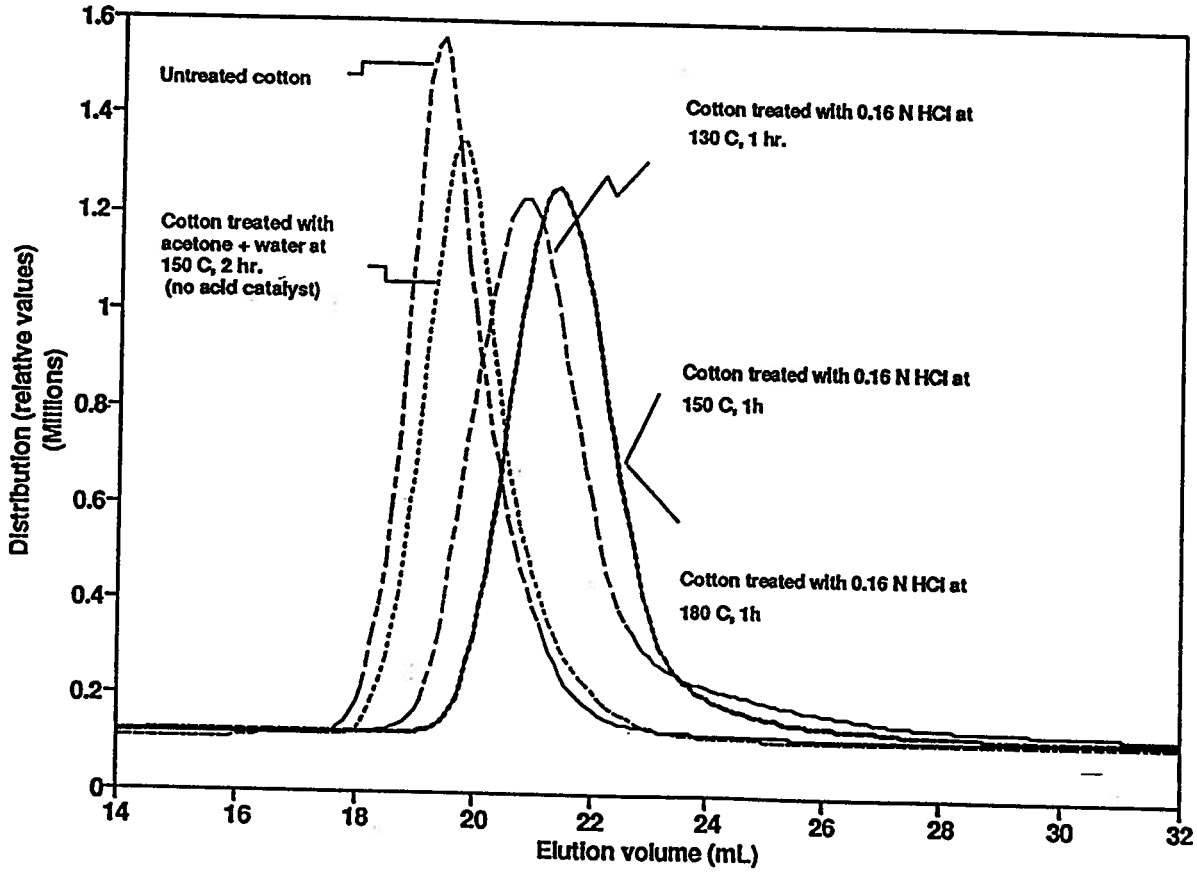


Figure 4.1.6.4. Effect of temperature on molecular weight distribution of cotton residues when HCl was used as catalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 1 hr; 0.16 N HCl).

Table 4.1.6.3. Effect of temperature on molecular weight distribution and polydispersity of cotton residues when TFA was used as catalyst in aqueous acetone (acetone:water: 90:10, liquor/solid ratio: 10/1; 2 hr; 1.5 N TFA).

Temperature Treatment °C	$\bar{M}_w$ ($\times 10^{-3}$)	$\bar{M}_n$ ($\times 10^{-3}$)	Polydispersity $\bar{M}_w/\bar{M}_n$
Untreated cotton (control)	902	296	3.05
130	165	86	1.93
150	158	83	1.89
180	137	78	1.77

Table 4.1.6.4. Effect of temperature on molecular weight distribution and polydispersity of cotton residues when HCl was used as catalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 1 hr; 0.16 N HCl).

Temperature Treatment °C	$\bar{M}_w$ ($\times 10^{-3}$)	$\bar{M}_n$ ($\times 10^{-3}$)	Polydispersity $\bar{M}_w/\bar{M}_n$
Untreated cotton (control)	902	296	3.05
130	164	51	3.22
150	171	82	2.09
180	108	54	2.00

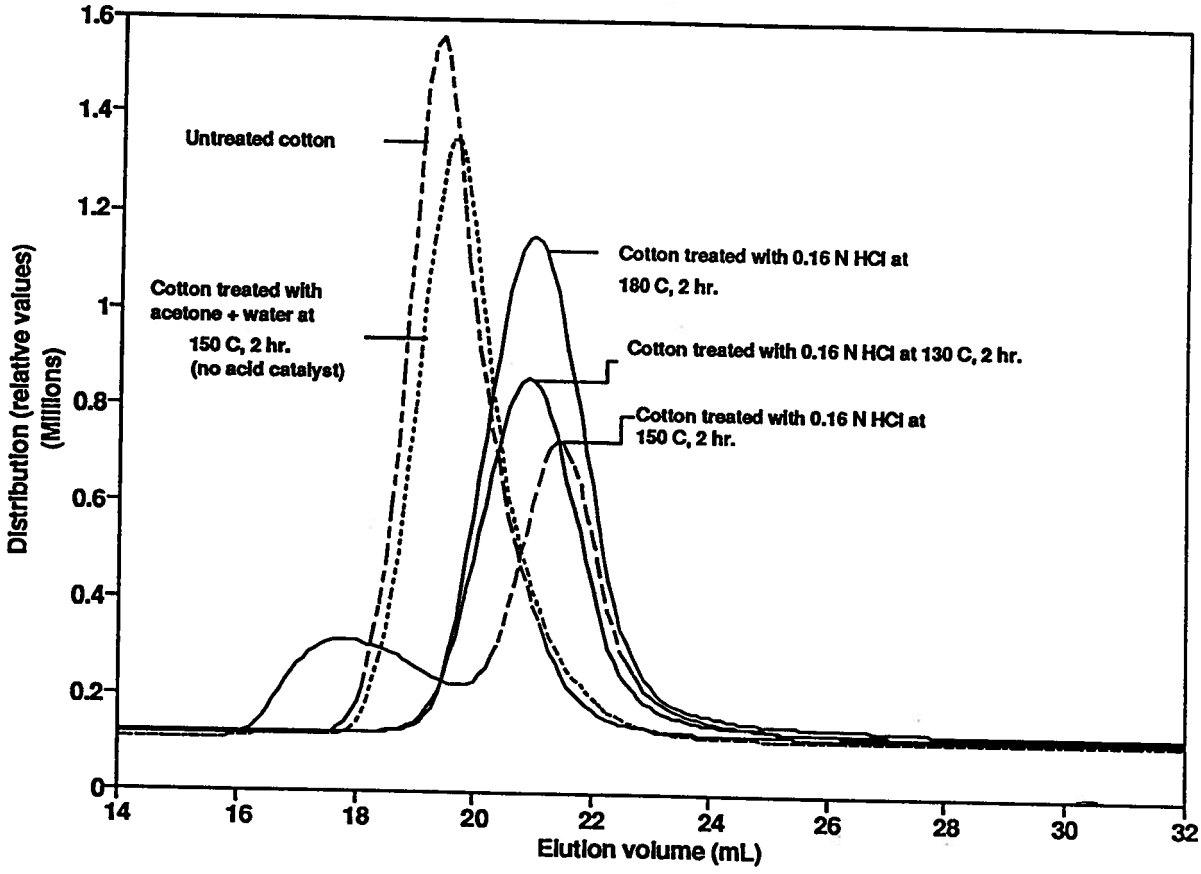


Figure 4.1.6.5 Effect of temperature on molecular weight distribution of cotton residues when HCl was used as catalyst in aqueous acetone (acetone: water: 90:10; liquor/solid ratio: 10/1; 2 hr; 0.16 N HCl).

Table 4.1.6.5 Effect of temperature on molecular weight distribution and polydispersity of cotton residues when HCl was used as catalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 0.16 N HCl).

Temperature Treatment ^{o}C	$\bar{M}_w$ ($x10^{-3}$)	$\bar{M}_n$ ($x10^{-3}$)	Polydispersity $\bar{M}_w/\bar{M}_n$
Untreated cotton (control)	902	296	3.05
130	150	74	2.02
150	1248	122	10.21
180	103	54	1.92

The results given in Table 4.1.6.3, 4.1.6.4 and 4.1.6.5 show that the solvent purification treatment brings about considerable degradation of the celluose chains with the increase of temperature during the treatment. However, the results illustrate that the polydispersity index decreases with the increase in temperature. The narrowness of polydispersity is a clear evidence that the solvent purification treatment causes a more uniform molecular weight distribution in the residual cellulosic material. Now, it is postulated that this uniform disproportionation of the treated celluloses could be due to the formation of isopropylidene groups at regular intervals on the cellulose chains. The presence of isopropylidene groups on the solid cotton residues has been confirmed, in this work, by the results obtained from GC, HPLC, and C-13 CP/MAS solid state NMR analyses. However, these analyses allow no statements as

to the distribution and location of isopropylidene groups on the cellulose chains themselves. Probably, the uniformity of disproportionation of the cellulose chain arises from repeated equivalent steric and electronic effects along the cellulose chain due to acetone reactions with cellulose.

Regarding the last statement (i.e., uniformity of cellulose chain attributed to equivalence of steric and electronic effects), there is no evidence that the chain length distribution of cellulose within a finite element of cellulose as the crystallite is uniform. To the contrary, while the molecular weight itself may be increasing with the crystallite size, the MWD pattern may not provided that a certain (high) crystallinity is maintained. If the crystallinity index drops to a certain limit (~ 75%) the MWD will broaden due to the contribution from chains running in the amorphous cellulose. In the present work, even though, an enhancement of crystallinity (see crystallinity section) is attained, the crystallinity index of the treated samples has not exceeded 76%. In addition, a similar trend of narrowness has also been indicated by polydispersity results, however, it did not approach unity that one may justify a cellulose sample of chains of similar lengths. On the other hand, cotton and ramie are considered to be single-phased types of cellulose, however, their lattice structure was found to be highly imperfect (Kulshreshtha et al., 1973). This observation lends support to the concept of the limited molecular uniformity of cotton residues achieved

through solvent purification treatment. In addition, the results obtained, in this work, on crystallinity, molecular weight distribution, and polydispersity are not applicable to the two-phase hypothesis of cellulose (Viswanathan, 1966; Viswanathan, 1967). In other words, the state of order in the fibrous structure of cellulose is much more complex than the oversimplified structural picture drawn by the latter theory. The two-phase concept visualizes the cellulosic material as a two-state-ordered matter; one completely crystalline and the other completely amorphous, present in all cellulosic materials but to different extents, the correlation coefficient for every analysis, no matter what the crystallinity of the sample, should be unity (Viswanathan, 1966; Viswanathan, 1967). However, there is enough evidence against the hypothesis of a two-phase structure in cellulose in the literature (Kulshreshtha et al., 1973).

4.1.6.3 Effect of Residence Time on Molecular Weight Distribution of Solvent Purified Cotton Residues

Fig. 4.1.6.5 illustrates the changes in molecular weight distribution resulting from the influence of reaction time on acetonation of cotton. As anticipated, the MWD curves show slight shifts towards the low molecular weight

distribution region with the increase in residence time. The results given in Table 4.1.6.6, explicitly, show the successive reduction in both weight-average and number-average molecular weights with the increase in residence time. The results also show that the polydispersity index becomes smaller with the increase in residence time. Also, Fig. 4.1.6.5 and Table 4.1.6.6 illustrate that the differences in changes between both molecular weight distribution and polydispersity has narrowed remarkably with increasing reaction time. Particularly, this effect appears to be clear between the 2 and 3 hr treatments. This little difference in change of MWD and polydispersity at extended reaction time can be attributed to the fact that hydrolysis reactions become predominant, at longer reaction times, in the crystalline regions and hence the frequency of disproportionation is increased. The results given in Fig. 4.1.6.5 and Table 4.1.6.6 are consistent with those obtained for weight loss, hydrogen bonding and crystallinity (Fig. 4.1.3.2.3.5, 4.1.2.7 and Table 4.1.5.6).

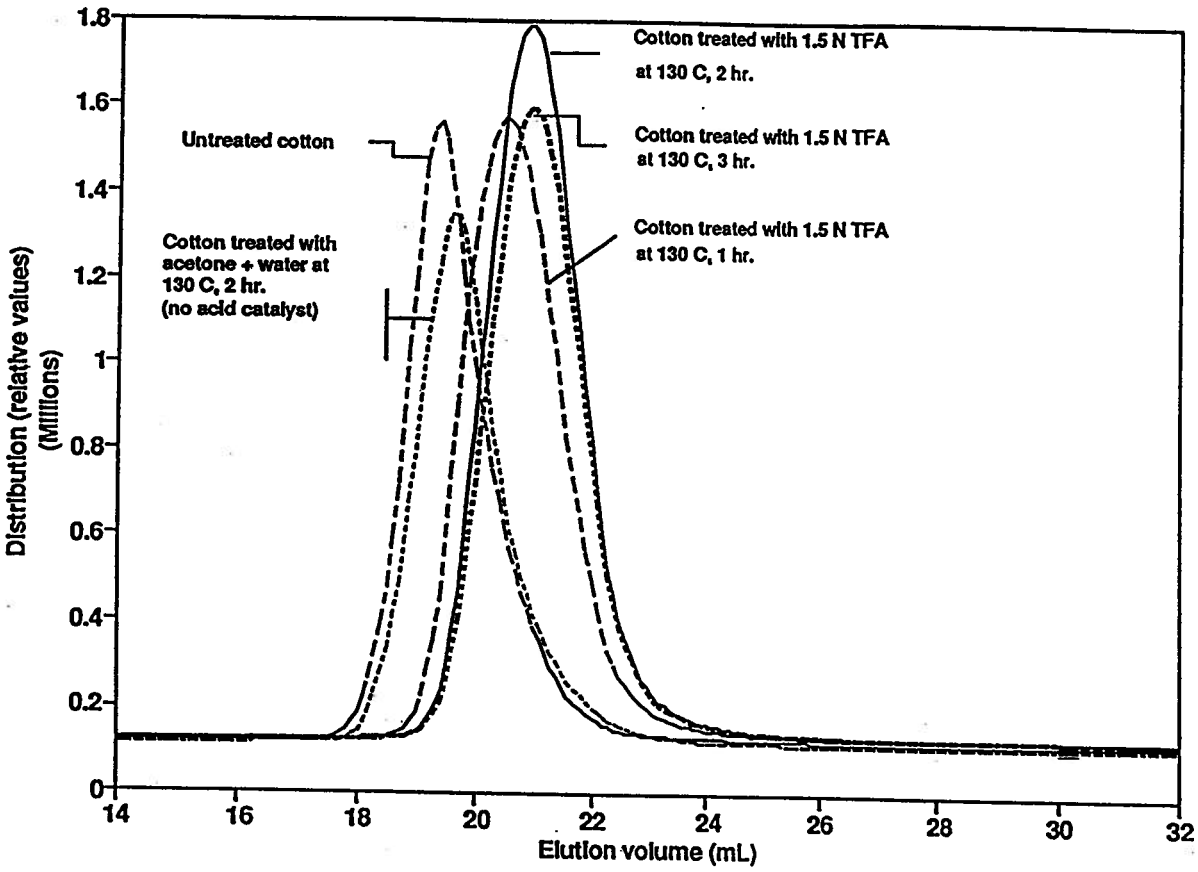


Figure 4.1.6.6. Effect of residence time on molecular weight distribution of cotton residues when TFA was used as catalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 130 ^{o}C; 1.5 N TFA).

Table 4.1.6.6. Effect of residence time on molecular weight distribution and polydispersity of cotton residues when TFA was used as catalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 130 ^{o}C; 1.5 TFA).

Residence Time (hr)	$\bar{M}_w$ ($x10^3$)	$\bar{M}_n$ ($x10^3$)	Polydispersity $\bar{M}_w/\bar{M}_n$
Untreated cotton (control)	902	296	3.05
1	213	111	1.91
2	155	86	1.81
3	152	84	1.81

From the results shown in Fig. 4.1.6.6 and Table 4.1.6.6 it is evident that the time factor has a lesser effect on disproportionation of cellulose chains during solvent purification when other parameters are kept constant. The lesser degradation of cellulose chains can be explained by the fact that the stereochemistry of isopropylidenated sugar units may bring about, more or less, the some effect on the adjacent molecules . This has implications on more steric and electronic interactions allowing the more accessible cellulose units to undergo rapid isopropylidenation and hydrolysis reactions. This assumption is based on experimental findings of other workers (Brewster, 1959; Lemieux et al., 1968; Lemieux et al., 1969; Stoddart, 1971) in the area of stereochemistry.

4.1.7 Viscosity Analysis - Changes in Viscosity of Cotton Residues during Solvent Purification Treatment

Viscosity measurements, which are relatively simple to perform, have been used widely because they can provide valuable information both on the physico-chemical behaviour of a cellulose and on the size of its molecules. In addition, viscosity is one important parameter for dissolving pulp analysis for both research and quality control work. Thus, the viscosity test makes it possible to check the degree of degradation brought about by hydrolysis reactions, which greatly influence the quality of the dissolving pulps.

The purpose of this investigation is to characterize the resistance of cellulose to degradation by solvent purification with the acidified acetone-water system.

4.1.7.1 Effect of Acetone Concentration on Viscosity of Cotton Residues during Solvent Purification Treatment

Fig. 4.1.7.1 shows that the viscosity of cotton residues, treated with different acetone concentrations in the solvent composition, decreases with the increase in acetone content. In addition, the statistical analysis illustrates that the treatments of cotton with different acetone concentrations for the viscosity are significantly different, see Fig. 4.1.7.1, (Duncan's multiple range test).

This result is in agreement with those obtained for the hydrgen bonding, weight loss, and crystallinity. In other words, the progressive increase in acetone concentration is met with a systematic decrease in hydrogen bond strength (accessibility), increase in carbohydrate removal, increase in crystallinity index (selectivity), and decrease in DP of the cellulose. In general, apparently, the decrease in viscosity of cotton residues treated with just acetone and water (no acid catalyst) is due to the action of acetone-water system and acids released from pectic substances present in cotton cellulose on strained glucosidic linkages. This stress on the glycosidic linkages is likely to result from the engagement of two adjacent cellulose units in isopropylidenation. The formation of isopropylidene groups on the cellulose molecules during acetonation is confirmed in this work by GC, HPLC, and C-13 CP/MAS solid state NMR analyses.

With regards to the hydrolysis reactions on cotton residues that took place during the solvent treatment (acetone/water) when no catalyst was added, are probably, on one hand, due to the acidic nature of acetone/water mixture (pH = 5.77) at higher temperature. This conclusion has been drawn when the initial acetone-water mixture (pH = 7.46) was dropped to 5.77 when heated for two hr at 150 ^{o}C, and the pH of cotton hydrolysate (identical conditions) dropped from 7.46 to 4.59 . Thus, the pH result indicates that the acidity of acetone/water system developed during solvent

treatment may lead to depolymerization reactions (protonation) along the cellulose chains. Such acidity of the acetone-water system was also indicated by Fong et al. (1969), and Waggoner et al. (1982). On the other hand, the contribution of acids released from cotton during solvent treatment to hydrolysis reactions might also be taken into consideration. The possible explanation for the release of acids from the cotton during treatment has already been cited in subsection 4.1.3.2.3. Similar hydrolysis reactions were observed earlier by Zarubin et al., (1989) on studying acetone-water pulping of different wood raw materials. However, their interpretation of the hydrolysis reactions that took place was soley reasoned by the action of the acetic acid formed during the pulping process.

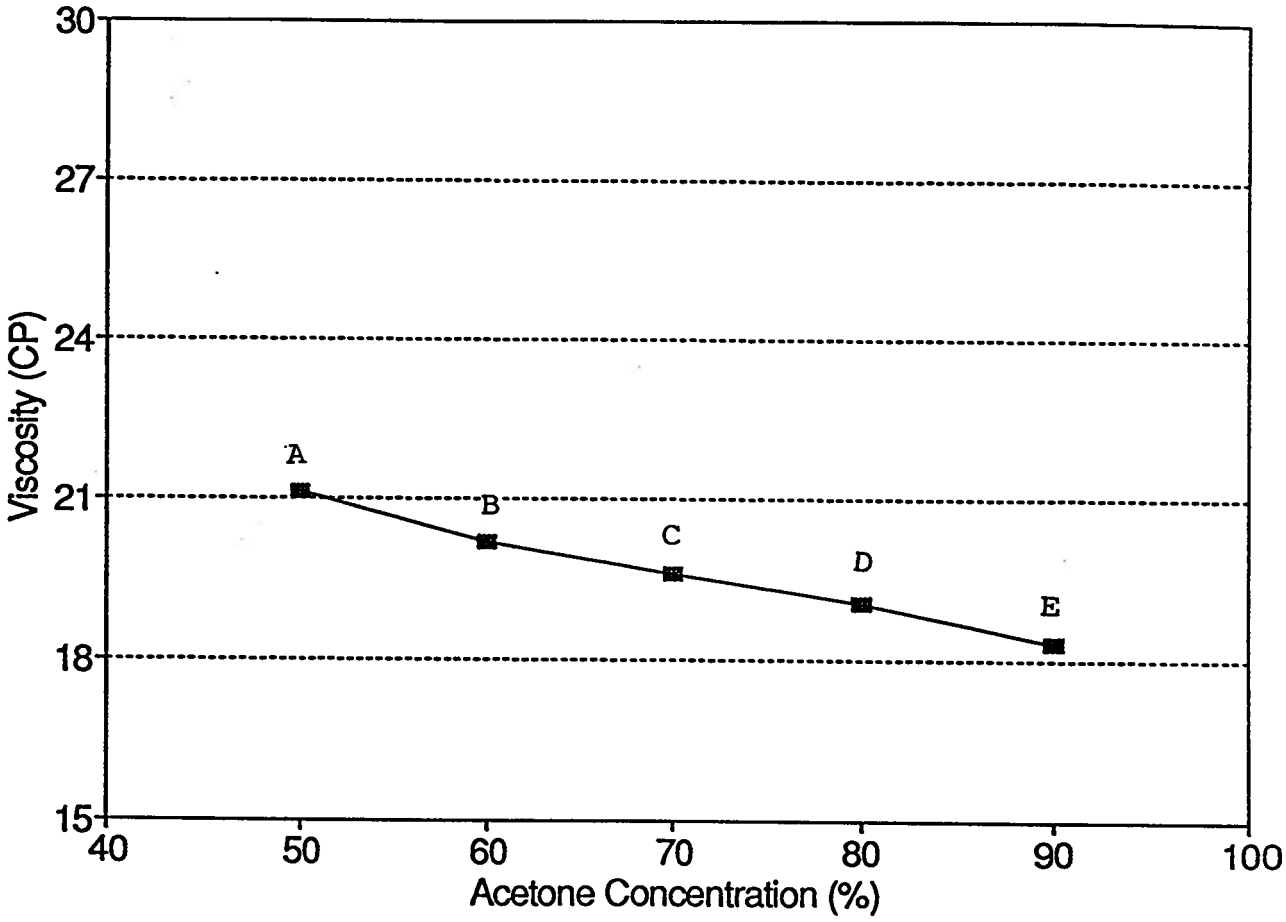


Figure 4.1.7.1. Effect of acetone concentration on vicosity of cotton residues when no acid catalyst was added (liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C).

* Means with the same letter are not significantly different.

** Significance at 95% confidence level.

The results given in Fig. 4.1.7.1 indicate the sensitivity of glycosidic linkages under isopropylidenation reactions to acids. In other words, usually, under conventional forced acid hydrolysis conditions (i.e., high energy and acidity) are required to protonate glycosidic oxygens. However, in the case of acetonation, these glycosidic linkages may, probably, be placed under considerable strain due to the formation of isopropylidene groups between the adjacent cellulose units. The gradual decrease of viscosity is attributable to the better solvation of cellulose molecules by solvent (i.e., at both levels - hydrogen bonding and isopropylidenation) at higher acetone concentrations.

4.1.7.2 Effect of Acid Concentration on Viscosity of Cotton Residues during Solvent Purification Treatment

Fig. 4.1.7.2 and 4.1.7.3 show the dramatic drop of viscosity (from 18.3 CP for the acetone:water treated cotton to 3.68 and 3.49 CP for TFA and HCl catalyzed $\bar{r}$uns, respectively) when (0.75 N TFA and 0.16 N HCl) acid catalysts respectively were used in the initial in solvent purification treatment of cotton. This is strongly indicative of the destabilization of glycosidic linkages due to the presence of isopropylidene groups on the molecules along the cellulose chain. The results given in Fig. 4.1.7.2 and 4.1.7.3 illustrate that further increase in acid

concentration had little contribution to the drop of viscosity after the initial acid concentration when the other factors such as solvent composition, temperature, liquor/solid, and reaction time are kept constant. However, the statistical analysis shows that the treatments of cotton with different acid concentrations for the viscosity are significantly different (Fig. 4.1.7.2 and 4.1.7.3), Duncan's multiple range test. The lower rate of viscosity loss at the higher acid concentration can be explained by the fact that: a- the limiting DP has been reached, and b- that the stereochemistry of already isopropylidenated sugar units would bring about, more or less, the some effect on the adjacent molecules. This has some implications on more H-bond disruption/destruction (i.e., destabilization of sugar conformations) allowing the more accessible cellulose units to undergo rapid isopropylidenation and hydrolysis reactions. Fig. 4.1.7.2 and 4.1.7.3 show that the viscosities obtained for HCl are lower than those obtained for TFA. This can, in part, be explained by the fact that HCl is a stronger acid than TFA and, in part, by the competing reactions that may take place in the presence of solvents with different properties such as acetone addition reactions (March, 1985) hydrogen bond formation etc. Consequently, such reactions could retard remakably the reactivity of TFA towards hydrolysis reactions.

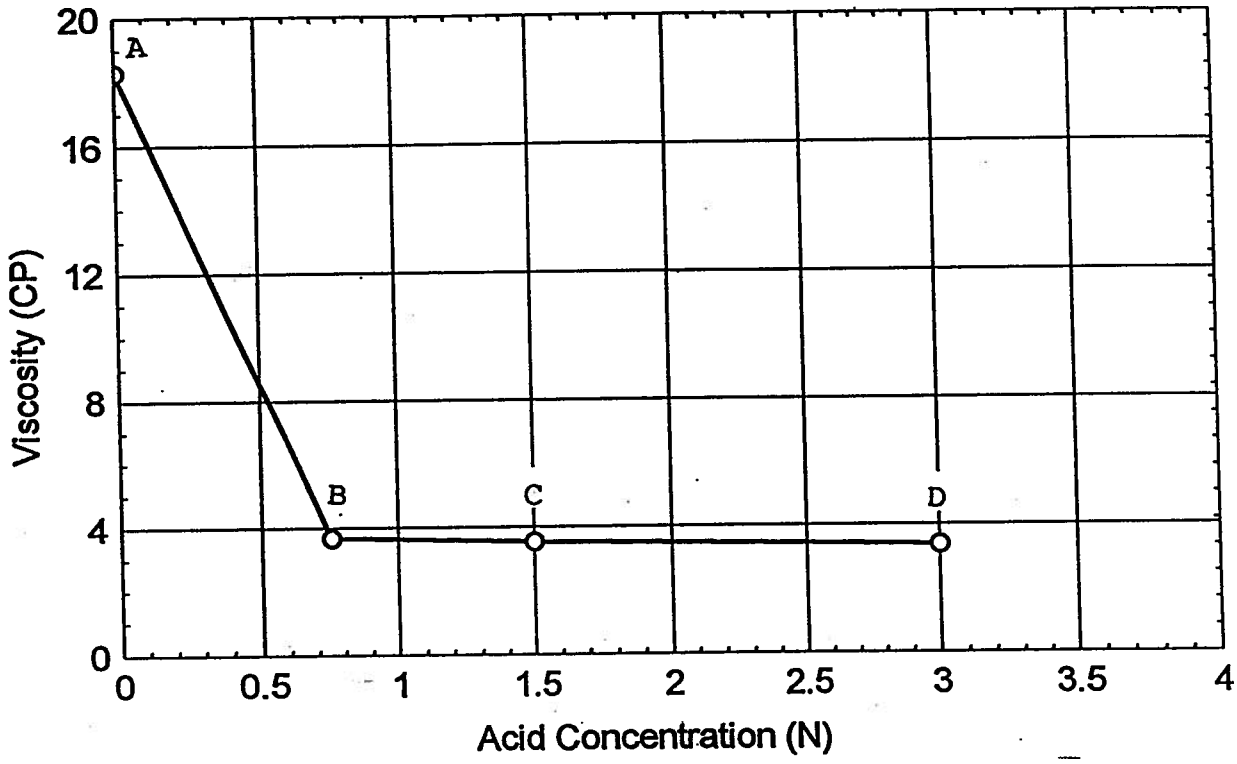


Figure 4.1.7.2. Effect of acid concentration on viscosity of cotton residues when TFA was used as catalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C).

* Means with the same letter are not significantly different.

** Significance at 95% confidence level.

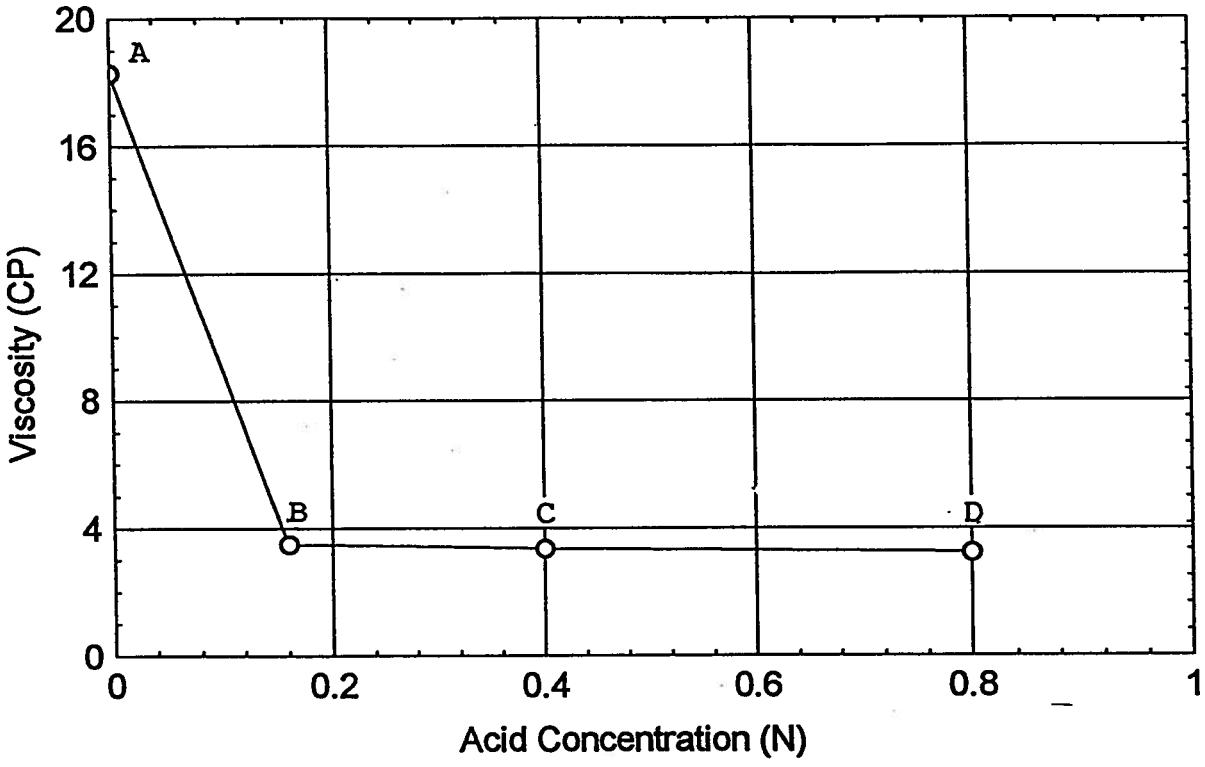


Figure 4.1.7.3. Effect of acid concentration on viscosity of cotton residues when HCl was used as catalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 150 ^{o}C).

* Means with the same letter are not significantly different.

** Significance at 95% confidence level.

4.1.7.3 Effect of Temperature on Viscosity of Cotton Residues during Solvent Purification Treatment

Fig. 4.1.7.4 and 4.1.7.5 show the effect of temperature on the residual viscosity of cotton residues following the solvent purification treatment. The results in both figures indicate a considerable drop in viscosity with increasing reaction temperature. The results, also, show the drop in viscosities continued to proceed with increase in temperature even though the limiting DP has been reached (the limiting DP is about 250-300 or 2.5-3.0 CP). Fig. 4.1.7.4 and 4.1.7.5 show that the viscosities obtained with TFA at different temperatures are higher than those obtained with HCl as catalyst. This limiting effect can be best explained by the difference in acid strengths of the two acids and, partly, by the involvement of TFA in competing reactions as described previously. Nonetheless, the statistical analysis indicates that the treatments of cotton at different temperatures are significantly different (Fig. 4.1.7.4 and 4.1.7.5), Duncan's multiple range test.

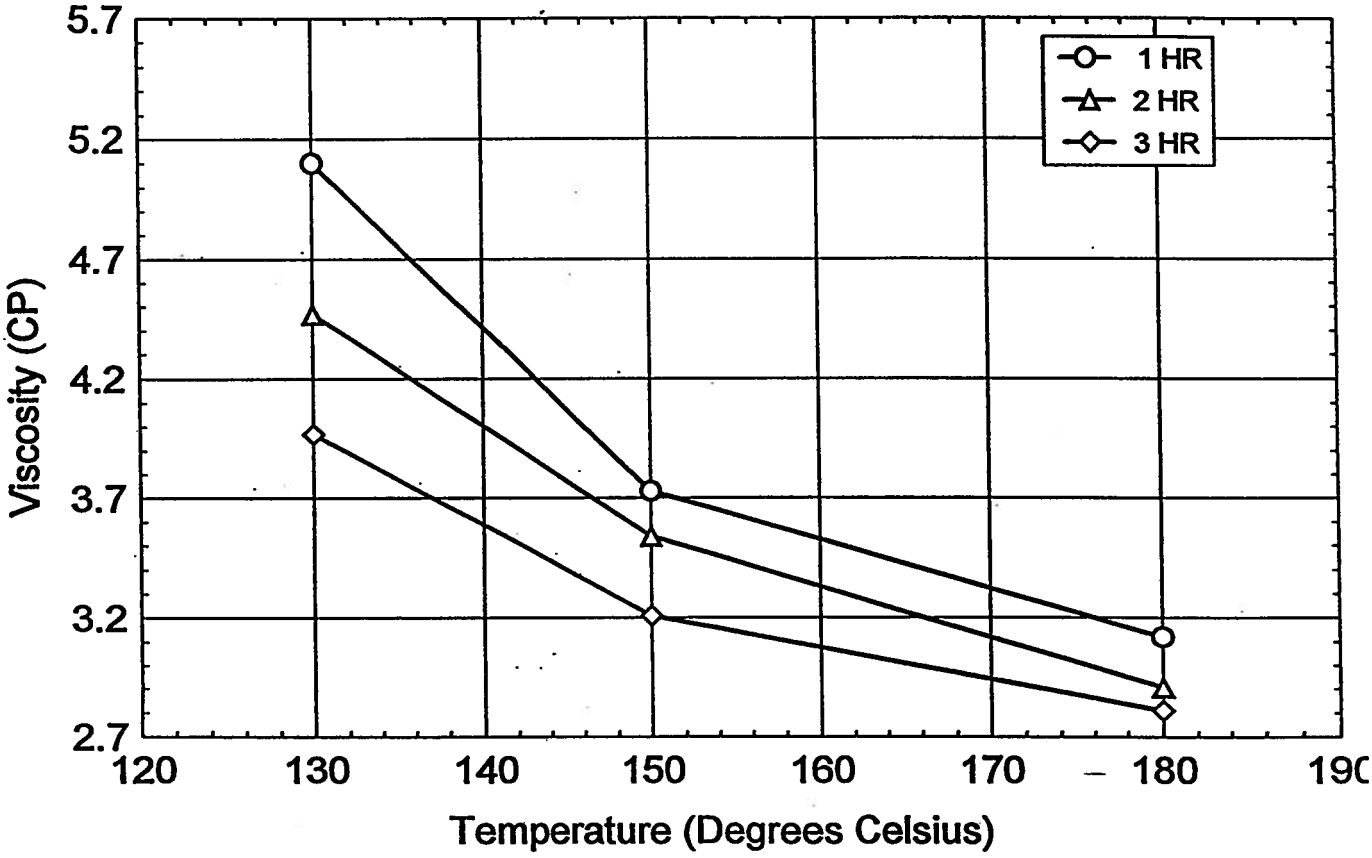


Figure 4.1.7.4. Effect of temperature on viscosity of cotton residues when TFA was used as catalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 1.5 N TFA).

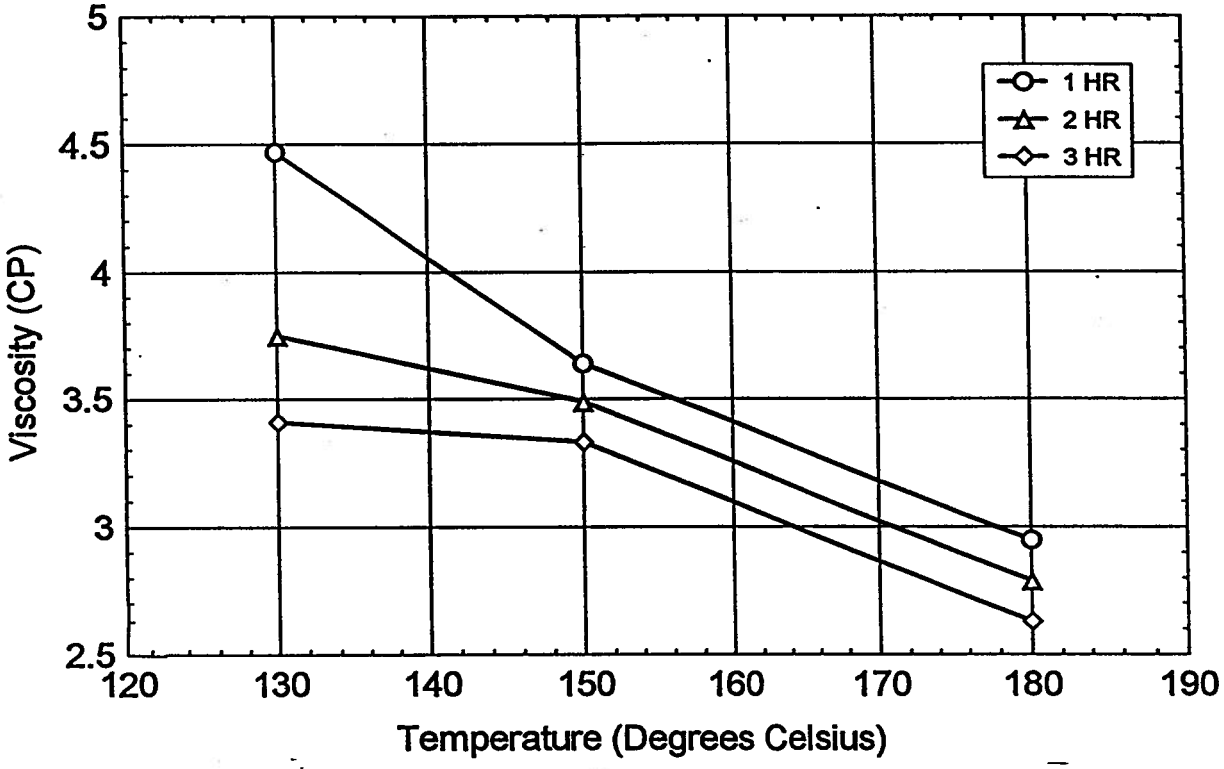


Figure 4.1.7.5. Effect of temperature on viscosity of cotton residues when HCl was used as ctalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 0.16 N HCl).

The results can be interpreted as follows; higher temperature increases the reaction rate of the system. Consequently, this would give rise to further stereochemical alterations (i.e., molecules are freer and faster to reorient, Bradley et al., 1993) that can bring about, to a greater extent, more H-bond disruption/destruction in the cellulosic material. In turn, more active sites (i.e., H-bond free hydroxyl groups) will be available to undergo isopropylidenation. Besides, the reactivity of acetone molecules increases with increased temperature as does the system pressure. This should also speed up the isopropylidenation process by the involvement of more acetone molecules with glucose units to yield isopropylidene groups along the cellulose chain.

4.1.7.4 Effect of Residence Time on Viscosity of Cotton Residues during Solvent Purification Treatment

Fig. 4.1.7.6 and 4.1.7.7 show the effect of residence time on viscosities of cotton residues during the solvent purification treatment. The results given in both figures show a slight drop in viscosity of cotton cellulose on increase of residence time. The results shown in Fig. 4.1.7.6 and 4.1.7.7, also illustrate that the effect of residence time on the viscosity drop at 130 ^{o}C treatment temperature is relatively higher than that at higher

temperatures (150 and 180 ^{o}C). Probably, this could be due to the fact that the hydrolysis reactions proceeed primarily in the amorphous zones. However, the statistical analysis shows that the treatments of cotton at different reaction times for the viscosity, for both acid catalysts, are not significantly different (Duncan's multiple range test).

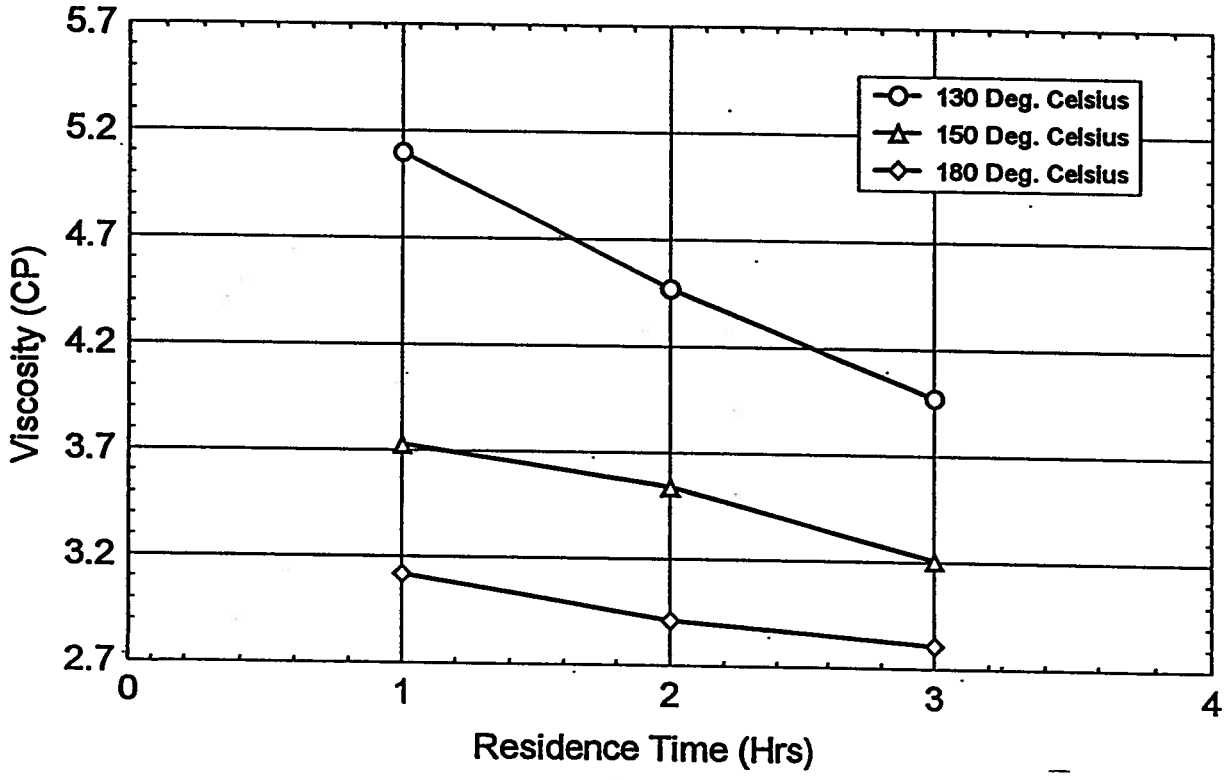


Figure 4.1.7.6. Effect of residence time on viscosity of cotton residues when TFA was used as catalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 1.5 N TFA).

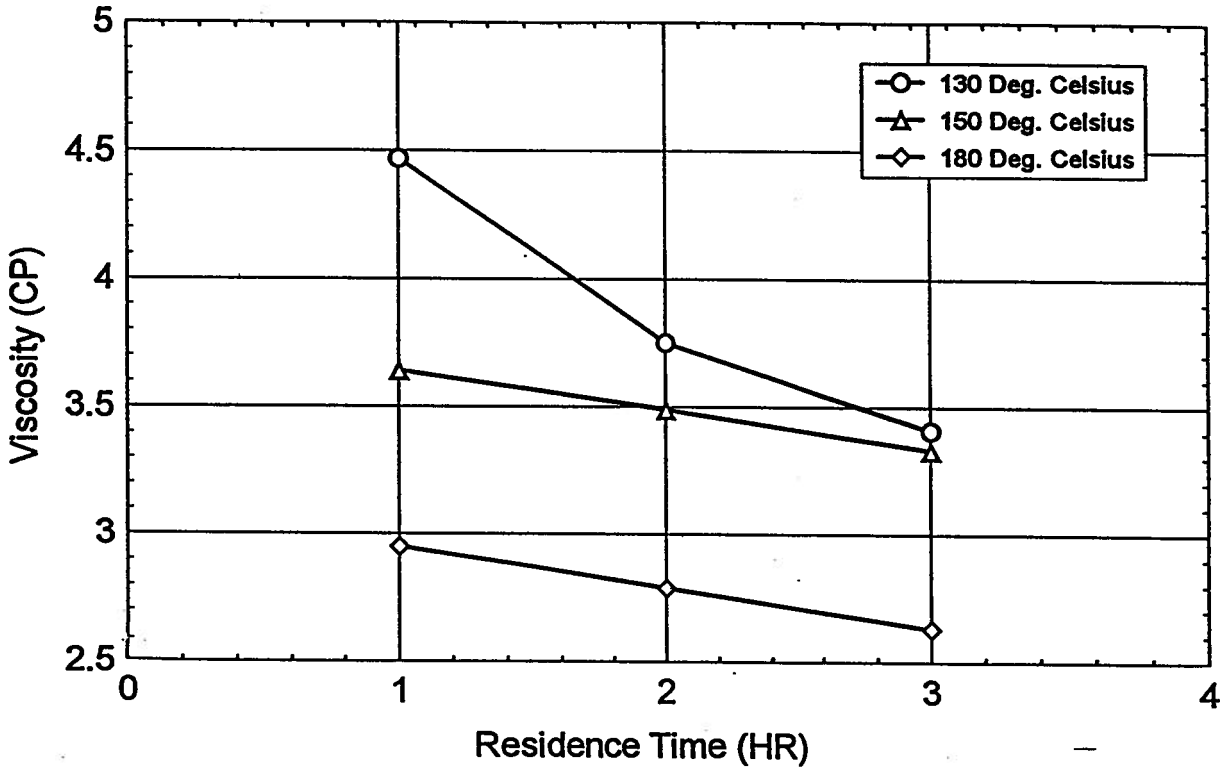


Figure 4.1.7.7. Effect of residence time on viscosity of cotton residues when HCl was used as catalyst in aqueous acetone (acetone:water: 90:10; liquor/solid ratio: 10/1; 0.16 N HCl).

The time factor is shown to have a lesser effect on drop in viscosity (DP) especially at the higher (150 and 180 ^{o}C) temperatures following the initial solvent purification treatment when all other parameters were kept constant (solvent composition, temperature, liquor/solid ratio, and acidity). The reduced rate of viscosity loss can be explained by the fact a- the limiting DP has been reached and b- that the stereochemistry of isopropylidenated sugar units may bring about, more or less, the some effect on the adjacent molecules. This has implications on more H-bond disruption/destruction allowing the more accessible cellulose units to undergo rapid isopropylidenation and hydrolysis reactions.

5 OVERALL MECHANISM OF PURIFICATION OF CELLULOSE IN ACIDIFIED AQUEOUS ACETONE

The mechanism of cellulose purification in acid catalyzed aqueous acetone has been proposed to be of a physico-chemical character. The physical phenomenon is based on the hydrogen bond disruption/destruction in crystalline cellulose by acetone as the solvent. On the other hand, the chemical hypothesis of the mechanism is suggested to be the formation of isopropylidene groups on carbohydrate chains that lead to disproportionation of the polymer and protection of the dissolved sugar ring. To investigate the validity of these assumptions cotton has been used throughout this work as a model compound, i.e., it consists of glucose units only. Nonetheless, trace amount of other substances were reported to be a part of its constituents (see section 4.1.3, HPLC Analysis).

The mechanistic study carried out by employing different techniques, on solvent purification of cotton using acetone in the presence of acid catalyst has established the following findings:

1- interaction of acetone with cellulose molecules through their hydroxyl groups brings about irreversible attenuation in hydrogen bonding of the cellulosic material (Fig. 4.1.2.1). This suggests that the hydroxyls of the cellulose have adopted new orientations (i.e., stereochemical changes)

as the result of acetonation. These structural changes have disrupted both the inter- and intramolecular H-bonds of the material, i.e., amorphous and crystalline regions (Figs. 4.1.5.1, 4.1.5.2, and 4.1.5.3). In addition, the changes in crystallinity index (increase) and crystallite size (decrease) (see Table 4.1.4.1) confirm that the acetonation of cellulose is achieved by intramicellar swelling.

2- the systematic increase in accessibility of cellulose with the increase of acetone concentration is linearly correlated with the subsequent increase in crystallinity index and decrease in crystallite size. This indicates a high degree of specificity is attained in removal of amorphous cellulose during the solvent purification treatment (see Fig. 4.1.2.1 and Table 4.1.5.1).

3- by using acid catalyzed aqueous acetone in solvent purification of cellulose both large amounts of acetonated reducing and nonreducing sugars were found in the hydrolysate. Two of the isopropylidene derivatives of sugars (different isomers) were identified as 1,2:5,6-diacetal glucofuranose and 1,2:3,4-diacetal galactopyranose (Figs. 4.1.3.5 and 4.1.3.6).

4- In a similar manner the deacetonated solvent purified cotton hydrolysate has offered a considerable quantity of simple sugars (epimers) such as glucose and galactose (Fig. 4.1.3.2.5).

5- the quantitative analysis of the reducing sugars in the cotton hydrolysate has shown that the predominance of

deacetonated sugar products is to be as high as 86.33% of the weight loss (Table 4.1.3.2.1).

6- the treatment at high temperatures (180 ^{o}C) has brought about significant removal of sugars (i.e., weight loss went up to 42.3% of the original cotton). This is explicitly illustrated in Fig. 4.1.3.2.3.3.

7- the structural investigation of the residual cotton, using C-13 CP/MAS solid state NMR, has confirmed the formation of isopropylidene groups on the sugar rings in the cellulose chain or chain ends. However, the quantitative analysis conducted in this regard has shown that only small amounts of isopropylidene groups remain in the residual cellulose (i.e., at the reducing and nonreducing terminals), (see section 4.1.4 and Figs. 4.1.4.3a and 4.1.4.3b). In other words, one isopropylidene group is fond per 400-500 cellulose units at the treatment; acetone:water: 90:10; liquor/solid ratio: 10/1; 2 hr; 0.16 N HCl; 150 ^{o}C).

8- C-13 CP/MAS solid state NMR spectrum has confirmed that the adsorbed amount of acetone by cellulose is too small for the unreactive solvent in comparison to that consumed on the formation of methyl groups.

9- by using acid as catalyst for aqueous acetone in solvent purification of cellulose, the viscosity of the treated material drops dramatically as shown in Fig. 4.1.7.3. This can be explained by the disproportionation of the fibres due to the formation of isopropylidene groups between adjacent cellulose units at regular intervals along the cellulose

chains. CuEn viscosity is decreased with the increase of temperature in the presence of the acid catalysts, as illustrated in Figs. 4.1.7.4 and 4.1.7.5 (from 28.5 to 2.7 CP). Similar trends are also observed for the molecular weight distributions of the solvent purified cotton residues. The treatment has offered uniform (symmetrical) molecular weight distrbutions (see Figs. 4.1.6.3 and 4.1.6.4 and Tables 4.1.6.3 and 4.1.6.4) which would be preferred for the dissolving pulp manufacture if the weight losses and decrease in viscosity could be suppressed.

The results of the present work, support the following mechanism of cellulose acetonation as illustrated in Fig. 5.1. below:

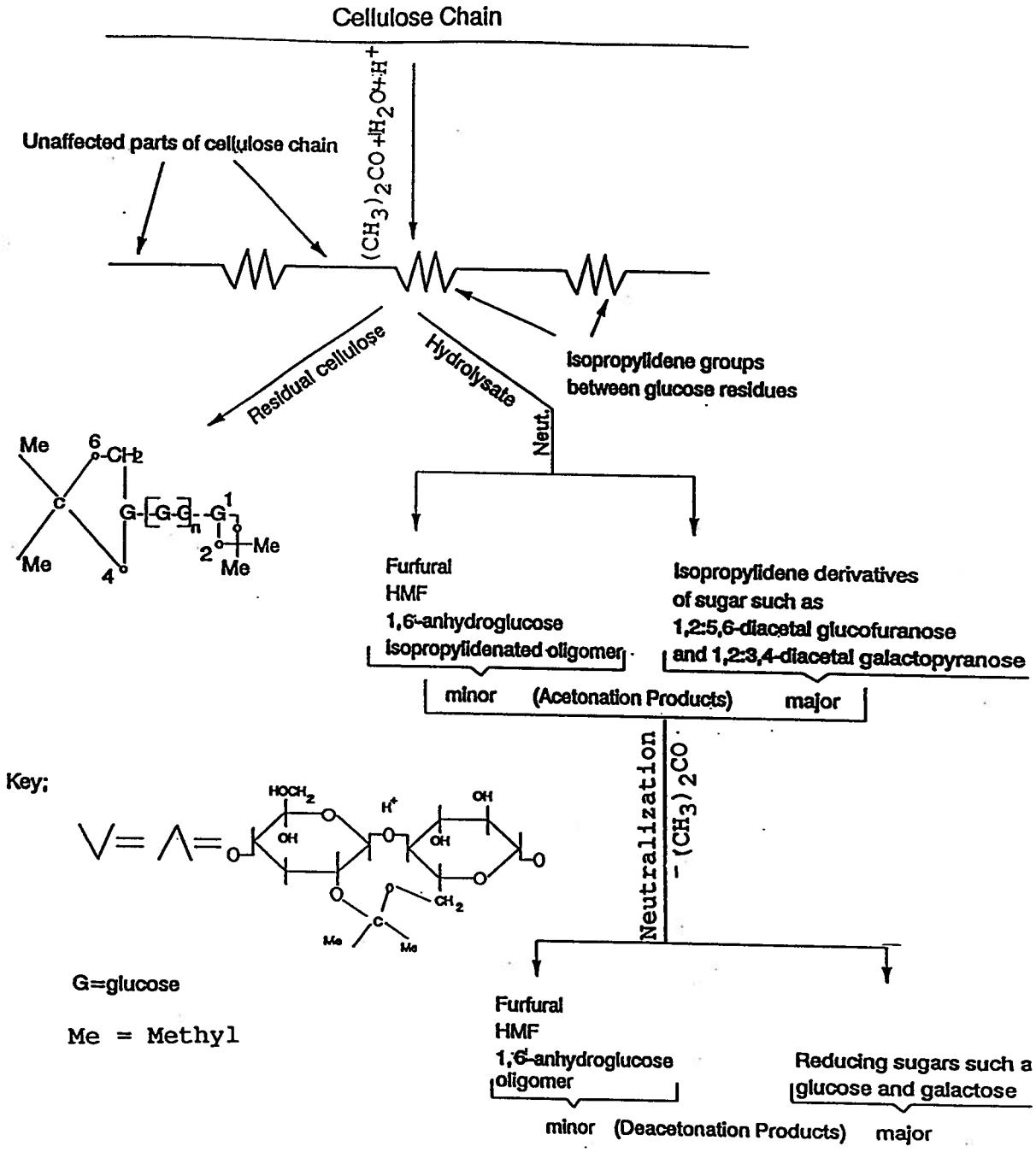


Figure 5.1. Mechanism of purification of cellulose in acidified aqueous acetone at higher temperatures.

6 SUMMARY

A detailed study on the mechanism of purification of cellulose in acidified aqueous acetone was carried out. The mechanism has been found to be of a physico-chemical character. The physical phenomenon has been verified to be based on the hydrogen bond disruption/destruction by the interaction of acetone with the cellulose (amorphous and crystalline). This action has resulted in irreversible changes in hydrogen bonding (weaker H-bonds), crystallinity (enhanced), and crystallite size (decreased). These changes are explicitly illustrated in Results and Discussion (chapter 4), section 4.1.2 and 4.1.5. The chemical hypothesis of the mechanism has been proved to be the formation of isopropylidene groups on carbohydrate chains that lead to disproportionation of the polymer and protection of the monomer sugar ring thus formed. The quantitative analysis conducted on the hydrolysate has indicated that the isopropylidene derivatives of sugar were the predominent product of the dissolved material. These experimental findings are demonstrated in Results and Discussion (chapter 4), section 4.1.3, 4.1.4, 4.1.6, and 4.1.7. For the investigation of the validity of these assumptions cotton was used throughout this work as a model compound, and different techniques (DRIFT, GC, HPLC, C-13 CP/MAS solid state NMR, X-ray Diffraction, GPC, and Viscosity) were employed.

Factors affecting solvent treatment such as acetone concentration, residence time, temperature, type of acid catalyst and acid concentration were also investigated. It is noteworthy to mention that the investigation of the factors was conducted in a manner that helped elucidation of the acetonation mechanism rather than optimization of the process. Elucidation and characterization of the purification mechanism was the main objective of this work. Parametric contributions to the mechanism of the process are as follows:

Acetone Concentration

The increase of acetone concentration was found to be associated with a significant systematic increase in absorbance height of OH stretching, i.e., provision of weak H-bonds (Fig. 4.1.2.1). In other words, the accessibility of cellulose was progressively increased with the increase of acetone concentration.

The weight loss was increased consecutively with the increase of acetone concentration (Fig. 4.1.3.2.3.1).

In crystallinity, the successive increase of acetone concentration was found to give rise to a systematic increase in crystallinity index, and decrease in crystallite size (Table 4.1.5.1). A confirmatory trend of acetone concentration was also shown by the viscosity results (Fig. 4.1.7.1).

Type of Acid Catalyst

Two acid catalysts were used in this study; TFA (organic), and HCl (mineral). The effect of the type of acid catalyst, on hydrogen bonding, hydrolysis (i.e., deacetonated sugar products and weight loss), crystallinity, molecular weight distribution, and viscosity, was examined. This was observed to be dependent on the molecular structure and properties of the acid (i.e., protic, ionizing power, nucleophilicity etc.). This is explicitly illustrated in various figures and tables of chapter 4 (Results and Discussion). HCl was found to be more effective than TFA in many different ways illustrated in chapter 4 (Results and Discussion).

Acid Concentration

The effect of acid concentration on hydrogen bonding, hydrolysis, crystallinity, molecular weight distribution and viscosity was found to depend upon the type of acid catalyst, i.e., it is dependent on molecular structure and the properties of the catalyst. This is indicated throughout the whole text of chapter 4 (Results and Discussion). However, it is important to note that the results illustrated in this work have shown that higher concentrations of TFA are effective but milder in the

hydrolysis reactions (i.e., minimum dehydration products), while those of HCl are detrimental and "aggressive" to the quality (DP) and quantity (yield) of the product, see Figs. 4.1.3.2.10 and 4.1.3.2.11.

Temperature

Different temperatures were applied in this work (130, 150, and 180 ^{o}C). From the experiments on hydrogen bonding, hydrolysis, crystallinity, molecular weight distribution, and viscosity it was apparent that temperature has a significant influence on the quality (DP) and quantity (yield) of the treated cellulosic material during solvent treatment. These results were shown in many figures and tables in chapter 4 (Results and Discussion), see Figs. 4.1.2.4, and 5, 4.1.3.2.3.2, and 3, and Tables 4.1.5.4, 4.1.6.3 and 4.

Residence Time

The effect of the reaction time, on different characteristics of the cellulosic material during solvent treatment, was investigated at different periods of time. The effect of residence time on hydrogen bonding, hydrolysis, crystallinity, molecular weight distribution, and viscosity was noticed to provide chances for better solvent-solute solvation conditions. However, the extent of

strength of the hydrogen bond with increase in reaction time was found to be dependent on the solvent and solute properties (Figs. 4.1.2.6 and 4.1.2.7).

Furthermore, the time factor was shown to have a lesser effect on the carbohydrate removal (weight loss) and drop in viscosity (DP) after the initial solvent purification treatment when other parameters were kept constant (i.e., temperature, solvent composition and acidity), see Figs. 4.1.3.2.3.4, 4.1.3.2.3.5, 4.1.7.6, and 4.1.7.7 and Tables 4.1.5.5, 4.1.5.6, and 4.1.6.5.

In summary, solvent purification of cellulose in the presence of an acid catalyst is a complex phenomena largely depending on the solvent concentration (acetone), the catalyst concentration (H^+) and type as well as the temperature and residence (reaction) time. At high solvent {acetone} concentration hydrogen bond disruption even in the crystalline domains of cellulose can be observed which is accompanied by formation of ketals in the solid phase followed by disproportionation or chain breaking (i.e., reduced DP). Solvent treatment does lead to physical purification whereby the crystallite size becomes more uniform especially as the limiting (leveling off) DP of the cellulose is approached. Substantially the same effects can be observed with a weaker organic acid, such as trifluoroacetic acid, however at much less destructive levels.

7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

1. The solvent purification treatment has brought about, within the residual cotton, significant, irreversible H-bond rearrangement that seems to cause permanent weakness (disruption) in the hydrogen bonding system. This irreversible hydrogen bonding rearrangement, as result of acetonation, confirms the reorientation (i.e., stereochemical changes) of hydroxyls of the cellulose molecules.

2. The systematic increase in absorbance height of OH stretching with the increase of acetone concentration is due to the increased interaction of acetone (HBA) with cellulose (HBD), i.e., provision of weak (nonlinear) hydrogen bonds.

3. The accessibility of cellulose is increased during the solvent purification treatment due to the interaction of acetone with cellulose molecules through their hydroxyl groups by provision of weaker hydrogen bonds.

4. The effect of the acid catalyst and concentration on hydrogen bonding are dependent on the molecular structure (i.e., type of atoms in the molecule) and properties of the acid (i.e., protic, ionizing power, and nucleophilicity).

5. Temperature has a significant influence on the hydrogen bonding of the cellulose during solvent purification treatment. This is explained by the better solvent penetration, and freer and faster reorientation of the molecules (i.e., increase of the reaction rate).

6. The effect of residence time on hydrogen bonding of the cellulose is explained by a provision of chances for better solvent-solute solvation conditions. However, the extent of strength or weakness of the hydrogen bond with increase in reaction time is dependent on the solvent and solute properties.

7. Acetonation of cotton provides for a remarkable stereochemical versatility. In other words, much is characterized by isomerization and interconversion reactions of glucose obtained on isopropylidenation of cotton cellulose.

8. The products of isopropylidene derivatives of sugars, such as 1,2:5,6-diacetal glucofuranose and 1,2:3,4-diacetal galactopyranose, resulting from acetonation of cotton, confirm that isomerization has led to the establishment of a dynamic equilibrium.

9. The identified diacetals (i.e., 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose and 1,2:3,4-di-O-

isopropylidene-α-D-galactopyranose) illustrate explicitly that isomerization has occurred in three forms of all sugars, i.e., constitutional, conformational and configurational.

10. The isomers of nonreducing sugars are fewer in number than those of the reducing sugar type. This is attributable to the difference in stability of the various isomers.

11. It is of significance, however, that isopropylidene derivatives of glucose have survived the high temperature hydrolysis conditions of cellulose even in the presence of water.

12. The removal of isopropylidene groups by hydrolysis and deacetonation under different treatment conditions (i.e., type of acid catalyst, temperature, and reaction time) resulted in a provision of different sugar isomers (epimers) in the hydrolysate.

13. It is evident that glucose has remained the major reducing sugar in the hydrolysate among the other epimers resulting from the removal of acetone.

14. 1,6-anhydroglucose, furfural, and hydroxymethylfurfural are minor by-products of the solvent purification treatment.

15. Although the sugar ring has some protection by isopropylidene formed during solvent purification treatment, high temperature exposure for prolonged time increases the chances of dehydration products (i.e., hydroxymethylfurfural).

16. From both primary (about 40%) and secondary (46%) hydrolyses the acetonation sugar products are the predominant part (86.33%) of the soluble hydrolyzed cellulose.

17. The successive increase of acetone concentration in the solvent composition (acetone-water) has been found to give rise to a systematic increase in weight loss.

18. The increase of temperature, while other factors are kept constant (i.e., acid concentration, residence time, and acetone content), has led to a significant increase in the weight loss of the cellulose.

19. The time factor is found to have a lesser effect on carbohydrate (weight) loss after the initial solvent purification treatment when other parameters are kept constant.

20. The weight loss of the cellulosic material has increased significantly with the increase of acid concentration of the different types of acid catalysts.

21. The greater increase (4.9% vs 33.5%) in the weight loss of solvent purified cellulose has been attained by the use of HCl rather than TFA as the acid catalyst.

22. The spectrum of C-13 CP/MAS NMR of the residual cotton solids after treatment with normal acetone, does not give chemical shifts in the methyl group region.

23. The C-13 CP/MAS solid state NMR spectrum of the residual cotton treated with C-13 labeled acetone has given two methyl groups at 26.5 and 31.8 ppm, respectively.

24. There is only one isopropylidene group per every 400-500 cellulose units of solvent purified cotton treated at 150 ^{o}C (acetone:water: 90:10; liqour/solid ratio: 10/1; 2 hr; 0.16 N HCl).

25. Most of isopropylidene derivatives of sugars formed during acetonation of cotton are rapidly solublized in the hydrolysate.

26. Disproportionation of the cellulose chains is the result of removal of isopropylidene derivatives of sugars in the solution during the hydrolysis reactions.

27. The process of the removal of isopropylidene derivatives of sugars in the solution offers residual cellulose with short chains isopropylidenated at the reducing and non-reducing terminals.

28. The isopropylidene derivatives of sugars formed in the residual cotton are monoacetals of pyranoid sugar structure, i.e., 1,2-O-isopropylidene-α-D-glucofuranose and 4,6-O-isopropylidene-D-glucopyranose.

29. The solvent purification treatment (i.e., acetone-water) of celluose has increased the intensities of 101, $10\bar{1}$, and 002 planes.

30. The successive increase in acetone concentration has resulted in a systematic increase of the crystallinity index of the cotton residues.

31. The increase of acetone content in solvent purification liquor of cotton cellulose has led to a systematic decrease in crystallite size of the residues.

32. With the increase of acetone concentration in the solvent composition, the accessibility of cellulose is progressively increased, i.e., weaker hydrogen bonds.

33. The systematic increase in accessibility of cellulose with the increase of acetone concentration is linearly correlated to successive increase in crystallinity index and decrease in crystallite size in acetonation treatment.

34. Catalyst and acidity in solvent purification treatment have no direct effect on crystalline changes. However, their involvement in the shaping of crystallinity and crystallite size can be used in determining how much they contribute to the accessibility of the cellulose, and the selectivity of the removal of the amorphous cellulose.

35. Temperature has a remarkable effect on the reaction rate of the solvent purification treatment. In turn, this would lead to considerable stereochemical changes, which affect both crystallinity and crystallite size.

36. Residence time contributes to crystallinity and crystallite size by provision of chances for further stereochemical changes, i.e., structral alterations.

37. Depolymerization of the cellulose (cotton), which has taken place in the unacidified acetone-water mixture (i.e.,

no catalyst added), is largely due to the mutual action of the acetone/water complex, resulted from the reaction of water molecules with the acetone at a higher temperature, and the acids from the pectic substances in cotton cellulose.

38. The increase in acid concentration, in general, has offered higher proportions of low molecular weight fractions of cotton residues in the solvent purification treatment.

39. Increase of temperature has led to production of shorter cellulose chains on acetonation of cellulose.

40. The molecular weight distribution (MWD) curves have shown shifts towards the low molecular weight distribution region with the increase in residence time.

41. The disproportionation of the cellulose chain, resulting from the increase of a parameter such as acid concentration, temperature, and residence time is usually accompanied with formation of narrower polydispersities in acetonation, i.e., more uniform molecular weight distribution.

42. The progressive increase in acetone concentration in the solvent purification treatment affords a significant systematic decrease of the degree of polymerization (DP) of

the cellulose. The drop in DP may be too severe for the purpose of dissolving pulp manufacturing.

43. Cellulose viscosity dropped dramatically (significantly) when acetone in the presence of acid catalyst has been used in high temperature solvent purification treatment of cotton.

44. Temperature has a significant effect on the residual viscosity of cotton residues following the solvent purification treatment.

45. The time factor has little (insignificant) contribution to the drop of viscosity (DP) after the initial solvent purification treatment when temperature, liquor/solid ratio, and acidity are kept constant.

7.2 Recommendations

1. Further studies on the mechanism of acetonation on other pulp components, such as xylans and lignin would be of importance.

2. Investigations should be carried out on the optimization of the solvent purification treatment for the attainment of high-yield dissolving pulp with characteristics similar to those recommended by the standards. Such process efficiency is expected to bring about significant impact on the economic feasibility of dissolving pulp manufacturing, as well as biomass conversion to liquid fuels without the need of involving higher efficiency biological agents such as enzymes in the cellulose conversion process.

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