

THE BEHAVIOUR OF WOOD CARBOHYDRATES IN TECHNICAL PULPING PROCESSES*

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INTRODUCTION

The predominant carbohydrate polymer in wood is cellulose and, irrespective of whether it is isolated from a softwood or a hardwood, it is very similar in chemical and physical properties¹. It contains both amorphous and crystalline areas and has a degree of polymerization in the range of 5,000 to 10,000. Cellulose comprises approximately 40 to 50 per cent of the weight of the tree^{2,3}. The hemicelluloses rank second to cellulose as the most abundant naturally occurring organic material and are mainly associated with the cell wall, although minor quantities of hemicellulosic and pectic material and other water-soluble carbohydrate polymers occur in the middle lamella². The hemicelluloses, which comprise 20 to 35 per cent of the wood weight, have been considered as amorphous materials of low degree of polymerization (50 to 200) interspersed primarily in the cell walls. Isolated hemicelluloses have been obtained in crystalline form, and recent results based on a study of delignified wood sections indicate an orientation of these polymers in the cell structure⁴. Thus, the hemicelluloses, or some members of this family of polysaccharides, may exist with both amorphous and crystalline areas. Lignin, which exists mainly in the middle lamella and to a lesser degree in the cell wall, occurs to an extent of about 17 to 25 per cent in most hardwoods and about 25 to 32 per cent in the softwoods. The lignin from hardwoods has a higher methoxyl content (20 to 22 per cent) than softwood lignin (14 to 16 per cent). The so-called "extractives" differ markedly in amount and nature in both softwoods and hardwoods. The average extractive content of wood is in the order of 2 to 8 per cent. These "minor" constituents are frequently of prime importance in determining the ultimate properties and end uses of the wood itself.

The common sugar and sugar acid constituents present in wood belong to the D-series with the exception of L-arabinose, L-fucose, and L-rhamnose. Cellulose and the glucomannans are joined predominantly, if not exclusively, by β -glycosidic bonds. The xylose family of polymers contains a β -linked backbone of anhydroxylose units to which are attached, in nearly all instances, an occasional 4-O-methyl-D-glucuronic acid unit by an α -glycosidic bond. Certain members of this family contain, in addition to the occasional above-mentioned uronic acid, an infrequent arabofuranose unit linked by glycosidic bonds of unknown configuration. There is some

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indirect evidence that this bond may be of the β -configuration⁵. The galactoglucomannans, arabogalactans, other galactose-containing polymers, and the complex "extracellular" polysaccharides of the middle lamella contain even more complex arrangements involving both α - and β -glycosidic bonds. Starch and pectin are each joined predominantly by bonds of α -configuration.

In the case of hardwoods, the average hemicellulose content is 20 to 35 per cent, the main constituent being D-xylose. Softwoods, on the other hand, average 20 to 30 per cent hemicellulose, the main constituent of which is D-mannose, with smaller amounts of D-xylose. The major xylose-containing polymer in softwoods is the 4-O-methylglucuronoaraboxytan which has a lower ratio of D-xylose to 4-O-methyl-D-glucuronic acid (about 6 to 1) than the predominant 4-O-methylglucuronoxylan type of polymer of hardwoods (about 10 to 1)².

It should be emphasized that each family of wood polysaccharides undoubtedly exists as a spectrum of closely related polymers differing subtly in degree of polymerization, degree of branching (if branched), ratio of constituent sugars in the case of heteropolymers, and in many other properties.

The polymeric carbohydrate fraction of a tree accounts for approximately 60 to 75 per cent by weight of the wood. It is these materials, especially the cellulose portion, which are desired in the highest possible yield and in the least degraded form from the technical delignification processes commonly termed "pulping".

The action of technical pulping processes on the above complex carbohydrate polymeric systems is widely varied and is dependent upon many factors⁶. The pH, temperature, time, chemical concentrations of liquors, the nature of the constituent building blocks of the polysaccharide, the carbon atoms involved in the glycosidic linkage, the configuration of the glycosidic bond, the presence or absence of side chains, the degree of substitution and location of acyl groups (formyl, acetyl), the polarity of the polymers, the position, type, location, and amount of the uronic acid and the degree of polymerization are some of the more important parameters and properties which contribute to the type and amount of degradation.

The purpose of this paper is to discuss the behaviour of cellulose and the various hemicelluloses during technical delignification processes. Because of the many excellent books and papers describing the various pulping methods^{7,8} no details on these processes will be given in this paper.

THE TECHNICAL PULPING PROCESSES

Chemical pulping may be defined as the treatment (cooking) of wood with chemical reagents to a point where fibres can be easily separated from each other (*i.e.*, pulped). The cooking process is often described as delignification; however, there is a small amount of lignin or lignin-like material remaining with the fibres (pulp). A large amount of carbohydrate material is dissolved with the lignin and some is destroyed during the pulping procedure. In most instances nearly all of the "extractives" are removed during this stage.

The two main pulping processes which are currently being used to produce

nearly all of the pulp in the world today are the highly acid sulphite process and the strongly alkaline kraft process. Many other processes, such as soda pulping, various two-stage sulphite modifications, neutral sulphite semichemical, and partial sulphite-kraft and *vice versa*, to mention but a few of the possibilities, are also currently being used in industry, but at the present time they produce a small percentage of the total tonnage of pulp.

In order to obtain pulps of high yield and high strength with the best over-all papermaking properties, pulping conditions modified from the present normal sulphite and kraft-type processes are required. Those hemicelluloses which confer upon a wood cellulose the most desirable properties for a specific end use must be retained rather than dissolved and destroyed (for the most part) as in the present delignification processes. As wood supplies become more scarce and competition in world markets increases, the various subtleties that are evident in wood celluloses produced from modified pulping conditions, especially where pH changes are involved, will become much more important and more economically feasible.

Historically, the sulphite pulping industry is based on the use of calcium bisulphite and sulphur dioxide ("combined acid plus free acid"). This was followed by ammonium base pulping and still later by the use of magnesium for the base. The present trend is toward the use of the soluble base pulping processes. The temperatures of the digestions in the above-mentioned processes are about 120 to 150°. The pH is in the range of 1 to 2. In this process the lignin is made soluble by sulphonation, giving rise to lignosulphonic acids. Modifications of this process in which cooking liquors having pH's ranging from 2 to 4.5-5 are also commercially employed. The economic success of the magnesium and sodium systems is contingent upon satisfactory recovery systems. The future of the sulphite industry looks very bright indeed from the point of view of soda base pulping over a wide range of pH.

The second of the two main processes currently employed is termed the sulphate or kraft process. The kraft process is an improvement on the older soda process which employs sodium hydroxide as the cooking chemical. The addition of sodium sulphide to a soda-type cooking liquor and the carrying out of the digestion at temperatures in the range of 150 to 175° (conventional kraft process) facilitates preferential lignin removal by the formation of low molecular weight thiolignins and thus decreases the fibre damage. Consequently, the lesser damaged kraft pulps produce stronger pulps than does the soda or sulphite process. The soda process, however, actually preceded the sulphite and kraft processes.

Wood celluloses (cellulose plus hemicelluloses) of varying degrees of refinement may be prepared by delignification processes in which the pH level ranges from the values of 1 to 2 for the sulphite process (and other acid processes, some of which are below pH 1) through *various intermediate levels and combinations thereof* (e.g., two stage sulphite, neutral sulphite semichemical, Sivola type), to the values of 12 to 13 for the kraft process. These wood celluloses, even when derived from the same wood, differ quite markedly in most instances in chemical and physical properties and in chemical composition. These differences are the result of characteristic degradative effects which occur during the delignification processes. Some

of these differences are probably due to subtle changes in the cellulose itself and to the presence of varying amounts of short chain glucans (β -cellulose). *The main differences in the wood celluloses, however, are due to changes in the structure, composition, degree of polymerization, solubility, yield, and the location of the hemicellulose components. The properties of the various hemicelluloses and their effect, individually and collectively, upon the ultimate end-use properties of the pulp has not been given the consideration it deserves. Certain types of hemicellulose have a much greater effect on the final properties of a pulp than other types of hemicellulose.* This is true whether the pulp was originally made for the dissolving industry (acetate, viscose) or whether it was specifically tailored for the paper industry. The latter pulps are obtained in higher yield and retain, or should retain, large amounts of certain of the hemicelluloses.

A comparison of the carbohydrate analyses of typical pulps prepared from western hemlock wood is given in *Table 1*. It is similar to those that have already appeared in the literature⁶. A detailed description of the carbohydrate composition of sulphite, kraft, and other pulps has been given by Hamilton, Partlow and Thompson⁹, and also by Jorgensen¹⁰.

Table 1. A comparison of the carbohydrate contents of the residues obtained from western hemlock wood by various pulping processes

	Acid sulphite	Bisulphite	Chlorine dioxide holocellulose	Modified kraft	Conventional kraft	Prehydrolyzed kraft
Galactose (%)†	0*	0*	4.6	0.6	0.6	0*
Mannose (%)†	8.1	9.8	20.3	8.1	9.3	1.6
Arabinose (%)†	0	0	1.0	0.5	0.5	0
Xylose (%)†	2.2	3.2	4.7	4.7	5.7	1.1
Rhamnose‡	0	0	P	0	0	0
4-O-Methylglucuronic acid§	P	P	P	P	0	0
Galacturonic acid§	0	0	P	0	0	0
pH	1-1.5	2.5-4.0	7-8	10-11	12-13	(3-4) 12-13
Temperature(°C)	130-150	150-170	25	160-175	160-175	150-180 160-170
Carbohydrate yield (%)‡	47	46	65	42	42	35
Cellulose yield (%)‡	41	38	43	35	34	34

*Trace amounts noted.

†Based on oven dry residue.

‡As determined by paper partition chromatography.

P = Present.

§Based on oven dry wood; corrected for lignin and alcohol-benzene extract.

The carbohydrate content of the chlorine dioxide holocellulose of western hemlock may be considered to be a close approximation to that of the actual carbohydrate portion of western hemlock wood. Also included are the analyses of the sulphite, conventional kraft, and prehydrolyzed kraft pulps of western hemlock, as well as a modified sulphite (pH 3-4) and a modified kraft (pH 10-11). It is interesting to note the complete absence

of rhamnose and galacturonic acid from all pulps prepared by commercial techniques, the absence of galactose and arabinose from the sulphite pulp (although the former does occur in trace amounts) and the absence of 4-*O*-methylglucuronic acid, in nearly all kraft pulps. The prehydrolyzed kraft pulp lacks the acid-labile arabinose and contains only minute amounts of galactose. The mannose and xylose contents are appreciably lowered (as compared with conventional kraft pulps), and the alkali-labile 4-*O*-methylglucuronic acid is absent in nearly all prehydrolyzed kraft pulps. The reasons for these variations have been the subject of a number of investigations over the last few years⁶.

Under sulphite pulping conditions the main sugars generally appear in the liquor in the following order: arabinose, galactose, xylose, mannose, and glucose¹¹. The order of appearance can vary with the actual pulping conditions employed.

For convenience, the behaviour during pulping of each of the more common wood polysaccharides will be treated separately.

THE BEHAVIOUR OF CELLULOSE DURING TECHNICAL PULPING PROCESSES

Cellulose is a polydisperse polymer of high molecular weight comprised of long chains of *D*-glucose units joined together by β -1,4-glucosidic bonds. The possibility that a very small percentage of linkages other than β -1 \rightarrow 4 exists¹². The presence of trace amounts of sugars other than *D*-glucose linked by bonds other than β -1 \rightarrow 4 is not excluded, although if such sugars and linkages occur they exist to only a very minor extent. The cellulose microfibril chains exhibit a very strong tendency to assemble themselves in bundles or areas of lesser or greater degree of order. The lateral order distribution function takes into consideration the gradual transition from an area of complete order (inaccessible area or crystallite) to an area of complete disorder (accessible or so-called amorphous area). In addition to orientation within the fibrils, the fibrils themselves exhibit a regular orientation which frequently is different for each layer of the cell wall. The degree of orientation influences the mechanical properties of cellulose in certain of its end uses. The concepts of lateral order distribution and orientation allow the satisfactory correlation of the supermolecular structure and technical behaviour of cellulose¹³.

As has been mentioned previously, cellulose is the most important product obtained from a technical pulping process. It is desired in the highest possible yield and with the minimum amount of degradation. Unfortunately, however, in all present pulping processes, the cellulose is degraded in chain length and is modified, to a certain extent, in structure.

Under acidic pulping conditions, the disordered areas in the cellulose microfibril chains (amorphous areas) are more susceptible to attack and the cellulose chains are hydrolyzed preferentially in the amorphous areas with a resulting loss in degree of polymerization (and ultimately in yield^{3,8}). Damage of the wood chip during the chipping operation prior to entering the digester leads to more extensive damage (and yield loss) to the cellulose due to the fact that the cellulose microfibrils are exposed to the high temperature acid conditions for a longer period¹⁴. During the earlier period

of cooking the lignin protects the cellulose; however, in the case of excessive chip damage this early protection is lost. In general, the greatest loss in cellulose and in carbohydrate yield occurs during the latter part of the pulping process.

The delignification processes carried out at pH's in the range of 2.5-4.5, in order to be effective, require higher temperatures than do the normal acid sulphite processes (pH 1-1.5). This increase in temperature partially offsets the more moderate pH conditions, thus, although the conditions are not so acidic, considerable hydrolytic degradation takes place due to the higher temperature¹⁵. The total carbohydrate yield (cellulose plus hemicellulose), depending, of course, upon actual pulping conditions, is slightly less than for delignification processes carried out at lower temperatures and at pH's in the range of 1-1.5. The actual cellulose yield is also slightly lower.

If, in the cellulose molecule as it exists in nature, there are carboxyl groups, carbonyl groups, linkages other than β -1 \rightarrow 4 and sugars other than D-glucose, the attack of the cooking acid will not necessarily be random. This, in part, will be due to the electron-attracting ability of the carboxyl and carbonyl groups or due to the different conformation and stereochemistry of the anomalous sugars [*i.e.*, mannose, xylose (no C-6)]. In the case of carboxyl and carbonyl groups this results in a partial positive charge on the C-1 glycosidic oxygen which would repel the approach of the hydrated hydrogen ion, thus increasing the resistance of this bond toward acid hydrolysis^{6,16-18}. The increased rates of hydrolysis which have been observed in oxidized cellulose have also been explained by this same inductive effect operating through the C-4 position of the carbonyl-containing anhydro sugar unit.¹⁹

The behaviour that cellulose undergoes under alkaline conditions at elevated temperatures is markedly different to that observed under the acidic pulping conditions. At temperatures up to about 150° the main attack on the cellulose molecule is from the reducing end by a stepwise degradation. This stepwise degradation of the terminal reducing group proceeds *via* a β -alkoxy carbonyl elimination reaction. The major acidic components from such a system have been shown to be gluco-isosaccharinic acids, although considerable quantities of other acids containing a lesser number of carbon atoms also are present. The original mechanism was postulated by Isbell²⁰ and, with minor modifications, has been shown to be correct by extensive studies carried out at the British Rayon Research Association^{16,21}.

The end-group degradation of cellulose does not continue indefinitely. The cellulose becomes very resistant to further attack due to the occurrence of a so-called "termination" reaction. The curtailment of the end-group degradation is brought about by the formation of glucometasaccharinic acids (rather than gluco-isosaccharinic acids) as the terminal (formerly reducing) group¹⁶ (*Figure 1*). Some evidence has been presented indicating that other termination reactions (in addition to metasaccharinic acid) are also operative²².

The effect of the end-group degradation reaction on the weight average D.P. of the cellulose is not very great. The shorter chain cellulose frag-

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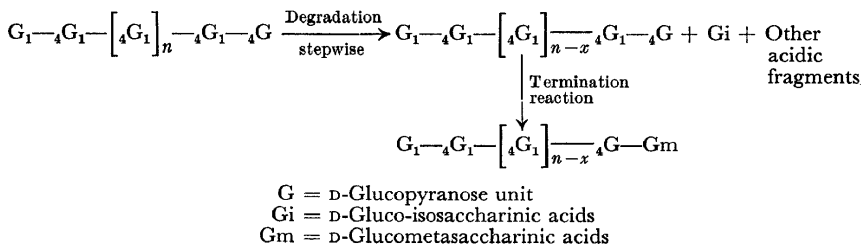


Figure 1

ments will be rapidly degraded to soluble fragments while higher D.P. material is reduced only by 40–50 D.P. units. At temperatures in the range of 150° a second type of degradation becomes important. This degradation is due to the cleavage of the glycosidic bonds by the hydroxyl ions. It has been indicated that reactions in alkaline media are similar at temperatures extending from 120–170°. However, as expected, the reaction velocities differ greatly. This cleavage naturally results in the formation of shorter fragments with reducing groups which, in turn, are degraded by the Isbell β-alkoxyl carbonyl reaction to acidic fragments.

The mechanism of alkaline hydrolysis is as yet unsolved. Evidence for the formation of anhydro sugars as intermediates in the alkaline hydrolysis of model compounds is being accumulated²³.

The temperatures which are used in most alkaline pulping processes are in the range of 140–180°. Thus the loss of carbohydrate material, by the above mechanisms, is considerable. Depending upon the pH, temperature, and time, the average D.P. of the cellulose is usually lower from an alkaline pulping process than from an acid pulping process. The chain length uniformity, however, is greater for the alkaline pulping process. The actual yield of cellulose is less from a kraft pulp than from a sulphite pulp. At similar lignin contents, the former will contain less total carbohydrate material, less cellulose, but more hemicellulose than the latter^{6,9,10}.

The above stepwise degradation, termination, and chain scission are the main reactions; however, other degradation reactions undoubtedly occur during alkaline pulping which also give rise to carboxyl groups and carbonyl groups at various positions in the chain. Prior reduction of the existing terminal reducing groups and reduction of such groups immediately upon their formation (due to alkali chain scission) would lead to greater recovery of the theoretical amount of cellulose from the tree²⁴.

THE BEHAVIOUR OF THE XYLOSE-TYPE HEMICELLOSES DURING TECHNICAL PULPING PROCESSES

The general behaviour of the xylose-containing hemicelluloses derived from coniferous and deciduous woods during various pulping procedures has been the subject of considerable investigation^{2,9,25,26}. Some of the properties of this family of polymers derived from various *pulps* prepared from western hemlock and western red alder are shown in *Table 2*⁶.

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Table 2. A comparison of the xylose-containing carbohydrates from a softwood and a hardwood

				Molar ratio of:—		
Source	Delignification technique	$[\alpha]_D^{23}$	Intrinsic viscosity*	Arabinose	Xylose	4-O-Methyl-D-glucuronic acid
Western hemlock	ClO ₂ holocellulose	- 54.5°	0.91	0.8	5.2	1.0
	Sulphite	- 61°	0.23	0	8.0	1.0
	Conventional kraft	- 105°	0.77	1.0	17.3	0
	Prehydrolyzed kraft	- 125°	0.33	0	100%	0
Western red alder	ClO ₂ holocellulose	- 72°	0.80	0	8	1
	Sulphite	- 78°	0.21	0	8	1
	Conventional kraft	- 108°	0.65	0	100%	0
	Prehydrolyzed kraft	- 110°	0.30	0	100%	0

* Measured in molar cupriethylenediamine hydroxide and expressed in decilitres per gram.

The main xylose polymer present in an alkaline extract of western hemlock holocellulose was shown to be a 4-O-methylglucurono-araboxyylan²⁷ and is represented by Figure 2. This same type of polymer is also present in southern pine⁹.

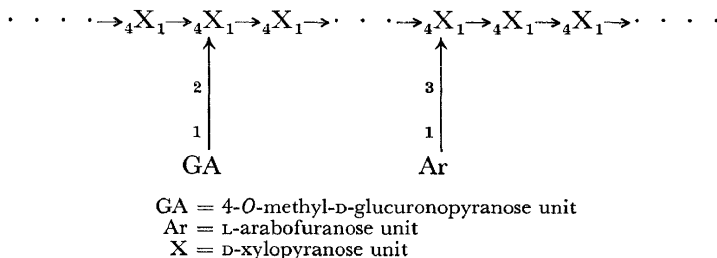


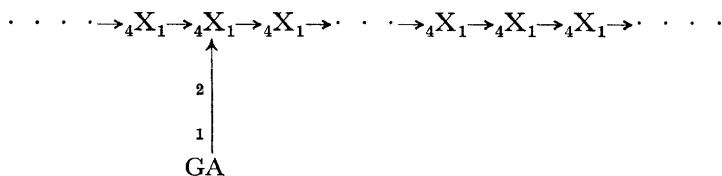
Figure 2

When xylose-containing polymers are extracted from a holocellulose with non-hydrolytic solvents, it has been found that they have a fairly high acetyl content. The acetyl groups were, for the most part, attached to the 3-position of the anhydroxylose units^{28,29}. Birch sulphite pulps have been reported to contain a partially acetylated 4-O-methylglucuronoxylan³⁰. Other work involving enzymatic hydrolysis of hemicellulose from Jack pine gave rise to a xylosidoglucose³¹. A complex glucoxytan has never been isolated previously; however, the spectrum of xylose-containing polymers may be broader than suspected.

After the sulphite cooks of western hemlock or southern pine, the only xylose polymer subsequently isolated was a 4-O-methylglucuronoxylan. The polymers in southern pine and western hemlock sulphite *pulps* were characterized by conventional methylation studies^{9,32}.

These results may be explained by the acidic hydrolytic conditions which occur during the sulphite cook. The acid-labile arabofuranose unit and most acetyl groups are cleaved from the 4-O-methylglucurono-araboxytan producing a 4-O-methylglucuronoxylan (Figure 3).

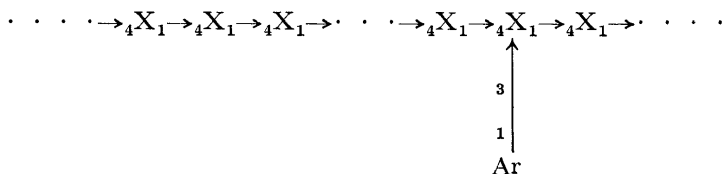
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GA = 4-O-methyl-D-glucuronopyranose unit
 X = D-xylopyranose unit

Figure 3

This reaction was verified by a model experiment using the actual isolated polymer from the holocellulose⁹. In addition, this artefact polymer is also degraded by acid hydrolysis to a much shorter chain length. This hydrolysis of the xylose-xylose glycosidic bonds is, of course, not random but is directed to the extent that the resistance of the glycosidic bond increases for those bonds closer to the uronic acid branch^{9,17}. It is assumed that the electron-attracting ability of the carboxyl group is transmitted through the pyranose oxygen of the ring to the glycosidic bond. This produces a partial positive charge on the glycosidic oxygen which would tend to repel the approach of the hydrated hydrogen ion.



Ar = L-arabofuranose unit
 X = D-xylopyranose unit

Figure 4

The conventional kraft *pulps* of western hemlock and southern pine wood have been shown to contain araboxylans⁹. The araboxylan which was isolated from the southern pine pulp was characterized by conventional chemical studies and is represented by Figure 4. When the readily soluble 4-O-methylglucurono-araboxylan of western hemlock *holocellulose* was subjected to a kraft cook for 1 hour at 160° a much less soluble polymer was isolated which was composed of arabinose and xylose⁶. This araboxylan was identical to the araboxylan isolated from the conventional kraft pulp. The prehydrolyzed kraft pulps of both southern pine and western hemlock were found to contain xylans. The xylan from the southern pine prehydrolyzed kraft pulp was characterized by conventional chemical techniques and found to have the structure represented by Figure 5⁹.

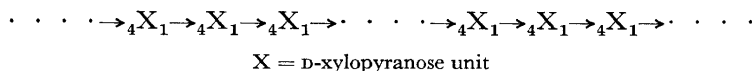


Figure 5

Hardwoods, such as western red alder, have been shown to contain 4-O-methylglucuronoxylans of high D.P. which are structurally similar to the 4-O-methylglucuronoxylan of the sulphite pulps of hemlock and

southern pine (*Figure 3*)². These polymers differ in the ratio of uronic acid to xylose present and also in the degree of polymerization. The glycosidic linkages involved in all these polymers are to all intents and purposes identical. This polymer from alder was converted to a short chain 4-*O*-methylglucuronoxylan (with very large losses) by the sulphite pulping procedure and to a xylan by both the conventional kraft and pre-hydrolyzed kraft pulping procedures. The xylan from the latter pulp is present in small amount and has a low D.P.

Initial studies on polymeric 4-*O*-methylglucuronoxylan indicated the selective removal of 4-*O*-methylglucuronic acid under alkaline cooking conditions. A time-temperature plot has been presented which denotes the points of complete uronic acid disappearance^{6,9}. More recent work^{33,34} has verified the original findings, but with some correction of the previously noted points of complete removal of 4-*O*-methyl-D-glucuronic acid. For example, traces of 4-*O*-methylglucuronic acid were still present after 30 minutes at 170°.

The actual mechanism of the uronic acid removal during the alkaline high temperature pulping processes is not clearly understood. Other mechanisms to explain this "uronic" acid removal are currently under investigation³³.

In kraft cooked pulp which has been prepared using an alkaline stage in the range of 165–180° most, if not all, of the uronic acid portions of the various polyuronides are destroyed^{6,9,35,36}. The pulp will, of course, have carboxyl groups present due to other degradation mechanisms.

In certain cases, particularly in some hardwoods, a small amount of 4-*O*-methylglucuronic acid is observed following the kraft digestion^{6,9,35}. This may perhaps be explained by the location of the hemicelluloses in the wood and lack of penetration of the alkali, due perhaps to too low an alkali concentration, too low a digesting temperature, or too short a time at temperature*.

It should also be noted that some of the arabofuranose residues are also removed by the high temperature alkaline digestions indicating the relative degree of stability at this 1→3 glycosidic bond.

As can be seen from *Table 2*, the D.P. of xylose-containing polymers as indicated by viscosity is much lower for the pulps prepared by acidic pulping conditions³⁷ or subjected to an acid stage prior to an alkaline delignification step. Some pulping processes carried out at intermediate pH levels give rise to xylose hemicelluloses of increasing D.P. approaching, in some cases, the D.P. of those obtained from holocellulose.

The adsorption (orientation, crystallization) of xylan polymers has been shown in kraft pulping³⁶. This may be related to the removal or partial

* Since this paper was completed (August 1, 1961) and presented, an article by Croon and Enstrom has been published³⁸ which confirms our findings on the importance of pH. Their ordinary sulphate cooks, which were carried out at pH's of 10.55 and 11.05, showed the presence of 4-*O*-methylglucuronoxylans. This is in agreement with the results presented in this paper where cooks carried out at pH of 10–11 showed the presence of 4-*O*-methylglucuronic acid, whereas conventional kraft cooks at pH's of 12–13 did not. (See *Table 1*.) The problem of what constitutes an "ordinary sulphate cook" or a "conventional kraft cook" is a problem of semantics; however, no such problem exists with respect to the effect of pH.

For more recent papers confirming the importance of pH in pulping see Refs. 59 and 60.

removal of (a) "uronic" acid, (b) removal or partial removal or translocation of acetyl groups, (c) removal or partial removal of the arabinose residues. *The extent of the above degradation, the D.P., and the location of the ultimate xylose-containing hemicellulose are also highly important.*

The presence of formyl and acetyl groups in wood celluloses has been recognized for some time³⁹. The presence of the acetyl groups on the native xylose-containing hemicellulose has been more recently disclosed and the position of the acetyl and the average degree of substitution has been determined in certain instances^{28,29}. The rôle which these groups play in the delignification of the wood has not been clearly demonstrated. The xylose hemicelluloses would be less hindered sterically by removal of the acetyl groups, and the adsorption by hydrogen bonds to one another, to other hemicelluloses, or to cellulose would probably be enhanced. Much more work must be done before this fascinating problem can be definitely solved.

THE BEHAVIOUR OF THE MANNOSE-CONTAINING HEMICELLULOSES DURING PULPING

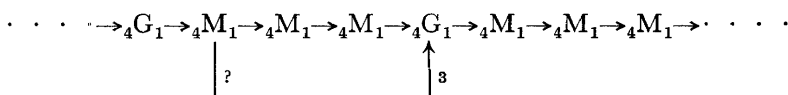
The mannose-containing polymers of conifers comprise approximately one-half to three-quarters of the total hemicellulosic material in the wood^{2,40,41}. In deciduous trees the mannose-containing polymers make up a very small percentage of the total hemicellulose^{2,42}. Although it was thought for some time that wood cellulose contained large amounts of mannose, it was shown, in 1956, that a very large percentage of the mannose in sulphite pulp occurred as a true diheteropolymer glucomannan⁴³. Further studies in 1957 showed that extraction of pulps or holocelluloses with high strength sodium hydroxide (about 10 per cent), in conjunction with mechanical action and slight acid hydrolysis, gave residues in high yield (about 30 per cent based on dry wood) of high degree of polymerization in which the total hemicellulosic material was reduced to less than 0.25 per cent for softwoods and less than 0.1 per cent for hardwoods (based on wood)^{2,44}. Rapson, in more recent studies, has shown even lower values for residual hemicelluloses⁴⁵. These results indicate that the residual extraction-resistant non-cellulosic cell wall polysaccharides, which remain associated with cellulose, as shown by hydrolysis (*i.e.*, mannose and xylose), are not part of the cellulose (except perhaps in trace amounts), but are much more probably due to inaccessible or highly insoluble polymers intimately associated with the cellulose microfibrils².

The mannose-containing polymers of conifers appear to be made up of at least two main families of polymers, the glucomannans and the galactoglucomannans^{2,6,9,46}. The possible presence of other polymers, such as a true mannan and galactomannan, is not excluded, although in general these polymers will probably not be present in large amounts^{2,40,44}. As a family of polymers or two closely related families, it is possible that the glucomannans vary not only within themselves in chain length and glucose-to-mannose ratio and sequence, but also contain varying amounts of galactose as a part of their structure⁴⁰. The number average molecular weight generally falls in the range of 70 to 130, although some depolymerization undoubtedly occurs in isolation. For the present it will be assumed that

both glucomannans and galactoglucomannans exist as separate but closely related families of polymers (with sub-families), each with its own spectrum of subtle changes in molecular architecture. These changes will have a variable effect on the physical and chemical properties of the polymers (*i.e.*, solubility, ability to orient, stability).

In certain instances polymers which are high in mannose, but contain also glucose and galactose, are most readily removed by low strength sodium hydroxide (below swelling strength) whereas, in most cases, extraction with high strength caustic (8–18 per cent) following lower strength extractions gives rise to polymers high in mannose and low in glucose (glucomannans with 1:3 or 1:4 ratio of glucose to mannose). In most instances, however, small amounts of galactose have also been shown to occur here as well as at lower caustic strengths⁴⁰. This follows the general rule that the more highly branched the polysaccharide, the greater will be its solubility.

As mentioned previously, the predominant sugar in hydrolyzed coniferous wood, apart from glucose, is mannose. Most of the mannose of softwoods is a part of the glucomannan and galactoglucomannan mixture in which the glucose:mannose ratio is approximately 1:3 or 1:4 (see *Figure 6*). Partial hydrolysis of the polymeric chain indicates that random distribution of the individual monosaccharide constituents is most probable, at least for the “backbone” portion of the polymers. Glucomannans have been isolated from a variety of conifers, as indicated in a recent review⁴⁷. Slightly different glucomannans having glucose:mannose ratios in the range of 1:1 to 1:2 have been isolated from western red alder² and other hardwoods⁴². Glucomannans have also been detected in western hemlock sulphite pulp and Norwegian spruce sulphite pulp. As with *all* polysaccharides isolated from pulps, the properties and structure are not necessarily the same as in the native wood. The majority of the glucomannans reported appear to be essentially linear or slightly branched polymers. In only a few instances has the position of the branch point been inferred⁴¹ or actually stated (position-3 of glucose)⁴⁸.



G = Glucopyranose unit
M = Mannopyranose unit

Figure 6

Table 3 lists the properties of the glucomannans which have been isolated from western hemlock and western red alder wood pulps. The persistence of the glucomannan in the sulphite pulp indicates a relative stability towards acid hydrolysis. Actual graded acid hydrolysis experiments suggest that the glucomannans are more resistant to acid hydrolysis than are the xylose-containing family of carbohydrates, although in certain instances the glucomannans appear to be more resistant to hydrolysis than cellulose³³. Glucomannans were also detected in the conventional kraft pulps of western hemlock and southern pine. Due to the properties of the araboxyylan contaminant, it is often difficult to obtain a pure glucomannan;

WOOD CARBOHYDRATES IN TECHNICAL PULPING PROCESSES

Table 3. A comparison of glucomannans of western hemlock and western red alder

Wood	Delignification technique	$[\alpha]_D^{23}$	Cuene I.V.	Molar ratio of:	
				Glucose	Mannose
Western hemlock	ClO ₂ holocellulose	- 35°	0.56	1	2.6
	Sulphite	- 37°	0.29	1	3.0
	Conventional kraft	*	—	1	2.5
Western red alder	ClO ₂ holocellulose	- 25°	—	2.0	3.0
	NSSC wood cellulose	- 32°	—	2.0	3.0

* This polymer was not pure but contained an araboxylan contaminant.

however, separation can be achieved by fractionating the glucomannan acetate of kraft pulps. Anomalous glucomannans have also been isolated from western hemlock sulphite pulp⁴¹.

The alkaline degradation of the predominantly straight chain 1→4 β-linked glucomannans is very similar to that of cellulose. Using model experiments and isolated glucomannans of markedly different intrinsic viscosities only about 15 to 20 per cent yield of the glucomannans was obtained following kraft cooks at 160°⁶.

During the alkaline pulping of glucomannans, the stepwise end-group degradation and termination reactions occur in conjunction with the high temperature chain scission reaction due to the hydroxyl ion. This is true both of the hardwood and softwood glucomannans. Reduction of the terminal end groups using sodium borohydride gives a higher carbohydrate yield as in the case of cellulose. The alkaline degradation of glucomannans is much more rapid than xylose-type hemicelluloses and seems to be more closely related to cellulose.

The presence of acetyl groups in wood has been mentioned previously and it is known that some of the acetyl groups are associated with the mannose-containing polymers^{25,49} (e.g., glucomannans, galactoglucomannans). Pulping in the presence of sodium borohydride³⁸ or by a two-stage process in which there is first a slightly alkaline pH followed by a lowering of the pH and completion of the cooking cycle, gave a much higher carbohydrate yield and nearly all of the increased yield could be accounted for in the increased amount of glucomannan associated with the pulp^{25,49}. Annergren and Rydholm^{25,49} theorize that this may be due to deacetylation which then enhances the opportunity for sorption of the glucomannan on the cellulose microfibrils. This stabilization of the glucomannan presumably results from the prevention (by adsorption and screening, complex formation) of the end-group β-alkoxycarbonyl degradation reaction. In the case of sodium borohydride-containing kraft cooks the fact that the amount of galactose does not increase proportionately is perhaps indicative of the existence of both glucomannans and galactoglucomannans.

It is interesting to note the marked stabilization of the glucomannan in comparison with the poor stabilization of the xylose hemicelluloses both in sodium borohydride pulping and in two-stage sulphite cooks (xylan content of the borohydride-reduced cooks was found to decrease.) The removal of some galactan residues may have an effect similar to, or perhaps

greater than, the removal of acetyl groups in allowing greater hydrogen bonding (as this results in less steric hindrance).

A number of workers have reported the probable presence of galactoglucomannans from a variety of sources. The following table, although by no means complete, indicates the specific rotation and sugar ratios of a number of galactoglucomannans from softwood holocelluloses (western hemlock) and three softwood conventional kraft pulps. The presence of a galactoglucomannan in wood was first demonstrated by Adams⁵⁰. Recently, Timell has reported the isolation of galactoglucomannans from a number of conifers⁴⁷.

Table 4. A comparison of the galactoglucomannans from various wood sources

Wood source	Delignification technique	[α] _D ²³	Molar ratio of:		
			Galactose	Glucose	Mannose
Western Hemlock	ClO ₂ holocellulose	-10°	0.8	1.5	5.0
	Conventional kraft	+2 to -2°	1.0	1.5	5.0
Southern Pine	Conventional kraft	+12.5°	1.2	1.0	3.0
Redwood	Conventional kraft	+17.5°	1.0	1.0	3.0

It is interesting to note that the specific rotation of the polysaccharides isolated from holocelluloses is levorotatory, whereas those from the pulps are dextrorotatory. This would indicate changes occur in the polymer during delignification.

The first characterization of such a triheteropolymer was carried out on the galactoglucomannan obtained from kraft wood cellulose produced from southern pine⁴⁶. Although a unique solution to the structure of this polymer is not possible on the basis of the data presented to date, a simplified structure consistent with the facts so far ascertained is shown below. It is understood that a mixture of a galactomannan and glucomannan would give similar results from methylation studies. All chemical methods failed to give any evidence of mixed polymers. Data by Timell⁴⁷ and Bishop⁵¹ using electrophoresis and/or ultracentrifugation on galactoglucomannans from other wood sources showed homogeneity of the polymer.

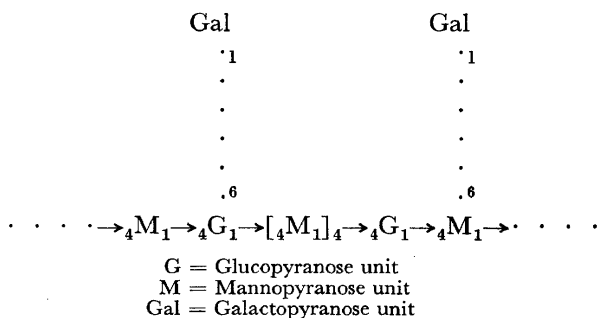


Figure 7

Galactoglucomannans are not found in sulphite or prehydrolyzed kraft pulps to any appreciable extent⁶. The low positive optical rotation of the galactoglucomannan indicates a predominance of β -glycosidic bonds but it does not preclude the possibility that some of the bonds may be, and probably are, of the α -configuration. The behaviour of the polymer during acid pulping conditions and during graded hydrolysis strongly indicates that most of the galactose residues are joined to the polymer by a labile linkage^{41,46}. Recent studies by Meier report the isolation of a galactosyl mannose and a galactosyl mannoiose from a spruce "glucomannan"⁵². The galactose residue of these oligosaccharides was linked by an α -glycosidic bond. Meier considers that these oligosaccharides are derived from a mixture of glucomannan and galactomannan.

The removal of galactose residues could, as predicted previously, leave a type of glucomannan⁴¹. It is possible that part of the glucomannan left following an acidic cook may be derived from this source. However, the availability to hydronium ions of the branched soluble galactoglucomannans, as compared to the highly "resistant", insoluble and inaccessible glucomannans, would indicate that the former would probably be destroyed to a great extent during the acid cooks. In model experiments using 0.25N oxalic acid at 100° for 6 hours, the galactoglucomannan was found to be very labile to acid hydrolysis⁴⁶. Thus, very little mannose would be derived from this triheteropolymer in sulphite or prehydrolyzed kraft pulps.

The relative stability of the galactoglucomannans to alkali was initially considered to be unusually high⁶. Subsequent investigations, however, have demonstrated a marked dependence on the polymer source, and intrinsic viscosities³³. Structurally, the galactoglucomannan has been shown to be a chain of 1→4 linked glucose and mannose anhydro units to which are attached branches, by 1→6 glycosidic bonds, terminated by galactopyranose units. The presence of branches on the 6-position should not affect the end group degrading mechanism. If, however, the molecule was constructed such that short branches were linked by 1→4 bonds and the main chain of the polymer was linked by both 1→4 and 1→6 bonds, greater alkali stability might be expected. Alternatively, the presence of some α -glycosidic bonds in this polymer would result in less degradation due to the greater stability of these bonds to alkaline hydrolysis. Previous studies have shown that amylopectin, which has α -1→4 and α -1→6 linkages when cooked under similar conditions, was isolated in 43 per cent yield⁶.

Comparison of the alkali stability of galactoglucomannans with glucomannans isolated from the same source indicates the existence of two different polymers. Significantly dissimilar yields were obtained for these hemicelluloses in alkaline media for identical time-temperature relationships. Since yield results also appear to be dependent on the previous history of hemicelluloses, the rate of alkaline degradation may be related in part to the initial intrinsic viscosities.

It should be noted that traces of xylose have been reported present in hydrolyzates of many glucomannan fractions. This could indicate incomplete separation of the xylose hemicelluloses or perhaps xylose as a constit-

uent of a glucomannan or galactoglucomannan. The former possibility appears the more probable. Mannose-xylose linkages could, of course, occur and glucose-xylose linkages have been reported³¹.

THE BEHAVIOUR OF THE MISCELLANEOUS CARBOHYDRATE FRACTIONS OF WOOD DURING PULPING

Very little is known of this complex mixture which, upon hydrolysis, can give rise to galactose, arabinose, xylose, glucose, mannose, rhamnose, and uronic acids. Polygalacturonic acid has been detected in a number of woods by Anderson and co-workers, while starch, arabogalactans and unusual mannose-containing polymers have been detected by others². When a commercial pectin and an algin were cooked with kraft liquor, all the uronic acid components were destroyed in less than 30 minutes, and the small amount of carbohydrate material which was isolated appeared to be neutral araban and galactan contaminants (in the case of pectin) and glucan and xylan (in the case of the algin), which had been present in the original samples. It would appear, therefore, that pectin, which is present in wood, but never present in wood pulps, has been removed from these pulps and degraded by the hydrolytic action of the cooking liquors⁶.

Starch has also been shown to be present in wood. This component undoubtedly varies in concentration with time of year. Starch is very susceptible to acid hydrolysis and, hence, would be degraded and removed during the sulphite cook. Starch was found to be quite resistant to alkaline degradation, but its marked solubility in hot alkali or hot water, together with its location in an accessible region, suggests it is dissolved and diffuses out of the kraft wood pulps. Pure amylose was recovered in 25 per cent yield from a 60-minute kraft cook at 160°, while amylopectin was recovered in 43 per cent yield from a similar cook⁶.

Other complex carbohydrate polymers exist in wood. These have not been isolated and characterized. Their properties in certain instances, however, resemble those of the various plant gums such as cherry gum, gum arabic, and Shasta fir gum⁵³. A comparison of the yield losses of cherry gum, gum arabic, and the 4-*O*-methylglucuronoxylan during a kraft cook at 160° showed that the cherry gum was rapidly degraded to non-isolatable products. Shasta fir gum behaved in a similar manner. The gum arabic was degraded by alkali in a manner quite similar to 4-*O*-methylglucuronoxylan. Such a behaviour might be predicted from the postulated complex structure of this polymer⁵⁴. Hydrolysis of the polymer before kraft cooking indicated the presence of galactose, arabinose, rhamnose, and glucuronic acid. Following the kraft cook, it was found that the polymer was now composed of galactose and arabinose only (no glucuronic acid was observed chromatographically). Such behaviour would be explained if the anhydrorhamnose units on the branch of the tentative structure were further removed from the main chain of the polymer than the uronic acid. It could also be explained by variations which undoubtedly occur in the structure of various samples of gum arabic.

While the above polymers are associated chiefly with the cambium and inner bark, they are probably representative of the many "extracellular" carbohydrates. The alkaline degradation, as noted above, is not entirely

related to end group cleavage as cherry gum does not reduce Fehlings solution. The behaviour of Shasta fir gum and cherry gum may be explained if uronic acids are incorporated in the main chain of the polymer as well as in the branches, as was the case for gum arabic. In this manner cleavage of the polymer at the uronic acid position will result in a large number of short chain molecules with terminal reducing groups susceptible to the action of hot alkali. These fragments would be rapidly degraded to non-carbohydrate constituents.

An arabogalactan has been isolated from the water-soluble extracts of many woods, especially western larch. The most recent work has been the isolation and characterization of the arabogalactan of Monterey pine by Brasch and Jones⁵⁵. These authors showed their polymer to be a highly branched galactan joined through positions 1, 3 and 6. The branches were terminated by arabofuranose units. This type of polymer would not be particularly sensitive to alkaline hydrolysis. The lack of arabogalactan in kraft pulps is probably the result of the dissolving of the polymer and its diffusion into the cooking liquor. The lack of arabogalactan in the sulphite pulp is undoubtedly the result of its lability towards acid hydrolysis.

CONCLUSION

Pulping procedures carried out at various pH levels introduce important chemical and physical changes in the resulting wood cellulose. The most obvious and most important chemical differences are those which arise in the "non-cellulosic cell wall polysaccharides" or, as they are commonly termed, "hemicelluloses". The absence (except in trace amounts in some instances) of such sugars as galactose, arabinose, rhamnose, and galacturonic acid in the sulphite and prehydrolysed kraft pulps arises from the acid-catalysed hydrolysis of the polymers containing these sugars or the selective removal of the sugars from the polymers. In general, these carbohydrate polymers are degraded to short chain fragments which dissolve in the cooking liquor, diffuse out of the chips and are thus removed from the final pulp. Pectin, starch, arabogalactans, galactoglucomannans (except for trace amounts), as well as small amounts of unidentified polymers, behave in this manner.

Certain sugars, particularly arabinose, are attached to various polymers as an acid-labile terminal unit. These sugars are rapidly and selectively cleaved from these polymers during acidic cooks. This behaviour accounts for the conversion of the 4-*O*-methylglucurono-araboxytan of softwoods to a 4-*O*-methylglucuronoxylan. This new polymer, as an artefact in softwood pulps and as the predominant original polymer in the hardwoods, is degraded by acid hydrolysis into molecules of lower D.P. Many, but not all, of these polymers dissolve in the cooking liquor and diffuse out of the pulp. The glucomannans of softwoods and hardwoods behave in the same manner under acidic pulping conditions, with the loss by solution in the liquors, of the shortest molecules.

Most of the galactose from the galactoglucomannan is readily removed under strongly acidic pulping conditions and the molecule is degraded

such that most, if not all, of the galactoglucomannan appears to be removed from the final pulp. Galactoglucomannans will occur, however, in modified sulphite, modified kraft and kraft pulps.

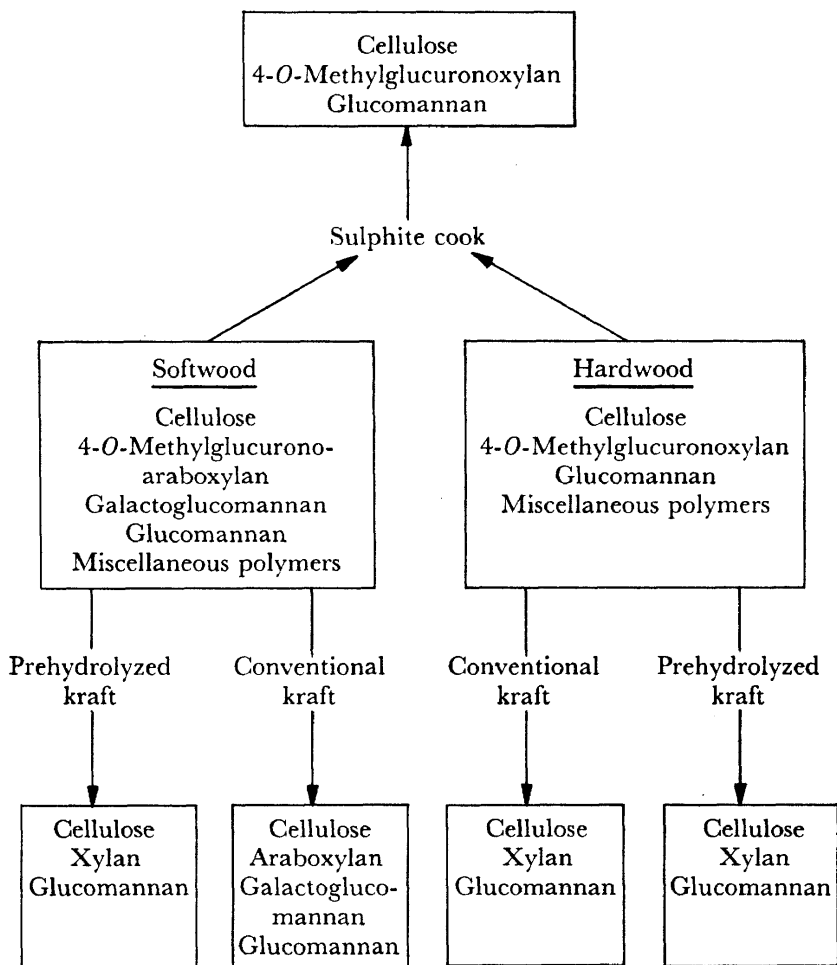
In the presence of the hydroxyl ion during the kraft and soda cooking procedures, different types of degradation occur. The best understood reaction is the end group degradation reaction resulting from an attack on the reducing group of a carbohydrate polymer by the hydroxide ion. In the case of cellulose, Samuelson and Wennerblom⁵⁶ have estimated that 40 to 50 glucose units are cleaved to isosaccharinic acid fragments, which in the process of formation, must be removed from the chain, exposing a new reducing group to attack. After some 40 to 50 anhydro units have been cleaved, on the average, a metasaccharinic acid is formed which remains attached to the polymer as an alkali-stable glycoside of the final reducing sugar, thus terminating the end group-alkoxy-carbonyl degradation.

Undoubtedly the xylose, glucomannan and galactoglucomannan polymers behave in a similar manner to the degradation of the cellulose. There will obviously be many modifications but, in principle, the degradation will proceed analogously. A substituent attached to a 3-position such as is present in the 4-*O*-methylglucurono-araboxylan which, in turn is converted under high temperature alkaline cooking conditions into an araboxylan, will cause a termination of the end group degradation. The presence of α -1 \rightarrow 6 glycosidic bonds will probably also result in the increased stability of certain polysaccharides such as the galactoglucomannans which exist in modified kraft and kraft pulps.

At these elevated temperatures, however, other complex reactions occur. The degradation studies on 4-*O*-methylglucurono-araboxylans, pectin and plant gums indicate that the presence of a uronic acid carboxyl group confers alkaline instability to the glycosidic bond which joins the uronic acid to the rest of the molecule. This instability results in the rapid removal of most, if not all, of the uronic acid when such a polymer is treated with alkali at temperatures in the range of 160 to 170°.

These complex reactions which occur during the kraft cook result in the production of araboxylan and xylans in the pulps from softwoods and hardwoods, respectively. The polymers have a somewhat lower D.P. than the original polymer in the wood due to the hydrolysis of xylose-xylose glycosidic bonds. The decrease in uronic acid content results in a *drastic decrease* in the solubility of the xylan and araboxylan in caustic. Polymers such as arabogalactans and pectin are rapidly dissolved in the alkali. In the case of pectin, the degradation would be to non-identifiable products. Substances similar to cherry gum and Shasta fir gum would also be rapidly degraded to non-identifiable products due to the presence of uronic acid in the main chain of the polymer. These conclusions are summarized in a very general manner in *Figure 8*.

Undoubtedly those hemicelluloses which are in contact with the pulping chemicals at high temperature for the longest time are highly degraded. The extent of degradation will, of course, be dependent upon the conditions and the structure of the polysaccharides themselves. The highly resistant polysaccharides (those requiring caustic of a solution strength



Note: The yield of polysaccharide, the degree of polymerization, structure and properties are different and are contingent upon the type of wood and pulping process. For simplification, only extremes of pH are considered.

Figure 8. A simplified scheme which indicates the general behaviour of some carbohydrate polymers of wood during technical pulping processes

of 8 per cent or higher to remove them from the pulp) will probably be degraded to a lesser degree.

The differences in the properties of pulps produced at different pH's [acid sulphite, bisulphite, neutral sulphite semichemical (similar to holo-cellulose preparation), modified kraft, conventional kraft, prehydrolyzed kraft, and all of the many possible combinations of acid, acid-base, base-acid] are due primarily to the amount, type, structure, chain length, location and general chemical and physical properties of the hemicelluloses. Some of the differences are due to subtle changes in the cellulose structure and chain length as well as in the amount and chain length of the short chain glucans (β -cellulose) which are always present.

Conditions must be selected such that the desired type of hemicellulose is left or deposited (adsorbed or crystallized) in the appropriate place in order that they will confer upon the ultimate wood cellulose those properties which will give it the maximum beneficial effects for a specific given end use.

A thorough understanding of the physical and chemical properties and of the location across the cell wall of the various hemicelluloses present in the different woods and from the different wood celluloses derived from these woods is essential before we can hope to utilize our wood supplies to their ultimate potential. Meier has carried out basic studies in this field⁵⁷. Such studies will lead to a thorough understanding of the type and extent of the degradation which each hemicellulose undergoes under technical pulping processes and will eventually lead to modified processes where the degradation is essentially eliminated (if possible) or kept to a minimum.

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