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Extraction of Lignin from Wood with Triethylene Glycol

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THE LIGNIN AS OBTAINED from wood is available in large amounts in two different forms: (1) in solution as a by-product of the pulp industry, and (2) in solid form as a residue in wood saccharification processes. In the latter process during treatment of the wood with dilute mineral acids, lignin undergoes changes caused by polymerization or condensation and it also contains variable amounts of carbohydrate residues mixed or combined with it.

Lignin obtained from pulp mills in the form of waste liquor may be recovered by precipitation as salts of lignosulfonic acid, as a sodium salt, or as so-called thiolignin. Only a few mills isolate even a part of such lignin, because of the high recovery costs. However, alkali lignin such as "Meadol" and thiolignin such as "Indulin" are produced in limited quantity and have become commercially available. A tremendous amount of work has been done on these lignins in an effort to find means for the utilization of this cheap organic material; but the lignin problem is still very real. It is a serious problem because extant commercially available lignins do not possess physical and chemical properties which make them attractive to industry.

It is the purpose of this paper to report a summary of some results obtained with a lignin extracted from lignocellulosic material by triethylene glycol ($\text{HOCH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{OH}$). This lignin exhibits different physical and chemical properties than the lignins mentioned previously. These differences may help to find new uses for lignin and even to promote a new and more efficient pulping process.

In the spring of 1949, in the Forest Products Laboratory of the University of Washington, research under a grant from the Engineering Experiment Station resulted in the discovery that, under proper conditions of use, triethylene glycol will completely defibrate wood chips and dissolve lignin (Grondal and Zenczak, 1950). When the triethylene glycol extract is diluted with water a reactive lignin is obtained as a precipitate.

Isolation of the Lignin Complex

Any lignocellulosic material such as wood chips, bark, or sawdust, is heated for one to four hours at 120-140°C with triethylene glycol containing 0.2-0.4 per cent of catalyst. Experiments at the Forest Products Laboratory of the University of Washington have been carried out in an electrically heated stationary digester with a capacity of five gallons under ordinary atmospheric pressure. The cellulosic residue is filtered from the cooking liquor and is washed with triethylene glycol and water. The lignin present in the cooking liquor is precipitated by the addition of one to two parts of distilled water. The precipitated lignin is filtered, washed with distilled water, and oven-dried at 50°C. This general procedure of extraction of lignin by triethylene glycol must be modified, depending upon the type of material that is extracted and the end-properties that are desired.

In the case of pulp production, the characteristics and quantity of the catalyst are very important. Certain metal chlorides, hydrochloric acid, or hydrogen chloride can be used. If pulp of maximum strength and high yield is desired, the hydrogen ion activity must be kept at a minimum and controlled.

Delignification is essentially a surface reaction. The reaction proceeds rapidly at first and then slows down as the concentration of the solvent decreases and that of the solute increases in the immediate area of contact. Therefore, circulation of the extracting liquor and pressure are desirable, although most of our experiments were conducted with completely satisfactory results at atmospheric pressure with no agitation.

Recovery and Refuse of Triethylene Glycol

The mother liquor, after the separation of the lignin complex, contains triethylene glycol, water, small amounts of nonprecipitated lignin, and minor amounts of water-soluble carbohydrates. Due to the difference in vapor pressure and the relative volatility of water and triethylene glycol, water is easily distilled off, and the losses of triethylene glycol are negligible. Concentrated glycol, containing up to 10 per cent water, was, in some cases, reused as cooking liquor.

The stability of triethylene glycol is remarkable. No ester formation or other decomposition reactions were noticed. In some instances, the same triethylene glycol was reused twenty times with good results. No accumulation of sugars or lignin degradation products was observed. This fact may be explained in the following way: The triethylene glycol lignin precipitates in the form of very fine colloidal particles of high-sorption surface areas, and therefore, solubilized carbohydrates may be adsorbed on the surface of the freshly precipitated lignin complex, and removed from the triethylene glycol cooking liquor. Also, some volatile carbohydrate decomposition products are distilled off when the triethylene glycol is concentrated by distillation.

Extraction of Lignin with Other Glycols

A total of twenty glycols and glycol ethers¹ were investigated under the same conditions, as possible substitutes for triethylene glycol (Table 1). The majority of those tested were completely unsuitable as lignin solvents because esters were formed when even traces of acidic catalysts were present. Some have a decomposition point too low for the temperature required; others are only partly soluble in water which, of course, makes recovery difficult and expensive. Ethylene glycol, which is relatively stable and water soluble, extracts only a part of the lignin (Hibbert and Rowley, 1930). This may be due to the orientation of the molecules at the solvent-lignin interface. The fact that the molecular structure of an alcohol has a profound effect on its ability to extract lignin was noticed during an investigation of monohydroxy aliphatic alcohols by Aronowsky and Gortner (1936).

Characteristics of the Lignin Complex

The crude, wet triethylene glycol lignin complex is a light cream-colored paste readily dispersible in water. Water emulsions are readily prepared with the compound. If a triethylene glycol lignin solution is poured into an excess of hot water, a colloidal solution is produced which exhibits a strong Tyndall effect. This solution is very difficult to filter or centrifuge. To obtain a precipitate of larger particles, the procedure must be reversed, and water should be added to the triethylene glycol lignin solution. In this case cold water precipitates particles of smaller size; hot water precipitates larger particles or even causes melting of the lignin so that it may be collected as a water-soluble viscous tar.

In the dry state, triethylene glycol lignin is an amorphous powder. The color varies depending on the source, the fineness of the particles, and the

¹ These were kindly supplied by the Carbide and Carbon Chemical Corporation, the Dow Chemical Company, the Shell Chemical Corporation, and the Celanese Corporation.

No.	Name	Formula	Boiling point °C	Solubility in Water	Observed Results—Remarks
1	Ethylene glycol	HO-CH ₂ -CH ₂ -OH	197	complete	Chips only partly defibrated
2	Ethylene glycol monomethyl ether	CH ₃ -O-CH ₂ -CH ₂ -OH	201	complete	Chips only partly defibrated
3	Ethylene glycol monoethyl ether	C ₂ H ₅ -O-CH ₂ -CH ₂ -OH	135	complete	Boiling point too low. No defibration below boiling point
4	Ethylene glycol monobutyl ether	C ₄ H ₉ -O-CH ₂ -CH ₂ -OH	171	complete	No defibration
5	Ethylene glycol monophenyl ether	C ₆ H ₅ -O-CH ₂ -CH ₂ -OH	116	insoluble	Insoluble in water. Low boiling point
6	Diethylene glycol	HO-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -OH	245	complete	Chips defibrated less uniformly than in triethylene glycol
7	Diethylene glycol monomethyl ether	CH ₃ -O-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -OH	305	complete	Chips defibrated less uniformly than in triethylene glycol
8	Diethylene glycol monoethyl ether	C ₂ H ₅ -O-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -OH	202	complete	Only partial defibration
9	Diethylene glycol monobutyl ether	C ₄ H ₉ -O-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -OH	230	complete	No defibration
10	Propylene glycol	CH ₃ -CHOH-CH ₂ -OH	188	complete	Partial defibration, ester formation
11	Propylene glycol monophenyl ether	C ₆ H ₅ -O-CH ₂ -CHOH-CH ₃	241	insoluble	No defibration
12	Dipropylene glycol	CH ₃ -CHOH-CH ₂ -OCH ₂ -CHOHCH ₃	232	complete	Partial defibration
13	Dipropylene glycol monomethyl ether	CH ₃ -O-CHOH-CH ₂ -O-CH ₂ -CHOHCH ₃	241	complete	No defibration
14	Dipropylene glycol monoethyl ether	C ₂ H ₅ -O-CHOH-CH ₂ -O-CH ₂ -CHOH-CH ₃	193	complete	No defibration
15	Dipropylene glycol monophenyl ether	C ₆ H ₅ -O-CHOH-CH ₂ -O-CH ₂ -CHOH-CH ₃	241	insoluble	No defibration
16	Tripropylene glycol monomethyl ether	CH ₃ -O-C ₂ H ₅ -O-C ₂ H ₅ -O-C ₂ H ₅ -OH	242	complete	No defibration
17	Trimethylene glycol	HO-CH ₂ -CH ₂ -CH ₂ -OH	214	complete	No sign of defibration
18	Hexylene glycol	CH ₂ -COH-CH ₂ -COH-CH ₂ -CH ₂ -COH	198	complete	Esters formed, no defibration
19	Diethylene glycol diethyl ether	(CH ₂ -CH ₂ -O-C ₂ H ₅) ₂ -O	188	complete	No defibration
20	2,3-Butylene glycol	CH ₃ -CHOH-CHOH-CH ₃	182	complete	No defibration
21	Triethylene glycol	HO-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -OH	287	complete	Complete defibration

conditions of the cook, from a very light cream or light grey to light brown. Dry crude triethylene glycol lignin was purified by dissolving it in pure dioxane to give about a 10 per cent solution. The solution was centrifuged and decanted. The residue was suspended again in fresh dioxane and centrifuged as before. The lignin was recovered by pouring the solution into anhydrous ether. The precipitated lignin was washed with fresh ether, centrifuged, washed twice with pure benzene and petroleum ether. It was finally dried in the open air and in a desiccator under vacuum.

Triethylene glycol lignin purified and dried in this manner, has a "sintering" point ranging from 130°C to 160°C, depending upon the mode of its preparation. Water acts as a plasticizer, i.e., the "sintering" point is lowered. The low sintering point and light color is one of the properties distinguishing triethylene glycol lignin from commercially available lignins which are not thermoplastic, or which have sintering points of 210°C or higher (Plungvian, 1940).

Triethylene glycol lignin exhibits a desirable degree of solubility in a variety of solvents. It is soluble at room temperature in 95 per cent methyl or ethyl alcohol as well as acetone-water mixtures and other polar aliphatic solvents. Good solubility in some substituted aromatic compounds and in heterocyclic and dicyclic compounds is also apparent.

The solubility of this lignin in dilute sodium hydroxide and sodium carbonate and its insolubility in the bicarbonate, indicate that it is phenolic in character. It forms a large number of water-soluble and water-insoluble salts with different metals. About 25 per cent by weight of the crude triethylene glycol lignin is soluble at room temperature in chloroform.

By fractional precipitation from triethylene glycol solution, a large number of fractions have been prepared. These fractions differ in melting point, color, and solubility behavior. For instance, some chloroform-soluble fractions have melting points below 110°C.

Triethylene glycol lignin gives a very positive pink color phloroglucinol tests; after treatment at reflux temperature with 2 per cent HCl, this phloroglucinol reaction is not shown.

Numerous analyses to determine the methoxyl content of different fractions have been carried out using the Viebock and Schwappach method. Differences in the values were within one per cent of the methoxyl content of the purified original triethylene glycol lignin. The original triethylene glycol lignin extracted from Douglas fir wood contained 15.3 per cent methoxyl, although differences within one per cent were noticed in lignins produced under different cooking conditions.

Circular chromatograms prepared from triethylene glycol lignin on filter paper resolved into three different colored zones. This suggests that triethylene glycol lignin is a multicomponent complex.

All attempts to hydrolyze the assumed glycol radical have been unsuccessful, although it is known that methoxyl is easily split from methanol lignins. It is possible that triethylene glycol does not enter the lignin molecule and that the isolation of lignin by extraction with triethylene glycol is a catalyzed solvolytic cleavage of a polymer in a very suitable solvent. It is of interest to mention that lignin is not extracted from wood by pure triethylene glycol, even if the wood has been previously subjected to prolonged acid hydrolysis and then washed with water until it is substantially neutral.

Another property shown by the triethylene glycol lignin not possessed by other lignins is an ability to self polymerize under the influence of heat. This property has been demonstrated in wood-gluing experiments. Douglas fir veneers were glued with the triethylene glycol lignin under conditions similar to those used with hot-setting, phenol-formaldehyde glues. The triethylene glycol lignin was applied in the form of a water dispersion. Three-ply specimens of the conventional design used in shear testing were prepared and tested dry and after boiling, according to Douglas Fir Plywood Association Specifications. Both dry and boiled shear values and wood failures were equal, or, in some cases, better than average values obtained with commercial phenol-formaldehyde glues.

These tests suggest a possibility of the development of a superior inexpensive waterproof glue for plywood and a binder for hardboard. In the preparation of glues, Douglas fir or hemlock wood lignin was used, but similar results were obtained with a triethylene glycol lignin extracted from hemlock wood and Douglas fir bark.

TABLE 2
SOME SHEAR AND WOOD FAILURE VALUES OBTAINED WITH TRI-ETHYLENE GLYCOL LIGNIN GLUE

Panel	Dry Test		Wet Test	
	Shear (lb./sq. in.)	Wood Failure (per cent)	Shear (lb./sq. in.)	Wood Failure (per cent)
Three ply, 1/8 inch Douglas fir veneer	310	95	200	91
	270	90	185	90
	294	81	165	88
	248	75	190	84
	330	99	220	100
	260	90	170	100

The triethylene glycol lignin reacts with furfural, furfural alcohol, phenol, aniline, and formaldehyde, forming resins. Although some of these reactions have been reported for the alkali lignin complex in the patent literature, it is believed that triethylene glycol lignin, being more reactive, gives condensation products of different and more promising characteristics.

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