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PREFACE

Lignin is the natural binder of living trees. Spent sulfite liquor (SSL) is a waste, polluting product from paper mills which contains over 60% lignin derivative. Use of spent sulfite liquor as a thermosetting resin binder for wood is in the process of commercialization. The polymerization of lignosulfonates has been extensively studied with limited success. The aim of this thesis is to identify the functional groups and reactive species responsible for the polymerization of spent sulfite liquor and further study the mechanism of polymerization.

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ABSTRACT

Ammonium-base spent sulfite liquor (NH₄SSL) was separated into fractions having different molecular weight ranges by ultrafiltration using the thin-channel system. The major constituents of NH₄SSL, namely lignin and reducing sugars, were analyzed for each fraction. This recent method successfully provided 80-90%-pure fractions of lignosulfonates possessing a narrow molecular weight distribution as well as NH₄SSL fractions containing a large concentration of low molecular weight reducing sugars. Contrary to the expected results, it was found that highly purified lignosulfonate fractions of different molecular weight ranges failed to thermoset while a purified reducing sugar fraction did polymerize under severe treatment of heat and pressure. Lignosulfonate is however contributing to the carbohydrate polymerization since the optimum reactivity of the NH₄SSL was obtained by adjusting the carbohydrate-to-lignin ratio by ultrafiltration or by simple addition of carbohydrate to the crude liquor.

The findings of this thesis cast serious doubts on current theory which suggests that it is furaldehyde derivatives alone which are the active ingredient in the carbohydrate polymerization. An alternative interpretation of the role of the various carbohydrates in the thermosetting process is as follows: Under a combination of heat and pressure the carbohydrates partially dehydrate to reactive acyclic

unsaturated aldehyde intermediates which can readily polymerize. This type of sugar condensation is sensitive to the carbohydrate chain lengths, the moisture content, and to catalysis by acids.

Lignosulfonic acid is not a stable intermediate in the desulfonation of ammonium lignosulfonate. The ammonium lignosulfonate itself is a weak acid which can catalyze the dehydration of carbohydrates. The unsaturated aldehyde derivative may homopolymerize and may also crosslink lignin with participation of both aldehyde groups and carbon-carbon double bonds.

INTRODUCTION

Wood in a simplified description consists of fibers of cellulose cemented together with lignin. Other lesser constituents are hemicelluloses and inorganics. The cellulose forms 50 to 60% of the wood, the lignin 20 to 30% and the hemicelluloses 10 to 25% (by weight) varying with the species. Inorganics are generally present in amounts of less than 1% (1).

Cellulose is a carbohydrate polymer of the sugar glucose; the glucose units within cellulose are linked in β -D fashion. Hemicelluloses are constituted of oligosaccharides and polysaccharides both soluble in aqueous alkali, and which contain sugar units such as arabinose, xylose, mannose or galactose in addition to glucose.

Lignin is also a high polymer consisting of aliphatic and aromatic portions. Its basic phenylpropane units are interconnected in a large variety of ways by carbon - carbon or ether bonds, giving lignin a complex cross-linked structure.

The manufacture of paper involves removal of lignin from the wood. The sulfite process consists of cooking wood chips under heat and pressure, solubilizing the lignin by converting it to salts of lignosulfonic acid.

During the pulping process most of the cellulose remains unchanged and is separated for use in the manufacture of paper. However, some of the polysaccharides break down to form wood sugars and other water-soluble substances. These also enter solution and are recovered in the raw cooking liquor along with soluble lignosulphonates. In general, spent sulfite liquor (SSL) contains approximately 60% lignin, 30% reducing sugars, and 10% inorganic materials. The Canadian pulp mills produce every year about 2 million tons of dehydrated SSL and only one mill in Canada is using part of this raw liquor for commercial application.

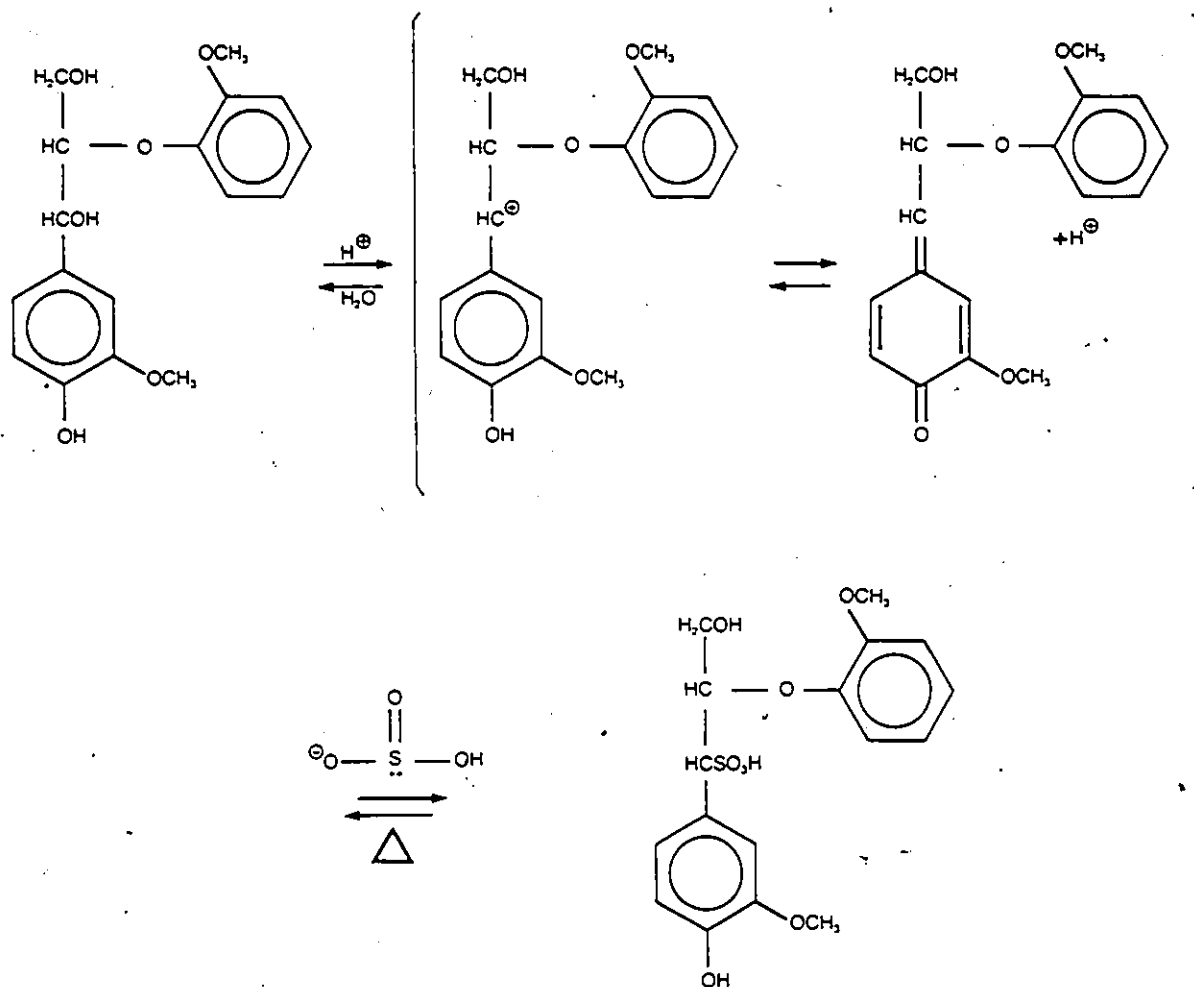
The fact that lignin materials are natural bonding agents for wood and that pulped lignin is of bakelite-like appearance has encouraged scientists around the world for the last 70 years to develop the use of this waste material as a bonding agent. If this were achieved the resultant economic advantages would be enormous. Worldwide there are more than 3,000 patents covering uses of lignins. Most of these, however, are not exploited.

A few years ago, it was found that calcium based spent sulfite liquor (CaSSL) may be utilized as a binder for wood composite when treated with sulfuric acid (2). More recently, it was also found that ammonium based spent sulfite liquor (NH₄SSL) may also be used as a thermosetting

binder for wood products without prior acidification with sulfuric acid (3). The thermal polymerization without acidification occurred only with ammonium based SSL. It seems (2,3) that lignosulfonic acid is released from calcium based SSL by adding sulfuric acid or by heating ammonium lignosulfonate. In both cases, the lignosulfonic acid, under heat and pressure, would then condense and polymerize into an insoluble state similar to the condensation reaction of conventional thermosetting binders. However, no serious attempt was made to understand the mechanism of polymerization of the sulfite liquor.

REVIEW OF THE CURRENT KNOWLEDGE

The formation of liginosulfonic acid from lignin model compounds has been studied in detail and a mechanism of reaction has been proposed to describe the formation of 4-hydroxy- α -[2-hydroxy-1-(*o*-methoxyphenoxy) ethyl]-3-methoxy- α -toluenesulfonic acid (4,5) (Scheme 1)



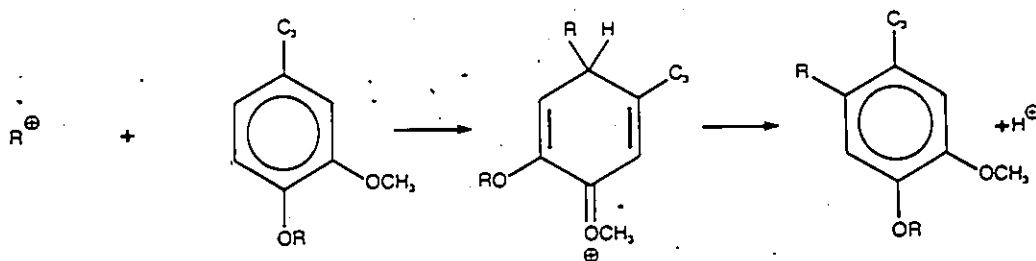
Scheme 1. Sulfonation and desulfonation process of lignin model compound.

The thermal desulfonation of lignosulfonic acid in aqueous solution or in the dry state is also known to occur and the same unstable intermediates were proposed to describe the desulfonation process (6,7,8) (Scheme 1).

The sulfonyl and hydroxyl groups located in the benzylic positions of lignin are both good leaving groups, thus the polymerization of lignin and of lignosulfonic acid are very similar and need not be differentiated, the sulfonic acid acting as a catalyst for the condensation of lignin.

1. CARBONIUM ION POLYMERIZATION

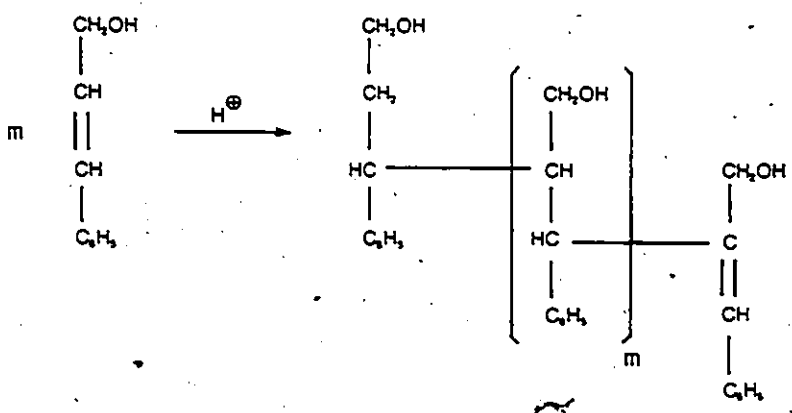
Lignin contains benzyl alcohol, cinnamyl alcohol and cinnamaldehyde groups which are readily converted to resonance-stabilized carbonium ions (R⁺) (7,9,10,11). Since many of the aromatic groups of lignin are strongly activated by alkoxy and hydroxyl substituents, electrophilic substitution can occur in ortho and para positions leading to the formation of a high polymer. This reaction is analogous to the well known condensation of phenol and formaldehyde.



Scheme 2. Electrophilic substitution.

2. VINYL POLYMERIZATION

Lignin contains cinnamyl alcohol and cinnamaldehyde end-groups which may condense as described in scheme 3 according to Freudenberg and Glennie (12,13).

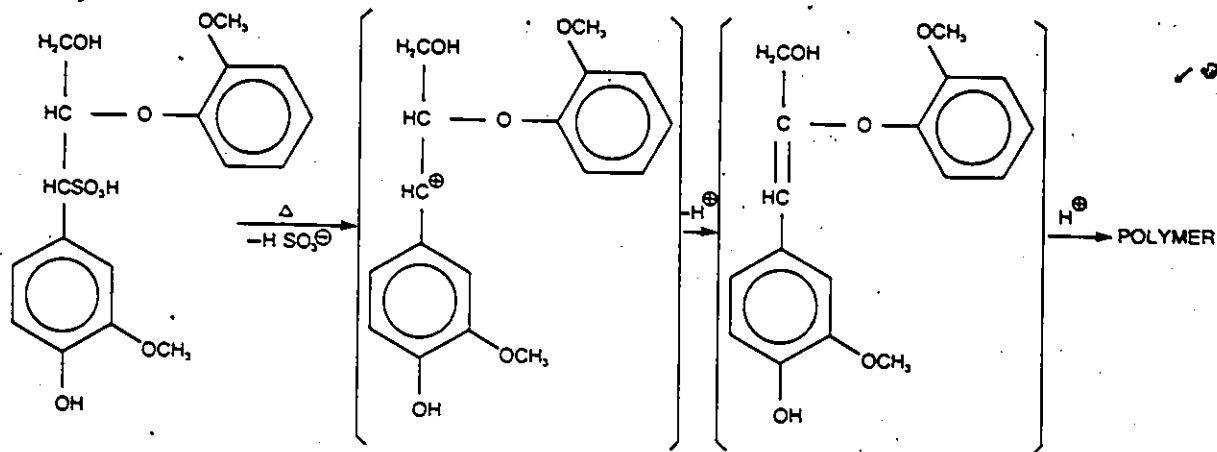


Scheme 3. End - Group Polymerization

These types of allylic alcohols are very reactive, coniferyl alcohol for example is unstable and polymerizes at room temperature under mild acidic conditions.

This type of polymerization may also occur from lignin repeating unit desulfonation (7) as illustrated in scheme 4.

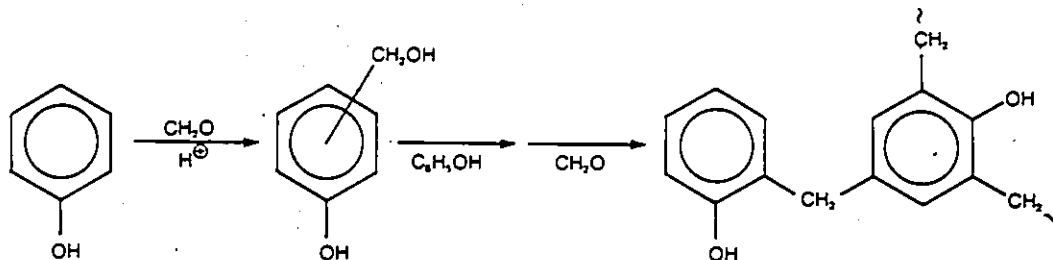
Scheme 4. Repeating Unit Polymerization



3. LIGNIN FORMALDEHYDE POLYMERIZATION

Lignin polymerizes during the course of the bisulfite cooking. Prolonged heating leads to formation of an insoluble polymer.

Spent sulfite liquor (SSL) contains other organic materials such as monosaccharides and formaldehyde. It has been suggested by Alder (14) that lignosulfonate reacts with formaldehyde by electrophilic addition and further condenses to provide a phenol-formaldehyde type of condensation reaction (scheme 5).



Scheme 5. Phenol-formaldehyde Condensation

4. LIGNIN-FURALDEHYDE POLYMERIZATION

It has also been suggested that in the bisulphite cooking process, monosaccharides are transformed to furaldehyde derivatives which react with lignin and lead to an insoluble polymer (15).

However, the recent work of Stenlund and associates (16) tends to demonstrate that neither formaldehyde nor furfural can explain the polymerization of lignosulfonate. Their claims rests on the results of an experiment in which bisulphite cooking of wood was carried out in the presence of radio-labeled formaldehyde or xylose. After the usual processing the resulting lignosulphonate displayed no radioactivity.

5. LIGNIN HYDROLYSIS

In 1979, Herrick and his group (17), using ultrafiltration to purify the lignin and gel permeation chromatography to measure its molecular weight, reported that even if the viscosity of acidic SSL increases, when heat treated the actual molecular weight of lignin decreases. The increase of viscosity was related to functional group changes in the lignin polymer which leads to molecular associations.

AIM OF THE RESEARCH

Spent sulfite liquor (lignosulfonate, SSL) was used successfully as thermosetting resin binder for wood products. There have been numerous attempts to identify the reactive species in the spent sulfite liquor polymerization reaction and numerous mechanisms of polymerization have been suggested to describe the condensation of lignosulfonic to insoluble materials. However, none of these have been able to explain entirely the empirical results.

This project was aimed at identifying the functional groups and reactive species responsible for the polymerization and insolubilization of the SSL by studying its mechanism of polymerization.

APPROACH

Lignosulfonate represents approximately 60% of dehydrated SSL by weight. In the pulping operation to make lignin soluble, its network is broken by chemical treatment to yield fragments of various sizes sulfonated to different extents. For example, these lignin fragments have been reported (18) to contain phenolic compounds with molecular weights as low as a few hundred or as high as several hundred thousand.

The sulfite also contains approximately 30% carbohydrates which are degraded mainly into hexoses and pentoses and also about 10% organic salts. It is evident that given the complexity of the SSL system, a limited amount of information would be obtained through the usual methods of analysis such as infrared spectroscopy, mass spectroscopy or nuclear magnetic resonance spectroscopy.

While most of the research on lignosulfonate polymerization has been carried out on model compounds (7, 10, 12, 14) or on monomeric degradation products isolated from SSL (13, 19) a few studies involving crude SSL have also been made (8, 9, 16) but little work involving purified SSL as starting material is reported (6, 17).

Our approach is to achieve the purification of lignosulfonates as a prerequisite to further study. The lignosulfonate and carbohydrate fractions would be separated and the purified lignosulfonate further fractionated to different molecular weight ranges. It should then be possible to establish some correlation between the reactivity of each fraction and its chemical composition.

METHODS OF PURIFICATION

The separation of spent sulfite liquor in its components has been studied extensively and many techniques have been used for purification and fractionation of SSL.

Gordon and Mason (20) reported the dialysis of SSL and its fractionation by successive conversion into basic salts and precipitation with ethanol. Jensen et al. (21) suggested ion exclusion and gel filtration methods to fractionate the waste liquor. Ferm and Nilson (22) preferred thin layer chromatography. Other methods of fractionation involving the precipitation and the differential solubility of various amino salts have also been used (23, 24, 25).

Ultrafiltration is a relatively new technique employed to fractionate polymeric materials based on their molecular size and configuration. It arises from the

development of anisotropic membranes with high hydraulic permeability made from a variety of synthetic polymers (26). The membranes are permeable to low molecular weight solvents but retain solutes which have molecular dimensions larger than a critical size corresponding to the "cut off level" of the membrane. Ultrafiltration has been used successfully to obtain sugar-rich fractions from waste sulfite liquor for fermentation to produce alcohol (27, 28, 29).

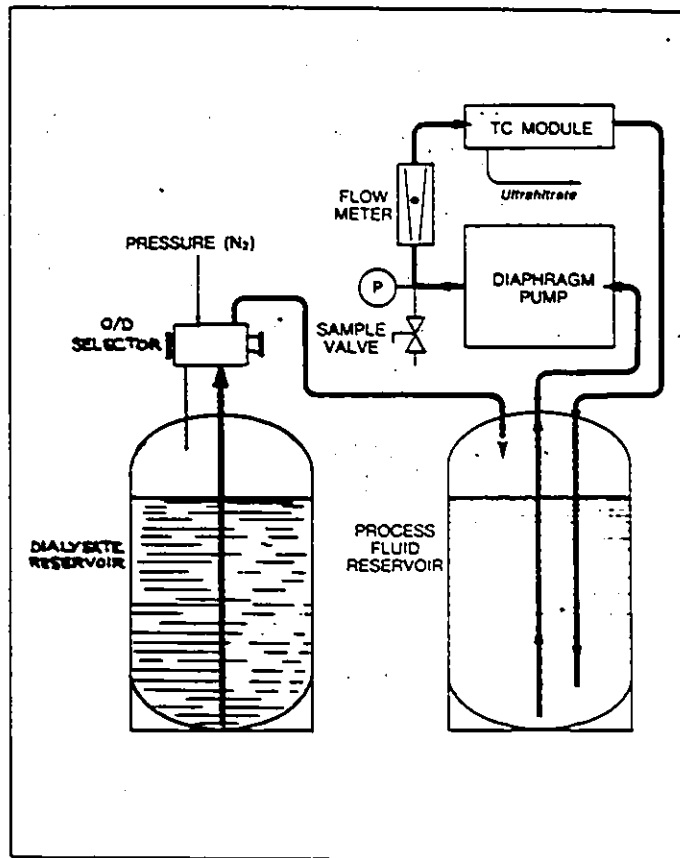
More recently Trivedi et al. used ultrafiltration to fractionate SSL to different molecular weight range and obtain "pure" high molecular weight lignosulfonates (30).

For our purposes an ultrafiltration technique using a thin-channel system TCSE from Amicon Corp. with Diaflo membranes of different pore sizes was used to fractionate SSL into different molecular weight ranges. Figure 1 shows the Diafiltration unit.

METHOD OF EVALUATION OF SSL

SSL is a complex polymer and even after purification and fractionation to a very narrow molecular weight range, no clear picture of its macromolecular structure can be obtained through the usual methods of characterization of organic compounds. Thus, a different method of evaluation of this polymer is required.

Figure 1. Thin - Channel Systems



TCE System with Diafiltration Unit

SSL is a heat hardening resin. A common way to investigate the rate of curing of a thermosetting resin is to subject the resin to different thermal treatments and measure its change of molecular weight (17) or its rate of insolubilization (6). Unfortunately methods to determine molecular weight of lignosulfonate using viscosity, vapor pressure or gel permeation (31, 32, 33, 34) are limited in application since lignosulfonic acid insolubilizes under mild heat treatment. Measure of the rate of insolubilization is also useless since the insolubilization of lignosulfonic acid occurs not only because of extensive polymerization but also by elimination of its sulfonic acid group.

Another simple method to investigate the rate of curing of a thermosetting resin is to compress the resin in a mold and heat it until it reaches the crosslinked insoluble, infusible stage. The time required, at a given temperature, to obtain the crosslinked stage is related to the reactivity of the material being studied. Reactive materials will crosslink easily and extensively while less reactive or unreactive materials may produce only a few crosslinks or none at all. Since the bonding property of a material is related to its ability to crosslink, an indirect measurement of the extent of crosslinking (or reactivity) can be obtained from an

evaluation of the mechanical Torsion Shear (T.S.) strength of an object in which the material being evaluated is used as binder. This thesis being written in the context of the study of adhesives for wood products, all torsion shear tests were performed on a molded wood disc of standard dimensions in which the adhesion was obtained by thermal crosslinking of the various substances being investigated. In practice (see experimental section) wood particles were coated with a few percent of the substance being investigated ("resin binder") and a solid disc was molded using heat and pressure to set the resin binder. The disc was then immersed in boiling water to eliminate any uncured resin binder and the wet torsion shear (T.S.) strength of the "boil proof" disc was measured.

Figure 2 shows the hydraulic molding press designed for this study. The Torque-shear Test (T.S.) is also illustrated in Figure 3.

It is understood that at a given resin content: press temperature, time and T.S. are interrelated. At low temperature a longer press time is required to cure the resin and the reverse occurs at high temperature. Different resin binders are evaluated by comparing their T.S. at fixed temperature and time. The T.S. test is very useful in that it is related to other physical properties of wood composites

Figure 2. Molding Press

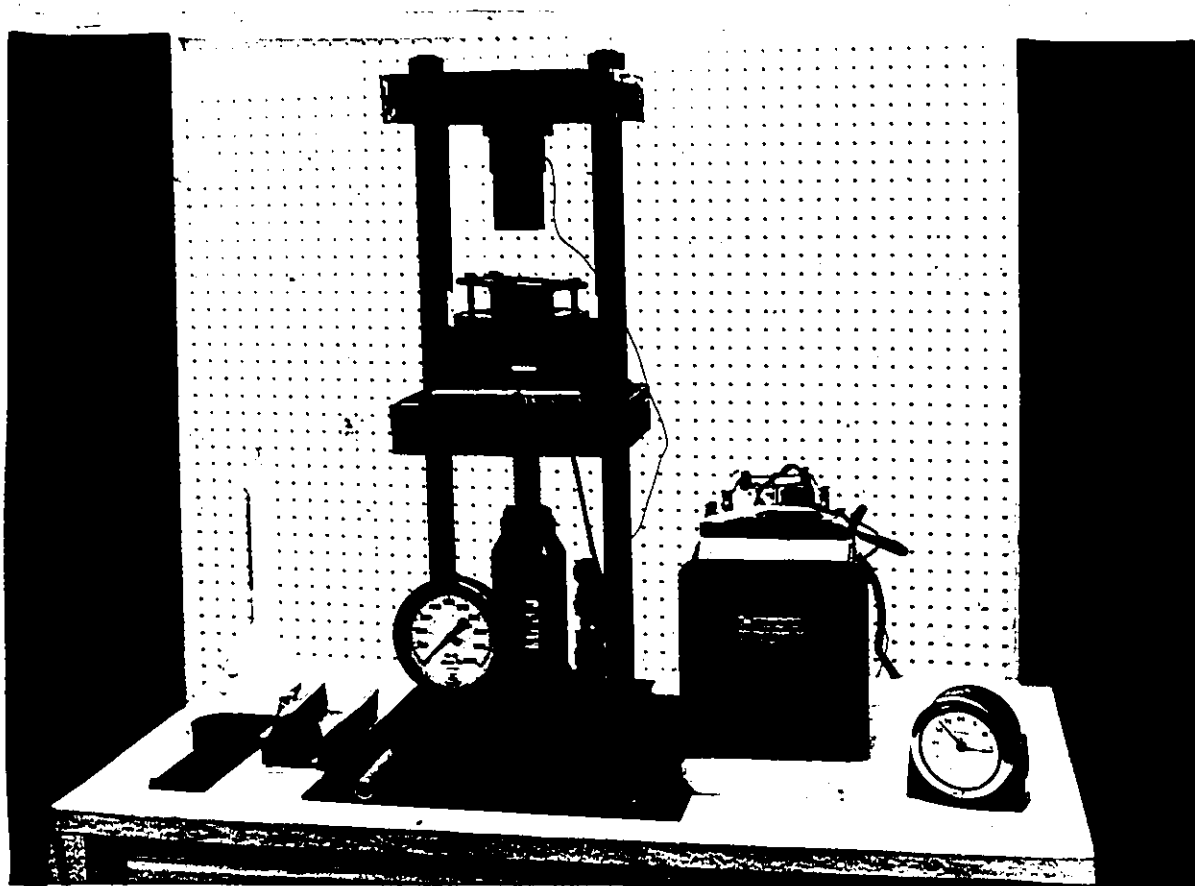


Figure 3. Torque-Shear Test



Torque-Shear Test on a 25. x 25 mm specimen with the bottom socket clamped in the vise and the top fitted to a 22.6 Nm torque wrench. A 25 x 25 mm specimen is positioned with half its thickness inside both top and bottom sockets.

such as their modulus of rupture (MOR) (35). In this study, it was estimated that a T.S. of 5.7 Nm corresponds approximately to a MOR of 68.9 MPa.

RESULTS & DISCUSSION

PART I. CHOICE OF LIGNIN THERMOSETTING STANDARD

The Torsion-shear (T.S.) test on molded discs is a valuable technique to study the rate of curing of both calcium based spent sulfite liquor (CaSSL) and ammonium based spent sulfite liquor (NH₄SSL). It is reproducible and requires only a small sample of chemical: about 2 g of resin binder was required for each test.

In the case of CaSSL, addition of an acid "catalyst" is required for the polymerization to occur. Acidification results in the formation of lignosulfonic acid as shown in scheme 6.



Scheme 6. CaSSL Acidification

Molded discs were made using 10% SSL contents made with various levels of acidity and pressed at 210°C with a pressure of 68.9 MPa for 10 minutes. The test results illustrated in figure 4 indicates that thermosetting occurs

Figure 4. Effect of Lignosulfonic Acid Content on T.S. Molding Disc Pressed at 210°C 10 min

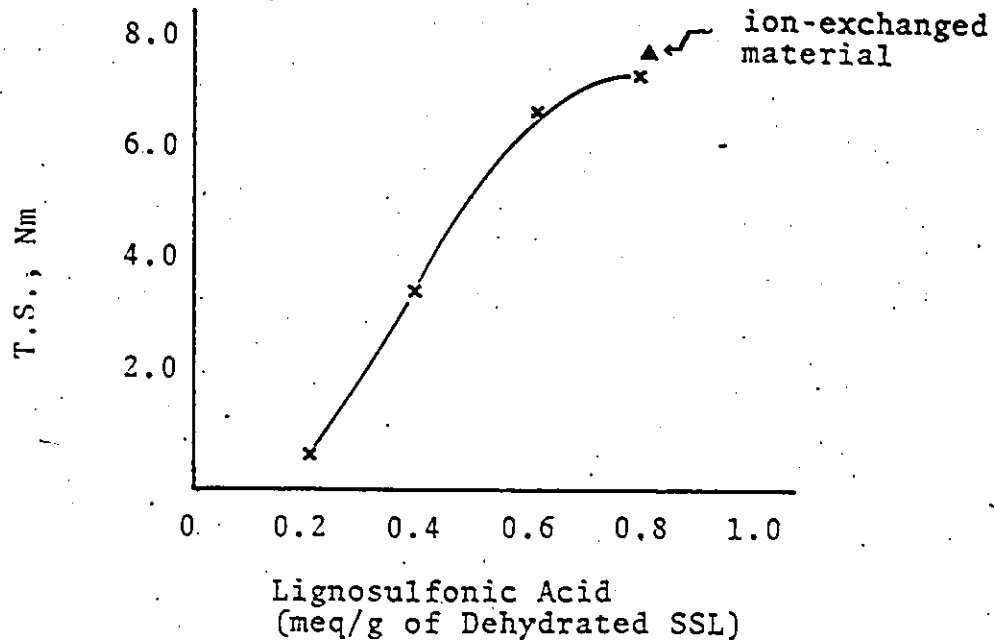
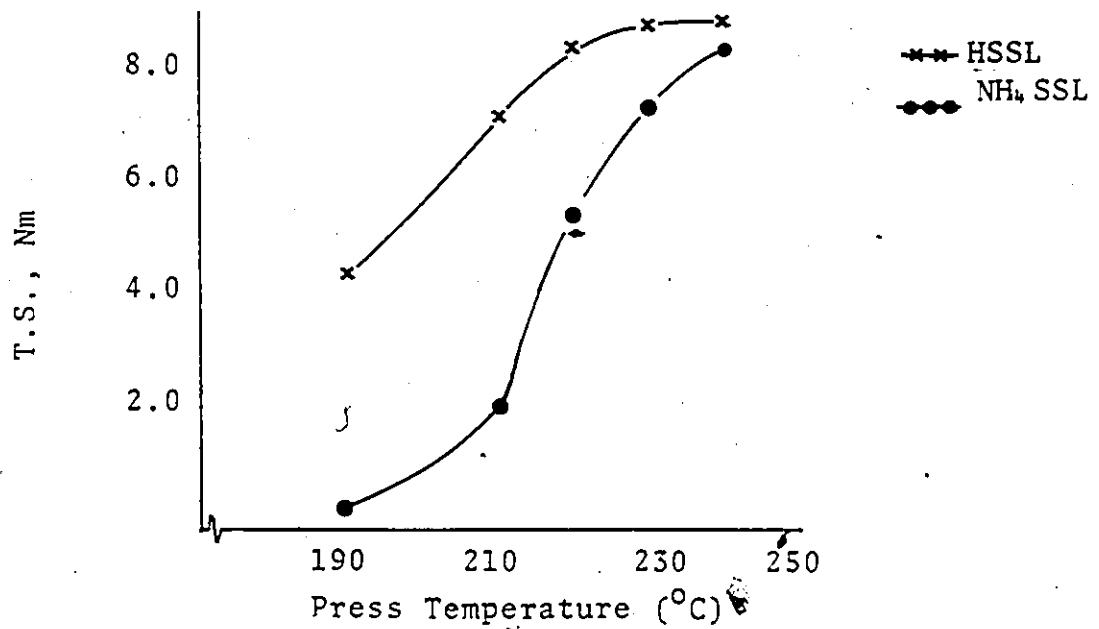


Figure 5. Effect of Press Temperature on T.S. Molding Disc Pressed for 10 min



as a function of acidity. The degree of crosslinking of the resin, as measured by the physical T.S. strength of a molded 25 x 25 mm specimen, increased with the sulfonic acid and its maximum strength coincides with the release of all the available lignosulfonic acid from its salt.

Figure 5 compares the rate of curing of ammonium lignosulfonate and lignosulfonic acid at different press temperatures. Lignosulfonic acid was obtained by ion-exchange of CaSSL. It can be observed that NH_4SSL cures slower than lignosulfonic acid, however similar T.S. strength was obtained if a higher press temperature of 240°C was used.

NH_4SSL is easier to handle than CaSSL as it cures without addition of an external acid catalyst; therefore it will be used in the following fractionation study. Preliminary results indicated that lignin may homopolymerize with participation of acid, however SSL contains many other constituents which may also participate in SSL polymerization (15,16) and purification of SSL is a prerequisite to further study.

NH_4SSL FRACTIONATION

The ultrafiltration technique is a convenient method to separate lignosulfonate fractions from ammonium spent sulfite liquor (NH_4SSL). A multi-stage ultrafiltration was carried out using a series of membranes of decreasing pore

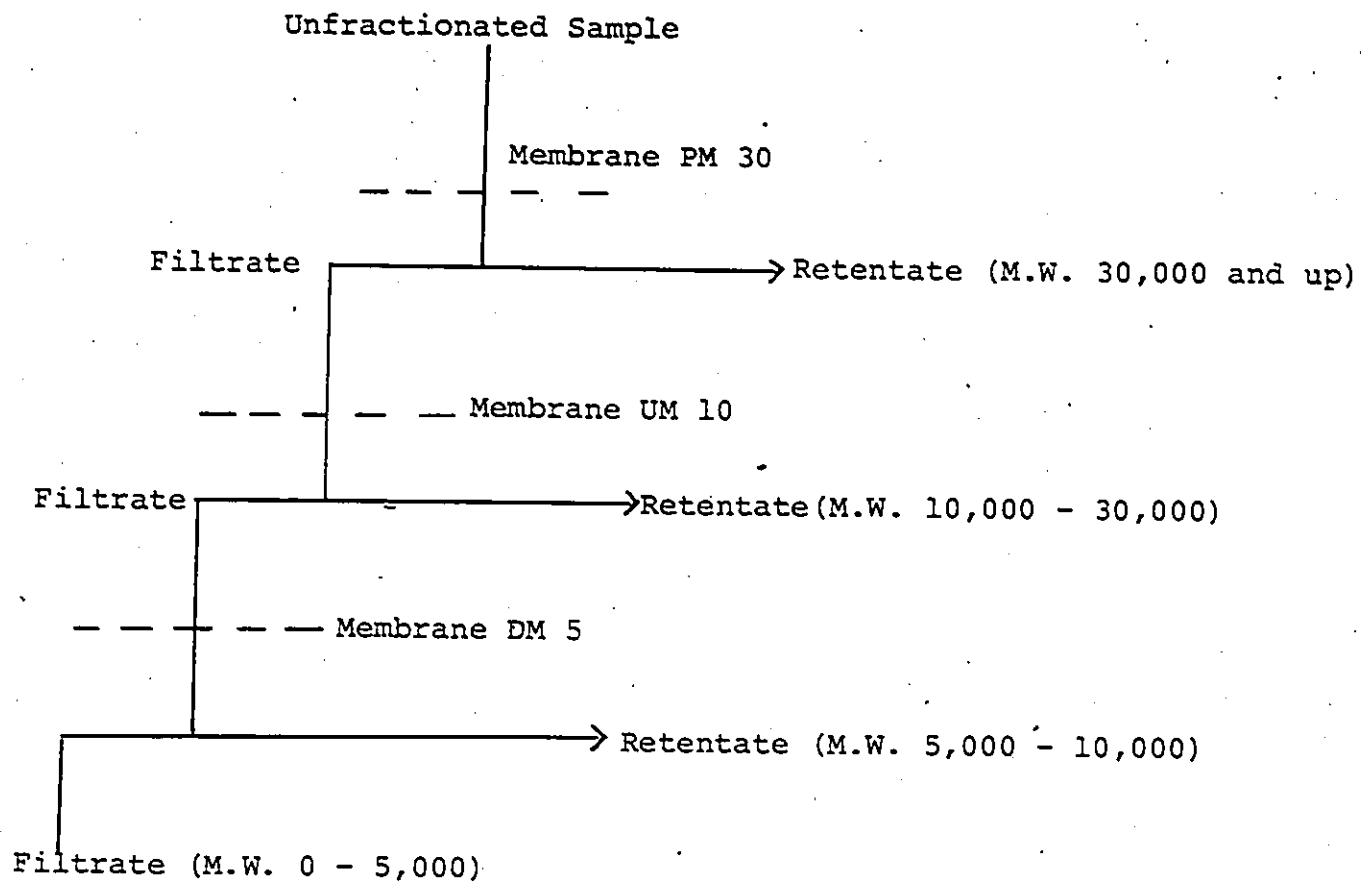
size according to the scheme given in figure 6. Four SSL fractions of different molecular weight ranges were isolated and their chemical analysis along with test results are set out in Table 1.

In agreement with previous findings (30) the lignosulfonates shows a large spread of molecular weight: 36% of the solids had a molecular weight above 30,000 and 25% under 5,000. Using the diafiltration system (figure 1) which allows addition of solvent to the solution being ultrafiltered, 90% pure high molecular weight lignosulfonate was obtained. A fraction rich in sugar (50% of solid) was also obtained from the filtrate of the UM5 membrane.

The molding discs were prepared with each NH_4SSL fraction and pressed under identical conditions. Surprisingly the purified lignosulfonate with molecular weight over 5,000 did not thermoset under severe heat treatment. The fraction containing a higher proportion of low molecular weight materials is more reactive than the fraction containing high molecular weight materials.

It should be noted that the current trend is to use high molecular weight SSL as advocated by Haron (36), Goss (37) and Papova et al. (38). In contrast, the results reported in this thesis show conclusively that for ammonium based SSL, low molecular weight fractions cure faster than their high molecular weight counterparts.

Figure 6



Multistage Ultrafiltration of NH_4SSL

Table I. Effect of molecular weight range on bonding properties of NH₄SSL

NH ₄ SSL Multistage Diafiltration	Weight of Original Liquor %	Lignin %	Reducing Sugars %	N %	S %	210°C, 10 min. T.S., Mn
FM-30 (M.W. 30,000 and up)	36	90	8	1.6	5.1	0
FM-10 (M.W. 10,000-30,000)	18	85	10	2.3	7.0	0
DM-5 (M.W. 5,000-10,000)	21	80	14	3.6	8.5	0
DM-5 (M.W. 0-5,000)	25	40	50	4.2	9.8	5.8

As can be seen in Table 1, the low molecular weight NH_4SSL fraction (0-5,000 MW) contains a high concentration of highly sulfonated phenolics since the sulfur and nitrogen contents increase with decreasing molecular weight of the fraction. The same low molecular weight fraction also contains a higher proportion of reducing sugars and salts. Further fractionation is required to identify whether one or all of these species are responsible for the binding properties of low molecular weight SSL.

Complete fractionation of the low molecular weight SSL into sugars and phenolic constituents was not successful. However some additional fractionation was obtained when the low molecular weight SSL was passed through a column filled with a strongly acidic ion exchange resin and a fraction enriched in reducing sugars could be isolated by this process. As can be seen in table 2 a clear trend to higher Torsion-shear values with higher concentrations of reducing sugars in the SSL fractions is observed. This suggests that the carbohydrate components make a critical and perhaps essential contribution to the polymerization of SSL.

CARBOHYDRATE ADDITION TO SSL

An alternative to ultrafiltration was obtained by adding an exterior source of carbohydrate to lignosulfonate.

Table 2. Fractionation of low molecular weight
 NH₄SSL with ion-exchange resin

NH ₄ SSL - Sample	Lignin %	Sugar %	210°C, 10 min. T.S. Nm
Unfractionated	68	22	2.0
DM-5 M.W. 0-5,000	40	47	5.8
DM-5 M.W. 0-5,000 further fractionation with 101-H	30	62	8.4

As shown in Table 3, addition of glucose to high molecular weight NH₄SSL produced a good resin binder. Table 4 further demonstrates that the mixture yielded a better resin binder than either carbohydrate or lignosulfonate used separately. The best formulation, that producing maximum torsion-shear strength, was obtained at a carbohydrate-to-lignin ratio of 55:40. This is a clear indication that both lignosulfonate and carbohydrate are contributing to the polymerization of SSL. It is also interesting to note that the fast curing binder was obtained with sugar as the major ingredient.

Table 3. Addition of D-Glucose to high molecular weight NH₄SSL

Ultrafiltrated NH ₄ SSL EM 10 M.W. > 10,000	D-Glucose g	Press Time 210°C Min	210°C, 10 Min T.S., Nm
100	0	25	0
50	50	10	6.2

Table 4. Molding disc with various ratio of D-Glucose - NH₄SSL

Ratio NH ₄ SSL: D-Glucose	Lignin %	Total Reducing Sugar %	210°C T.S., Nm
6:0	68	22	2.0
5:1	57	35	4.5
3.5:2.5	40	55	8.1
1:5	14	87	4.0
0:6	0	100	0



PART II

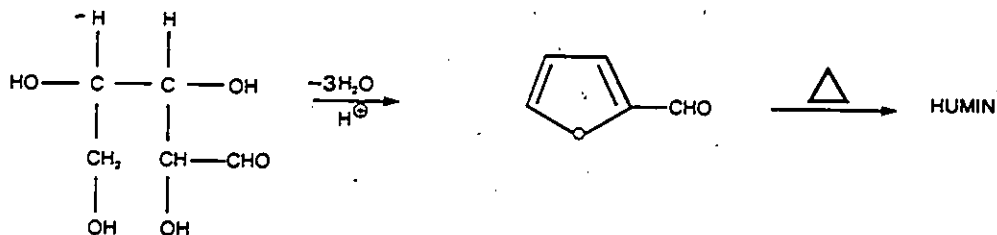
CARBOHYDRATE AS THERMOSETTING RESIN

The thermosetting and binding properties of SSL have commonly been considered to be a lignin polymerization reaction (36-41). Little consideration was attached to the carbohydrates which are minor constituents of the SSL (20 - 30% on solid).

Industrial preparations of furaldehyde derivatives by the thermal degradation of pentoses or hexoses in acidic conditions are well known (42). Also it is generally accepted that carbohydrates polymerize under neutral or acidic conditions in both the dry state or in aqueous solutions through formation of furan compounds which condense to produce insoluble and infusible humin (43-45). Recent studies by Heyns (46), Shafizadeh (47), and Prey (48) support the assumption that carbohydrates polymerize through formation of furan compounds (Scheme 7).

Scheme 7.

Pentose polymerization



A monosaccharide can be converted to a furan derivative using a heat treatment and an acid catalyst. The reactive furan derivative is then used as a thermosetting resin (49). The results of our work on thermal polymerization of carbohydrates cast serious doubts on the assumption that carbohydrates polymerize through the formation of furan compounds and suggest that under the action of heat and pressure, the carbohydrates readily dehydrate with formation of highly reactive unsaturated acyclic aldehydes which can condense to a cross-linked polymer without requiring the prior formation of furan intermediates.

CARBOHYDRATE'S REACTIVE SPECIES

A series of carbohydrate degradation products or related polyfunctional molecules were selected and their ability to polymerize under a combination of heat and pressure to produce a "boil proof" molding disc was evaluated.

A serious technical problem was encountered in the comparison of the various compounds which were tested (Table 5) due to the fact that some of them had a low boiling point (50) and may escape the press before polymerization temperature is reached. Thus, to accelerate their polymerization 1% sulfuric acid was added as shown in Table 5.

TABLE 5. CARBOHYDRATE DEGRADATION PRODUCTS AND RELATED POLYFUNCTIONAL MOLECULES AS WOOD BINDERS.

COMPOUND	FORMULA	BOILING POINT (BP) AT 760 mmHg °C	SOLVENT	H ₂ SO ₄ % DRY RESIN	238°C-10 MIN T.S., Min
D-GLUCOSE		...	H ₂ O	0	8.6
D-GLUCOSE		...	H ₂ O	1	9.2
GLUCITOL		400	H ₂ O	1	0
GLUCONIC ACID		...	H ₂ O	1	0
1,3-DIHYDROXY-1-PROPANE		...	H ₂ O	1	0
2-FURALDEHYDE*		161		0	0
2-FURALDEHYDE		161	CH ₃ OH	1	0
2-FURALDEHYDE**		161	CH ₃ OH	2	2.6
5-(HYDROXYMETHYL)-2-FURALDEHYDE		330	H ₂ O	0	1.7
2-FURYL HYDROXYMETHYL KETONE		...	CH ₃ OH	1	0
ACROLEIN CONTAINING 0.1% HYDROURNONE		52	CH ₃ OH	1	3.5
CINNAMALDEHYDE		250	CH ₃ OH	1	2.5

* Sample pre-treated in pressure reactor at 170°C under 12.5 MPa(O₂) for 16 h.
 ** One compressed to a higher density of 0.86 g/cm³ instead of 0.80 g/cm³ used elsewhere in this study.

The results summarized in Table 5 show that the aldehyde functional group (51,52) as well as certain structural features are essential to produce bonding since neither glucitol or gluconic acid, nor 1,3-dihydroxy-1-propanone were capable of bonding. All the substances showing adhesive properties possess either a combination of alcohol-aldehyde or ene-aldehyde functionalities (Table 5). D-Glucose under high press temperature and long press time produced a "boil proof" molded disc without the need for an acid catalyst. Addition of acid increases its reactivity and although its ultimate value of T.S. appearing in Table 5 is not affected, similar results could be obtained at a lower (210°C) temperature with an acid catalyst.

Surprisingly all the furaldehyde derivatives tested were far less reactive than D-glucose. The opposite was expected since they are generally accepted as "active species" in the carbohydrate polymerization process (46, 47, 48). A sample of 2-furaldehyde after treatment at 27.6 MPa provided by compressed nitrogen and 175°C for 16 h was still soluble in acetone and failed to thermoset under press conditions. The 2-furaldehyde was capable of bonding wood only when catalysed with 2% sulfuric acid and when the disc was compressed at a density of 0.96 g/cm³ instead of 0.80 g/cm³ as generally used elsewhere in this study.

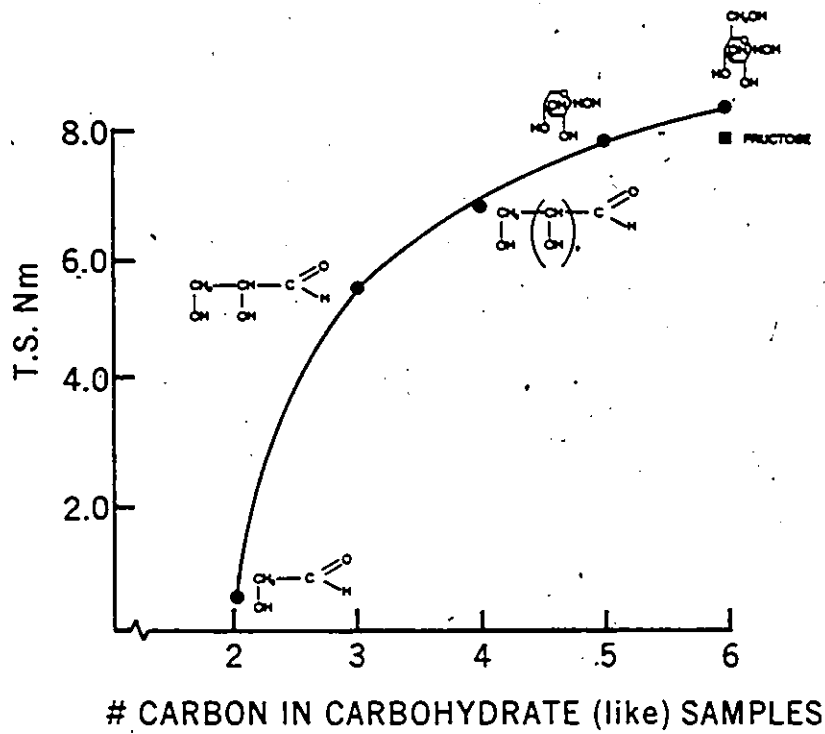
An alternative to polymerization through formation of a furaldehyde intermediate was evidenced with use of acrolein or cinnamaldehyde with respective boiling points of 52°C and 250°C which both succeeded in producing a "boil proof molded disc" in the presence of a small quantity of acid. These results suggest that carbohydrates may also polymerize through formation of an acyclic unsaturated aldehyde. To gain further evidence regarding this possibility a number of additional carbohydrates of varying structures were examined as described in the following pages.

It should be noted that a positive result was obtained with cinnamaldehyde, a compound which possesses structural features commonly found in lignin end groups such as coniferaldehyde.

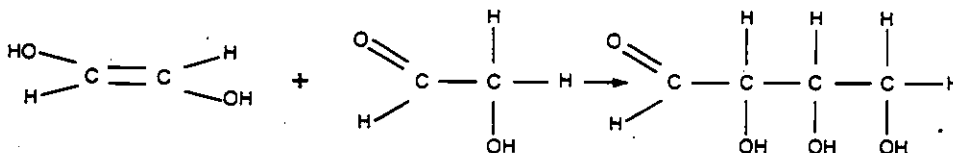
CARBOHYDRATE POLYMERIZATION CAPABILITIES

A series of carbohydrates of different chain lengths (including glycolaldehyde) were used to make molded discs under similar pressing conditions. The discs were made using an excess of each chemical as well as high temperature and long press time to obtain an optimized curing and strength from each compound. The relation between the carbon content and the bonding efficiency is illustrated in figure 7. Heynes

Figure 7. Effect of Carbohydrate's Chain Length on T.S.



and Klier (53) have reported that glyceraldehyde decomposes in a different manner than higher molecular weight sugars under similar heat treatment. By contrast our study shows that heat in combination with pressure caused sugars with carbon content from C₃ to C₆ to produce similar polymers as evidenced by a comparison of their infrared spectra (I.R.) and their ability to bond wood as illustrated in figures 7, 8 and 9 respectively. As expected, a large drop in T.S. strength occurred from glyceraldehyde to glycolaldehyde. However, it is surprising to find that even a 2 carbon "sugar like structure" provided some bonding. It may be assumed that an aldol condensation occurs with formation of a sugar with higher carbon content (scheme 8):



Scheme 8. Aldol condensation

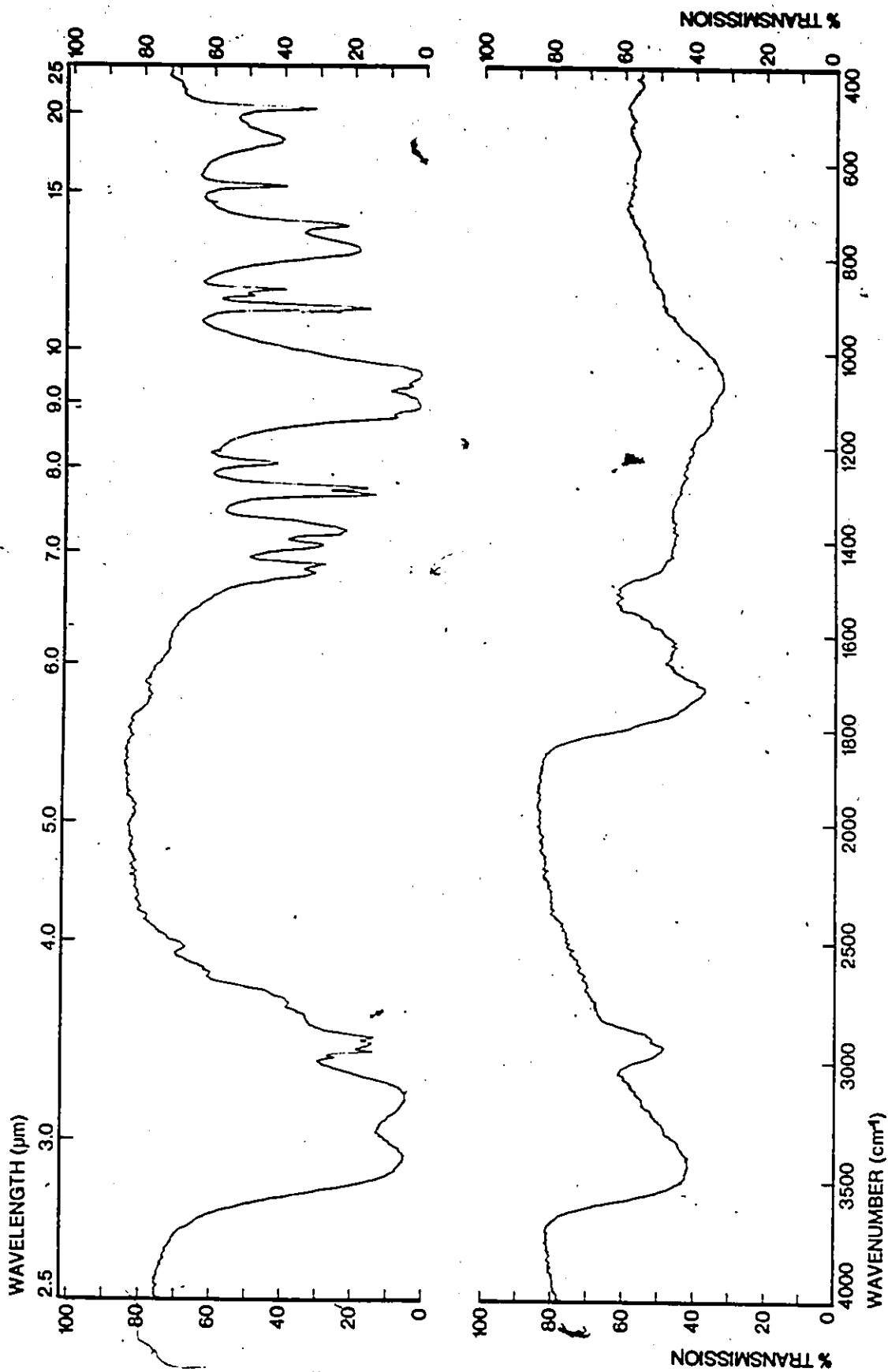


FIGURE 8. Infrared Spectra of DL-Glyceraldehyde (KBr, Disc) Before and After Polymerization 10 min. at 230°C and 13.8 MPa.

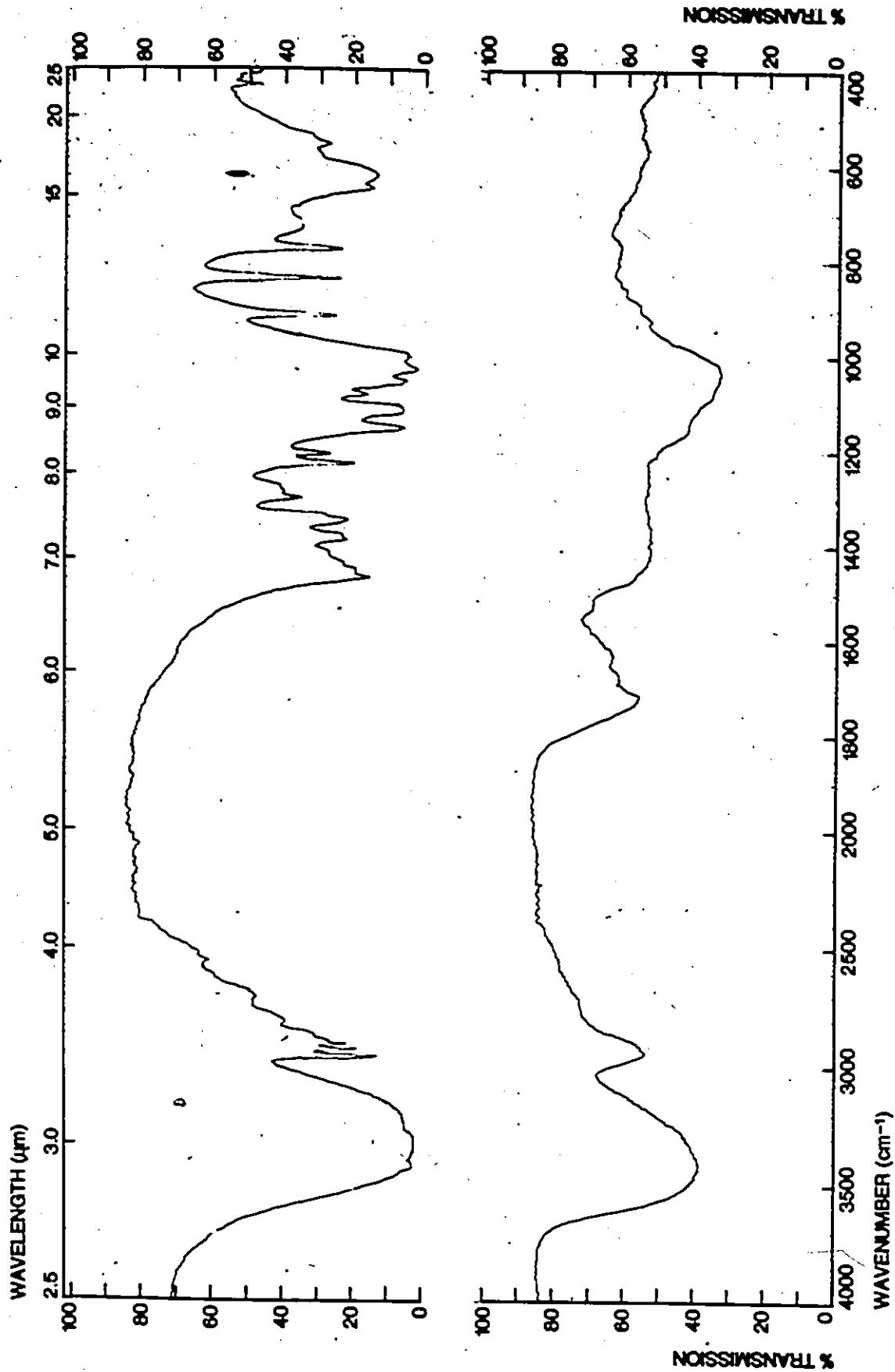


FIGURE 9. Infrared Spectra of D-Glucose (KBr, Disc) Before and After Polymerization 10 min. 230°C and 13.8 MPa.

This product could dehydrate to a furan derivative which would polymerize further. However, this is unlikely as seen in Table 5, furan compounds are less reactive than monosaccharides. More probably an acrolein type product of dehydration leads to the cross-linked polymer.

POLYMERIZATION OF GLYCERALDEHYDE

Small amounts of DL-glyceraldehyde, D-glucose and 5-(hydroxymethyl)-2-furaldehyde were respectively polymerized between two teflon sheets using a combination of heat and pressure similar to the conditions used for the formation of molded discs.

Figures 8 and 9 present the respective I.R. spectra of DL-glyceraldehyde and D-glucose before and after polymerization, 10 min. at 200°C and 13.8 MPa showing the appearance of a band at 1730 cm^{-1} characteristic of carbohydrate polymers obtained by thermal polymerization (54). The similarity of the two I.R. spectra after polymerization, ascertain the similarity of the two polymers.

In contrast, figure 10 presents the I.R. spectra of 5-(hydroxymethyl)-2-furaldehyde taken after 20 and 120 min of similar heat treatment. The I.R. spectra of the original material was included as reference. Even after 20 minutes in the

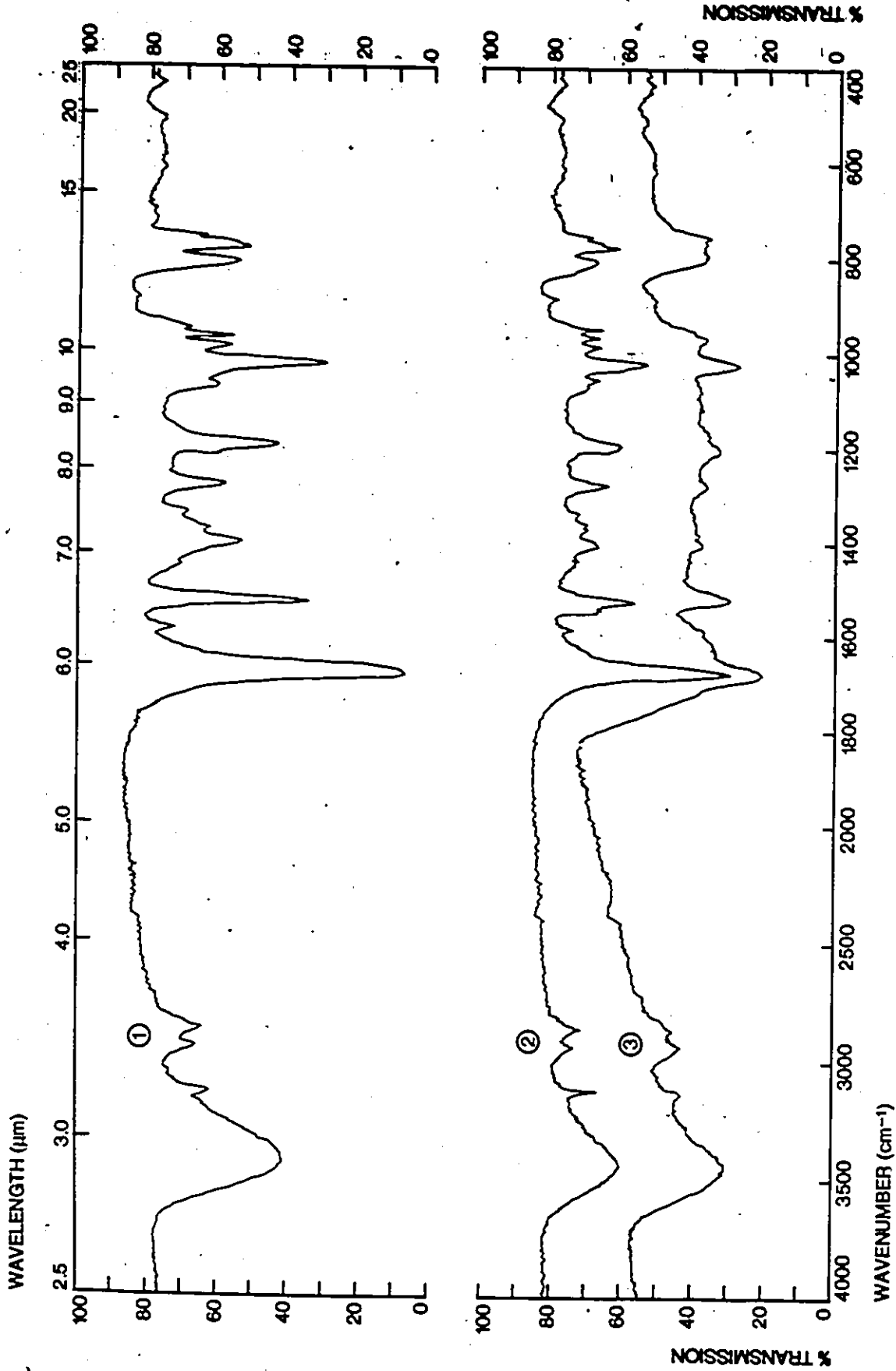


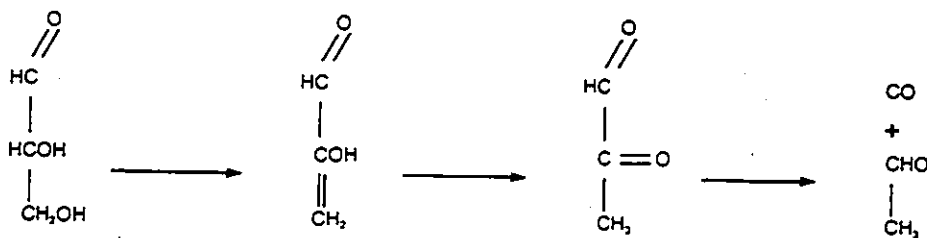
FIGURE 10. Infrared Spectra of 5-(Hydroxymethyl)-2-Furaldehyde Polymerization (KBr, Disc)

- 1) Starting Material
- 2) After treatment 30 min. at 230°C and 13.8 MPa
- 3) After treatment 120 min. at 230°C and 13.8 MPa

press, the furan derivative failed to insolubilize and its I.R. spectrum did not show any significant changes. After 120 minutes of that severe heat treatment the furan was insolubilized, but its I.R. spectrum still showed the large carbonyl band at 1680 cm^{-1} and was different from the I.R. spectra of the other polymerized carbohydrates.

The elemental analysis of DL-glyceraldehyde and its polymer presented on Table 6 indicates that glyceraldehyde polymerized through elimination of water. The polymer was resistant to hydrolysis by aqueous acid, perhaps due to the absence of hemiacetal or glycosidic bonds.

It has been reported that under action of heat alone, glyceraldehyde gives acetaldehyde as the largest product of degradation (53). The following mechanism of degradation was proposed by Fleury (55) and Shafizadeh (56):



Scheme 9. Glyceraldehyde degradation.

Table 6. DL-Glyceraldehyde condensation product
elemental analysis

Sample	Elemental Analysis			Boil in H ₂ SO ₄ 20 h. Reducing Sugar %
	C %	H %	O %	
DL-Glyceraldehyde	40.6	6.7	52.7	100
DL-Glyceraldehyde 240°C - 10 Min	59.1	5.1	35.8	0
(Calculated) DL- Glyceraldehyde, less 1.5 Mole H ₂ O	57.1	4.8	38.1	-

Under the action of heat and pressure, glyceraldehyde can dehydrate with formation of a highly reactive α, β unsaturated aldehyde which would readily polymerize to the infusible stage. The polymerization can occur with participation of both unsaturated and aldehyde function. Methylglyoxal is also very reactive and was reported to polymerize at 72°C (57).

LIGNOSULFONATE -- CARBOHYDRATE POLYMERIZATION

The thermal polymerization of SSL proceeds with contributions from both lignosulfonate and carbohydrate. Pure anhydrous carbohydrate can be used as binder, provided high temperature and long press time are used. A fast curing resin was obtained by mixing carbohydrate and NH_4SSL in the ratio of 55:40.

It is known that NH_4SSL decomposes at high temperature with release of SO_2 (8). It was suggested that lignosulfonic acid is the intermediate in desulfonation of NH_4SSL (3) the strong sulfonic acid would catalyse the dehydration of sugar and further polymerization of SSL. Recently Laamanen (58) has made some thermoanalytical studies on lignosulfonate and suggested that NH_4SSL dehydrates with formation of lignosulfonamide, in accordance with the following equation.



Scheme 10. NH_4SSL Dehydration




To gain further insight into carbohydrate - lignosulfonate polymerization, the effect of acid catalysis on carbohydrate polymerization, and lignosulfonic acid formation from NH_4SSL was studied.

A series of molded discs were made using glucose as resin binder in the presence of several different catalysts. The test results are summarized in Table 7. It is evident that adding acid catalyzes the curing of carbohydrate. A rough correlation can be observed between the strength of the added acids and their catalytic effect on the curing rate.



Qualitatively, similar results were obtained by Houminer and Patai (59) who studied the weight loss on thermal decomposition of D-glucose in the presence of various acids and salts. The sensitivity of the resin's curing rate to moisture further confirms that water is a product of the reaction. These results also suggest that ammonium lignosulfonate would not decompose through formation of sulfonamide since P-toluene sulfonamide did not catalyze polymerization of glucose while adding P-toluene ammonium sulfonate did catalyze the polymerization of D-glucose to some extent. However when NH_4SSL was mildly pyrolyzed (200°C, 10 minutes) no trace of lignosulfonic acid was detected and as shown on Table 8 NH_4SSL decomposed with the loss of sulfur and nitrogen in a 1:1 molar ratio. Addition of glucose to NH_4SSL increased the weight loss on

TABLE 7. D-GLUCOSE CONDENSATION CATALYST

CATALYST	CATALYST % DRY D-GLUCOSE AT 40% H ₂ O SOLUTION	PRESS TEMPERATURE °C	T.S., Nm
NIL	0	230	5.1
NIL*	0	230	0
HEXAMETHYLENETETRAMINE	5	220	0
(NH ₄) ₂ CO ₃	5	220	0
CH ₃ -  -SO ₂ NH ₂	5	220	0
CH ₃ -  -SO ₃ NH ₄	5	220	2.1
H ₂ NCH ₂ CH ₂ COOH	5	220	0
NH ₄ HSO ₄	5	220	2.8
 -SO ₃ H	2	210	8.5
H ₂ SO ₄	2	210	8.6

* 10% Moisture content, all others were anhydrous.

Table 8. Thermal decomposition of D-Glucose - NH₄SSL
210°C, 10 minutes

Sample	Initial Reducing Sugar %	Weight Lost %	S% Loss Mole/g x 10 ⁻³	N% Loss Mole/g x 10 ⁻³	OCH ₃ % of Initial Weight
NH ₄ SSL PM 10 > 30,000	6.0	5.8	21.0	21.5	12.5
NH ₄ SSL PM 10 > 30,000 + D-Glucose (1:1)	50.0	12.0	11.2	10.8	6.4
D-Glucose	100.0	0.5	-	-	-

pyrolysis because of sugar dehydration. The amount of nitrogen or sulfur lost was not affected. These results suggests that lignosulfonic acid formation is not required to catalyze the dehydration of the carbohydrates and further SSL polymerization.

It should be noted that the protons needed for the polymerization of SSL may be provided either by organic acids formed in the degradation process or by the "acidic" ammonium salt itself, or both.

CONCLUSION

These experiments clearly demonstrate that carbohydrate and sulfonated groups can both contribute to the polymerization of SSL. Dehydration of the carbohydrates is catalyzed by ammonium lignosulfonate or lignosulfonic acid which are both acid catalysts. Under a combination of heat and pressure an intermediate, presumably the acyclic unsaturated aldehyde, can readily homopolymerize and copolymerize with lignosulfonate and desulfonated lignin via participation of both aldehyde and carbon-carbon double bond functionalities. Since the exact mechanism of carbohydrate - lignin condensation is unknown, further studies on SSL polymerization are required.

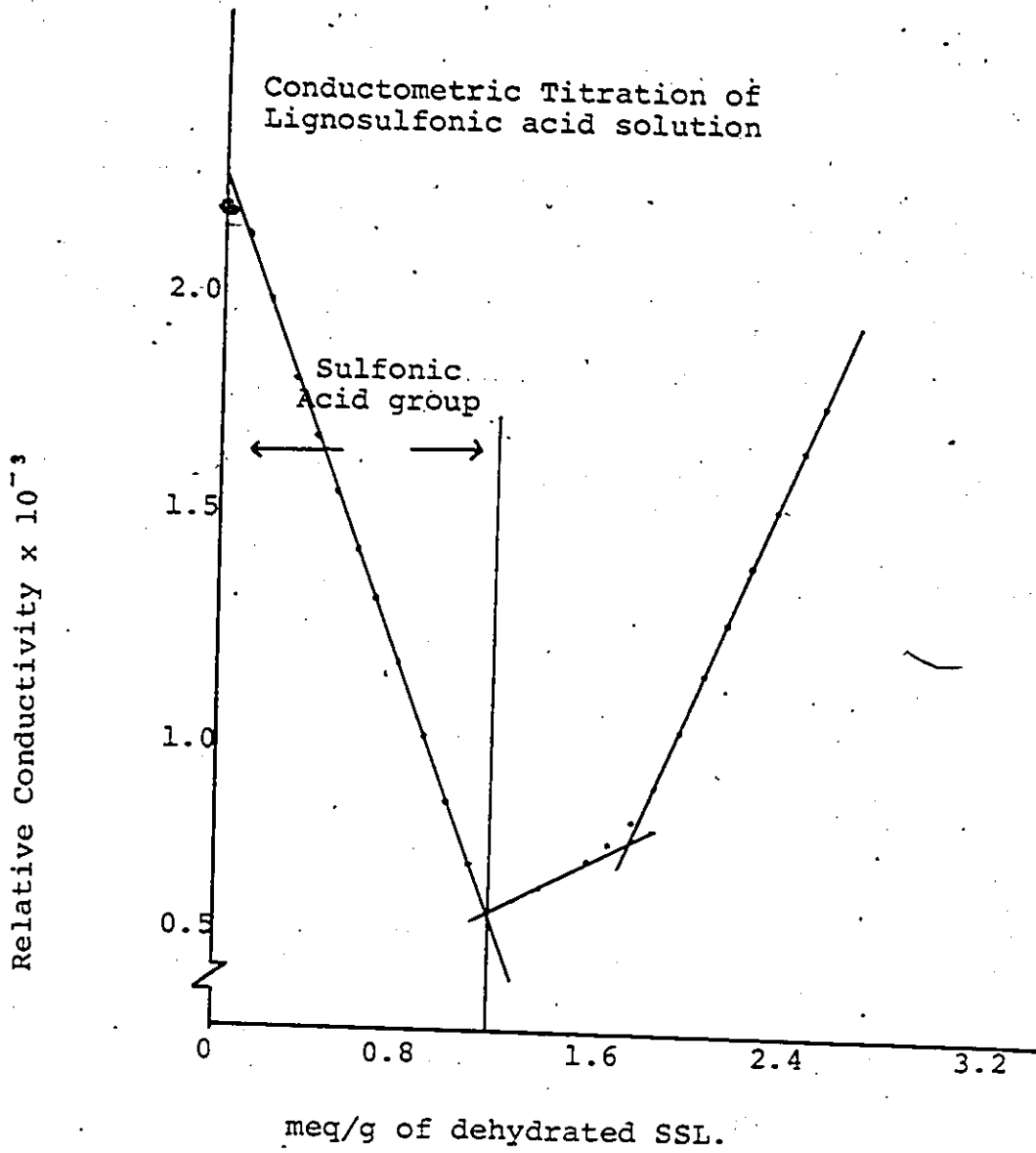
EXPERIMENTAL

METHOD OF ANALYSIS

1. Solids content was determined by TAPPI Standard Method TM 629M-53. Weight instead of volume was used for calculation.
2. Amount of reducing sugars was determined by the Swedish Method CCA-11 suggested by Yorston (60-61).
3. Hydrolysis of polymerized glyceraldehyde was carried out in 0.5N H₂SO₄ at 100° for 20 hours. Glucose was used as control (62).
4. Lignin was determined in aqueous solutions based on their absorbance at 280mm, using a Pye Unicam U.V. spectrophotometer model SPG-400. A calibration curve was made using a pure sample of spruce lignosulfonate (RAS II) supplied by Dr. W.Q. Yean (63).
5. Nitrogen was analyzed by the Dumas method in a Coleman Nitrogen analyzer Model 29.
6. Sulfur was analyzed by TAPPI Standard Method TM 629 M-53.
7. Methoxyl, carbon and hydrogen analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

8. Lignosulfonic acid was determined by conductometric titration of a solution containing 1.000 g of the SSL resin at 25°C with 0.1N NaOH through a method similar to that of Kyogolsu and Hachihama (6) (Figure 11).
9. Ash content was determined on SSL powder ignited in a crucible at 800°C for 16 h.
10. The calcium content of CaSSL powder was determined according to the official method of analysis of the Association of the Analytical Chemists (64).

Figure 11



RESIN ORIGIN

Two SSL liquors were obtained, from two different Canadian mills. CaSSL was supplied by Reed Ltd., Quebec City, Quebec. NH₄SSL was drained off from the digester of a mill owned by the Canadian International Paper Company at Hawkesbury, Ontario. Carbohydrates and derivatives were obtained from chemical suppliers.

RESIN EVALUATION

The resin was evaluated in liquid or powder form, with or without catalyst, by production and evaluation of a molded disc.

Excluding the resin formulation and the press conditions which may vary, the same general procedure was used.

RESIN - WOOD BLENDING

A binder was used for both powdered or liquid resins at 10% of dry weight of wood particles. Poplar wood particles of average dimension, 11.0 x 1.0 x 0.3 mm, were obtained by hammermilling veneers and dried to zero percent moisture. Powder resin was added to wood particles at 10 percent of wood dried weight and mixed with a rotary blender. Where liquid resins were used, the liquid was

sprayed-on wood during blending, the solvent if any was removed later with a stream of preheated air at 80°C.

PRESSING OF RESIN COATED PARTICLE

Resin coated particles (22.7 g) were introduced into a cylindrical mold (56 mm diameter) preheated at 210 to 240°C as desired and the press, illustrated on figure 2, was then closed to stop (11 mm) for 10 minutes using a hydraulic pressure of 68.9 MPa. Only one disc size (56 mm diameter by 11 mm) and one density 0.80g/cm³ was used in this study.

RESIN TESTING

The internal strength of the disc or the degree of curing of the resin, was evaluated by means of a Torsion-shear technique as illustrated in figure 3. A specimen of 25 x 25 x 11 mm cut from the center of the disc was immersed in boiling water 30 minutes. The specimen was cooled 30 minutes in water at 20°C and its mechanical strength measured with a standard torque wrench equipped with 25 mm wrench sockets. For every binder formulation, 3 discs were made and all the data appearing in this study is the average of three T.S. measurements.

RESIN FORMULATION

Powder

All the powder was obtained by spray-drying or freeze-drying SSL or was directly purchased from chemical suppliers. These were ground with mortar and pestle to pass a 100 mesh Tyler sieve before being mixed with wood in a rotary blender.

The glucose - SSL mixture was also mixed uniformly with a mortar and pestle, to pass through a 100 mesh Tyler sieve.

Liquid

Liquid formulation was used for studies described in Table 5 and 7 because some binders or additives were liquid at room temperature. The preparation of the solution was straightforward. The binder was dissolved in water or methanol at 40% solid content and the desired quantity of catalyst (calculated on the binder weight) was added to the solution while stirring.

CALCIUM SPENT SULFITE LIQUOR (CaSSL) ACIDIFICATION

A - Four batches of CaSSL were acidified respectively with 2,4,6 and 8% of concentrated sulfuric acid, based on SSL solids, to convert calcium lignosulfonate to lignosulfonic acid and calcium sulfate. Calcium sulfate

could be removed readily by filtration. The filtrates, containing mainly lignosulfonic acid, were dried to powder. A laboratory spray-dryer (BOWEN No BE-1031), at a feed rate 100 ml/min and a temperature of 135°C at inlet and 95°C at outlet, was used to produce the SSL powder in this study. The lignosulfonic acid content was determined on the powder by conductometric titration.

B - A control was made using ion-exchange resin to release all the available lignosulfonic acid from calcium spent sulfite liquor. A 400 ml portion of CaSSL at 25 percent solid was eluted with water through 800 ml of Rexyn-101-H. (Fisher Scientific Co.) (Rexyn bed capacity of 2.1 meq/ml). The resin was contained in a 3.5 cm x 150 cm vertical pyrex glass column. The eluted lignosulfonic solution (HSSL) was transformed into 65 g of powder by spray drying.

Ash Content 0.02%

Calcium Content 0.11%

NH₄SSL FRACTIONATION

A - the NH₄SSL liquor was fractionated with a thin-channel ultrafiltration system TC5E from Amicon (Figure 1) using successively Diaflo Membrane PM-30, UM-10 and DM-5 with respective nominal molecular weight cut offs of 30,000, 10,000 and 5,000 (Figure 6).

Thus NH₄SSL (20 kg) at 10% concentration was diafiltrated and washed with 60 kg of distilled water through a PM-30 membrane. The retentate (20 kg) having a nominal molecular weight over 30,000 was concentrated at 50% solids. The permeate (60 kg) was concentrated at 10% concentration and diafiltrated with three volumes of water through UM-10 membrane. The retentate having a nominal molecular weight between 10,000 to 30,000 was concentrated at 50% solids. The permeate (60 kg) was concentrated at 10% solids and again diafiltrated with three volumes of water through DM-5 membrane. The retentate and permeate having respectively nominal molecular weight 5,000 to 10,000 and 0 to 5,000 were concentrated to 50% solids with a vacuum rotary evaporator at 65°C and 5 mm of mercury. The fourth fraction was further transformed into powder by spray-drying.

B - Low molecular weight NH₄SSL with nominal molecular weight 0 - 5,000, was further fractionated by elution through ion-exchange resins. A sample of ammonium lignosulfonate of 400 g at 25% solids was eluted with distilled water through 800 ml of Rexyn - 101-H (Fisher Scientific Co.) in its acid form (Rexyn bed capacity of 2.1 meq/ml). The solution was then neutralized to pH 5 with ammonium hydroxide and freeze dried. A sample of

NH₄SSL of 42 g solid containing 62% reducing sugar was obtained.

GLYCERALDEHYDE POLYMERIZATION

A portion of 5.0 g of DL-glyceraldehyde was introduced at the center and in the middle of two teflon sheets with a size of 60 x 60 cm. The teflon sheets were placed between two plywood sheets size 60 x 60 x 0.6 cm and pressed at 240°C for 10 minutes under a pressure of 20.7 MPa with a press of the same dimension. A glyceraldehyde condensation product of 2.6 g was recovered. Elemental analysis, acid hydrolysis and reducing sugar content was performed on the residual polymer and on the starting material and their respective I.R. spectra were recorded. The same treatment was given to D-glucose and 5-(hydroxymethyl)-2-furaldehyde excepted that the furaldehyde derivative was pressed for 20 and 120 minutes. Infrared Spectra of residual polymers and starting materials were recorded.

2-FURALDEHYDE HEAT AND PRESSURE TREATMENT

In a 400 ml pressure reactor, a portion of 20 g of 2-furaldehyde was pressurized at 24.1 MPa with compressed nitrogen and immersed in a bath of oil at 175°C for 16 hours. The sample was still soluble in acetone

after treatment and was used to make discs.

PYROLYSIS

Purified NH_4SSL of nominal molecular weight of 30,000 was dried in a vacuum oven at 60°C and 5 mm mercury to constant weight. A known weight of 0.0600 g of the dried sample was placed in the combustion boat which in turn was placed in a pyrolysis unit (Lindberg HVI-Duty S.B.) preheated at the selected temperature. The sample was heated at 210°C for 10 minutes, its weight loss was recorded and elemental analysis was performed on the residual powder. Every data appearing in the study is an average of three experimental measurement. Pyrolysis of anhydrous D-glucose and pyrolysis of a mixture of purified NH_4SSL (M.W. > 30,000) and D-glucose (50:50) was also performed under identical conditions.

CLAIMS TO ORIGINAL WORK

1. NH_4SSL was purified and different fractions of known molecular weight were examined.
2. Fractions containing highly purified lignosulfonate of narrow molecular weight range as well as fractions containing a large concentration of carbohydrate were obtained.
3. The major constituents of the NH_4SSL liquor (lignin, reducing sugar) were analyzed for each fraction.
4. The thermosetting and binding properties of each SSL fraction were evaluated using molded disc and Torsion-shear Test Methods.
5. Highly purified lignosulfonate of different molecular weight ranges did not thermoset under action of heat and pressure.
6. Pure anhydrous carbohydrate was dehydrated and produced a resin binder without use of a catalyst.
7. Addition of pure ammonium lignosulfonate to a carbohydrate increased the rate of polymerization of the carbohydrate.

8. A fast curing binder was produced by adjusting the carbohydrate to lignin ratio by both ultra-filtration or simple addition of a carbohydrate to the NH_4SSL .
9. The relation between monosaccharide carbon length, functional group, structure, and ability to polymerize was examined.
10. Glycerinaldehyde was polymerized under action of heat and pressure and the polymer was characterized.
11. A direct relation between acid strength of catalyst and rate of curing of carbohydrate was shown to exist.
12. A mechanism of polymerization of carbohydrates through acyclic unsaturated aldehyde condensation was proposed.
13. Ammonium lignosulfonate is transformed into its polymer without the formation of lignosulfonic acid as a stable intermediate.

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