JOURNAL OF THE JAPANESE TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY

Vol. 4. February 1950 No. 1

COMMERCIAL LIGNINS (I)

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ABSTRACT

Lignins* from a number of sources are now being produced in commercial quantities in the United States from pulp mill wastes and from bark. Progress in the utilization of lignin is encouraging even though so far only a relatively small part of the amounts now being burned or wasted get to the market. The academic distinction between fundamental and applied research is being rapidly breached, establishing the properties of lignins as a basis for research in new applications. Properties such as surface activity, adhesion, rubber reinforcing, etc. are entering into promising industrial phases.

Lignin is produced in tremendous quantities in nature. It is the second most abundant component of practically all plant life, amounting to about 25% of most woods and 12-15% of most annual crops, both farm and wild.

That such an abundant raw material has been the subject of many scientific investigations is not surprising. In addition, it has been the target for discussion by many writers and prognosticators during the last two decades. Many unsuccessful attempts have been made to determine its exact chemical structure. More important perhaps are the numerous attempts to develop uses for lignin, particularly where its disposal is a nuisance in certain manufacturing operations. Only in the last twenty-five years has there been any marked success in consuming even some of the annoying wastes. The great bulk of the lignin available is, however, still untouched.

The function of lignin in plant life is not clear. Even its method of combination is a subject of considerable discussion. In 1947, during the first known conference specifically aimed at a discussion of lignin chemistry and utilization held by the Northeastern Wood Utilization Council (New Haven, Conn.) it was pointed out that information was still meager. Controversial discussions occur even on our basic knowledge of the subject.

SIGNIFICANCE OF THE WORD LIGNIN

As is known, in 1838 Payen isolated a substance which was distinct from the other constituents of wood. He called this material lignin. Since that time the term has been

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applied to a great multitude of materials. All have the same material, the non-cellulosic portion of plants, as a base. Because of variations in the starting material, and more important, in the methods of processing, many different lignins have been produced.

The only technical meaning of the word "lignin" is the empirical one of analytical chemist who states that lignin is that part of the plant which does not dissolve in concentrated acid under prescribed conditions.

The insolubility of lignin in sulfuric acid is a necessary qualification but not a sufficient description. Attempts to demonstrate uses for lignin have often been retarded by the multiplicity of substances labelled lignin. It may even be that a clearer realization of this fact by the numerous research workers trying to elucidate the structure of the lignin molecule would have reduced the number of their disagreements and debates, and seen them much further along than they are.

The word "lignin", standing alone can only be a generic designation. To minimize ambiguity it will be necessary for all workers to learn to qualify the term with words connoting both the source of the lignin and the means for its separation from that source. There is ample evidence that the properties of lignins vary with both process and source. Thus, we must learn to distinguish among sulfate pine lignin, sulfite spruce lignin, ethanol extracted spruce lignin, acid hydrolyzed corn cob lignin, etc.

THE ABUNDANCE OF LIGNINS

The total amount of all lignins produced annually by nature can hardly be estimated. Much is returned directly to the soil as plant life dies, falls to the ground, and slowly decays. It is estimated that the lignins in unused portions of farm crops in the U. S. A. amounts to over 30,000,000 tons annually. This also is returned to the soil, aiding in maintaining good growing conditions. Such lignins cannot be strictly termed a waste.

In the lumber industry, a large part of the lignins are essential to the final product, and are thus used. However, 7,500,000 tons are present in saw mill wastes in the U.S.A. alone. Small amounts of the saw mill waste are made into wood flour, or go into other uses. Most of it is burned as fuel, merely as a means of disposal. The lumber industry in the U.S.A. also produces an estimated 15,000,000 tons of woods waste. This, however, is not a true waste, since it returns to the soil.

The most readily available large sources of lignins are those associated with the production of wood pulp for paper. The amount of lignins available from American pulp mills is estimated at 3,500,000, tons annually. Some pulps, such as mechanical and some semi-chemical, retain all or most of their lignins, and thus do not contribute substantially to the readily available supply.

The total amount of lignins separable from cellulose is between 50 and 60% of the quantity of pulp produced by chemical processes. Wood pulp production in the U. S. A. has been increasing rapidly, and is now close to 12 million tons per year; of this sulfate amounts to about 50%; sulfite 22%; soda 4%; groundwood and semi-chemical pulping account for remainder. Pulp production has trebled in 25 years.

Most of the wood pulped consists of softwoods, although the use of hardwoods has been increasing and it is estimated that over a million cords of it will be pulped in North America in 1950. In general, most of the wood pulped by the sulfate processes is pine,

and this gives some idea of the importance of pine. There is, however, an ever increasing trend toward the use of more hardwoods throughout the world, evidenced by the fact that today's world consumption is almost ten times larger than before the war. This is brought about by a decreasing supply of conifers even in the areas which were predominantly covered by them, coupled with the development of better techniques for utilizing hardwoods.*

A potential source is the residue from wood hydrolyzed as the first step in the production of sugars or alcohol, the so-called Scholler lignin. The ligneous residue resulting from the acid hydrolysis of wood for the production of sugars, alcohol or yeast is also a nuisance. But the process is worth only in special cases or locations in comparison with other methods for producing alcohol unless an appreciable income can be derived from the lignins. There are no American plants in operation on this process at the present time, so the economics are not too clear. In the early stages of the development it was estimated that 1¢ profit per pound for the lignins would be sufficient to make the process self-supporting under American conditions, and this much heralded wood hydrolysis project for alcohol production never got into full scale production. It was a war time measure, and may perhaps only be fully operated in case of emergency, although efforts are now being made to use the existing plant for the manufacture of wood "molasses" for cattle feed.

A lignin is also available in the manufacture of furfural from oat and rice hulls and corn cobs. The furfural residue lignin is a development of the Quaker Oats Company and Industrial Solvents Corporation. As much as 400 tons per day are reported to be available.

Another type of lignin offered for sale, from high temperature steam pulping for the production of fiber board, is relatively less important. It is at present available from only one company, and little is known about it. Bark is also available in huge tonnages as a possible source of lignins.

LIGNIN SOURCES

The types of lignins offered commercially in the U.S.A., their trade names, and manufacturers are given in the table which follows. Since the wood hydrolysis process could be operated at any time, it is included for completeness. The properties and manufacture of the lignins are considered in detail later.

Table: COMMERCIAL LIGNINS

PROCESS	WOOD (where distinctive)	TRADE NAMES	MANUFACTURERS
Acid Hydrolysis		(Scholler Lignin)	U.S. Gov't or lessee (not operating at pres.) Timber Engineering Co.
		Teco Lignin (Treated Scholler Lignin)	
	Oat Hulls	Isofil	Quaker Oats Co.

*The authors have made several hardwood pulping installations and believe that the neutral sulfite semi-chemical process is among the best adaptable for this purpose. This process, however, gives rise to smaller amounts of lignin residue, which is less readily recoverable.

PROCESS	WOOD (where distinctive)	TRADE NAMES	MANUFACTURERS
Steam Hydrolysis Soda	Rice Hulls		(Industrial Solvents Corp.)
	Corn Cobs		Masonite Corp.
	Coniferous	Benaloid	Mead Corp.
	Deciduous	Meadol	Howard Smith Paper Mills (Canada)
Sulfate	Coniferous	Tomlinite	West Virginia Pulp & Paper Co.
		Arborite	International Paper Co.
Sulfite		Indulin	Robeson Process Co.
		Binderene	Marathon Corp.
		Goulac	
		Glutrin	
		Marasperse	
Mechanical	Douglas Fir Bark	Maratan	
		Silvacon	Weyerhaeuser Timber Co.

CHARACTERIZING LIGNINS

Lignins are thus available from many woods and can be produced by many processes. The various lignins have been made in sufficient amounts and enough comparative experimental work has accumulated to allow a general description of lignins.

The first characterization that might be applied concerns their purity. We now know that many commercial lignins contain considerable quantities of substances which are definitely not lignin. Thus, Scholler lignin contains pentoses, hexoses and their polymers, undissolved cellulose, resins and many other identifiable substances.

What then are lignins? It is not the purpose of this paper to go into the structure of lignins, as the subject has been covered by many others in several countries.

Lignins are friable solids without any visible structure, that is, they appear amorphous even under a microscope. They have a density of 1.3 and a refractive index of 1.6. They are usually brown in color, though specimens of very light colors have been isolated from some woods by solvent extraction.

Lignins are insoluble in water, mineral acids, and hydrocarbons. They are soluble in aqueous alkaline solutions and in many oxygenated solvents and amines. Lignins form irreversible gels with water and these have marked dilatant properties.

The elementary composition of lignins ranges from 61 to 65% carbon, 5.0 to 6.2% hydrogen and the balance oxygen. From a recent discussion sponsored by the Northeastern Wood Utilization Council, most chemists appear to agree that the Structure is at least partly aromatic. Lignins appear to consist of a mixture of polymers of a monomer molecular weight 840-880. The monomer is characterized by one phenolic hydroxyl and a number of alcoholic hydroxyl groups resembling secondary or tertiary alcohol groups. A variable number of methoxyl groups are also present. The number of methoxyls appears to depend on the source of the lignin and the treatments used for its separation.

Thus, hardwoods, yield lignins containing more methoxyl than softwoods. The 20-21% of methoxyl in hardwood lignins corresponds to six methoxyls per monomer; the 14-15% methoxyl in softwood lignins suggests four methoxyls per monomer.

The above description is sufficient for chemists to identify lignins in commerce and, more important, to consider a wide variety of uses.

Investigations in progress at the Polytechnic Institute of Brooklyn show that samples of the principal commercial lignins are now fairly uniform when tested in various ways.

LIGNINS FROM SULFITE WASTE LIQUOR

While the sulfite pulp industry is not a direct source of lignins it is an abundant source of a derivative of lignins—the ligninsulfonic acids contained in the sulfite waste liquor. These sulfonic acids have long had a number of uses. Ligninsulfonic acids can be more or less completely desulfonated to yield lignins and some lignins are being made in this way in connection with the manufacture of vanillin from sulfite waste liquor.

The most obvious difference between lignins and ligninsulfonic acids is that the latter are extremely water soluble while lignins are insoluble in water.

The sulfite pulping process, as commonly practiced utilizes only about 50% of the wood raw material. The nonfibrous wood components solubilized in the cooking process, including the lignins, are allowed to run to waste in most mills.

This waste in the U.S.A. alone totals about 2,500,000 tons of solids annually. Of this about 60%, 1,500,000 tons, are ligninsulfonic acids; sugars amount to another 400,000 tons. The rest is accounted for by about 150,000 tons of sulfonated sugars, 100,00 tons of aliphatic acids, mainly formic and acetic. The balance, 350,000 tons, is largely calcium and sulfur compounds.

It is becoming imperative for acid sulfite mills to find outlets for their lignins which will not be so burdensome as to force them out of business. The practice in the past was largely to dump the lignin-containing material into adjacent streams and rivers. This was found to be a nuisance as it killed or harmed wild life in and about the waterways. Recent federal legislation on the subject is increasingly strict. Many state legislatures have passed, or are considering the passage of, laws forbidding or restricting such dumping.

The calcium lignosulfonates in sulfite waste liquor are believed to be polymers in which the molecules of calcium lignosulfonate vary in size as is evidenced by diffusion, salting out and viscosity studies. It has thus been estimated that molecular weights of calcium lignosulfonates in sulfite waste liquor vary from 2,000 to 15,000. The sulfonic sulfur content of calcium lignosulfonates vary from one sulfur per two building units to one sulfur per four monomer units.

Calcium lignosulfonates undergoes many characteristic reactions. Thus they may be alkylated, halogenated, nitrated, hydrogenated, oxidized and hydrolyzed in either acid or alkaline mediums. These reactions are of commercial importance, as in the alkaline hydrolysis of calcium lignosulfonates for the production of vanillin, acetovanillone, catechol, guaiacol and other phenols.

Sulfite waste liquor has long found a number of limited uses based on its physical and chemical properties. In most cases these valued properties cannot be attributed specifically to the lignins or ligninsulfonic acids present. Thus, the liquor concentrated by evaporation is used as an adhesive ingredient of linoleum cements and as a binder as in making some types of cores and molds for casting metals. It is unlikely that the ligninsulfonic acids are anymore valuable than the sulfonated sugars for these purposes.

The lignosulfonates are known to be surface active and sulfite waste liquor has found a considerable number of applications as a dispersing, wetting or emulsifying agent.

The search for large scale uses for sulfite waste liquor continues. Only a small portion of the available supply is being utilized. Sulfite waste liquor is offered in the

form of a dry powder, as "lignin pitch" and in syrup form containing about 50% solids, as "lignin liquor", by a number of manufacturers. In addition to calcium base sulfite waste liquor, the sodium and magnesium base liquors, as well as liquors comparatively free of bases are available. Liquors of reduced fermentable sugar contents are also being sold. Until an economical process for recovering lignins from sulfite waste liquor is developed, the people requiring large tonnages of lignin itself can consider sulfite waste liquor only as a potential source of supply.

LIGNINS AND VANILLIN

The ligninsulfonic acids in sulfite waste liquor can be converted to vanillin and if more used could be developed for vanillin and its related compounds this means of utilizing sulfite waste liquor could come into general use.

The Marathon Howard process, operated commercially since 1937, reduced to practical use some of the many researches relating to lignin and vanillin. It also made practical the separation of lignin sulfonates from the other ingredients of sulfite waste liquor. Only one vanillin plant is operating in this country and the sulfite waste liquor from the Marathon Paper Mills at Rothchild, Wisconsin could supply the world's current needs for vanillin.

Vanillin can also be made from other lignins or lignin containing materials. Only the lack of large scale uses retards such developments.

THE MARATHON HOWARD PROCESS

This process is of interest not only for the manufacture of vanillin but also for the ligninsulfonates that it makes available. The Marathon-Howard process is a fractional precipitation procedure whereby the sulfite waste liquor is drained off from the cellulose fibers in the blowpit and processed by the controlled addition of lime. The first fraction, obtained by adding lime to the raw sulfite waste liquor in amounts to the raw sulfite waste liquor in amounts to give a pH of 10.5 is separated as a sludge in a settling tank. This sludge, consisting of calcium sulfite and lignin fraction, is returned to the sulfite mill as part of the make up system for producing calcium bisulfite cooking acid. The overflow from the settling step is treated with additional amounts of lime reagent to produce a flocculated yellow precipitate of basic calcium lignosulfonate which is continuously separated on a rotary vacuum filter as a filter cake of 30 to 35% solids. The filtrate from this operation is given a stripping treatment with lime, producing a sludge which is returned to the first stage in the process and a clear effluent which is passed into the river. This effluent has a B.O.D. value of only a third of that of the untreated waste liquor. The basic calcium lignosulfonate filter cake comprises from 60 to 80% to the lignin present in the waste liquor, and is the starting material for numerous lignin products and derivatives produced in commercial quantities at the Marathon Company plant in Rothschild, Wisc. The use of such lignin starting material has the following important advantages: 1) The product gives completely water-soluble lignosulfonates when either neutralized, acidified, or treated with alkali, and such solution has a concentration of 27 to 30% solids. 2) The basic calcium lignosulfonate filter cake is essential-

ly free from carbohydrates and other non-ligneous organic matter and the solubilized products from it may be conveniently dried to non-hygroscopic, free-flowing powders. 3) The basic calcium lignosulfonate obtained from the described lime precipitation process is a fairly well defined fraction of lignosulfonates from which the low as well as the high molecular weight lignosulfonates are absent. This is of value for various industrial applications.

Through processing of the basic calcium lignosulfonate, a number of water soluble lignosulfonates have been produced and are available commercially in carload quantities. Thus the neutral calcium lignosulfonate is used as a dispersant under the trade name "Marasperse C". Various grades of sodium lignosulfonates are used as a dispersant and boiler water treating agent. A magnesium lignosulfonate blended with specific vegetable tans is marketed as a tanning agent. The basic calcium lignosulfonate is also in part passed through a press which reduces its moisture content to around 50 to 55%, and thence through a tube dryer to produce a black, granular product sold as Maratex, and used as a grinding aid and binder.

Part of the basic calcium lignosulfonate is also the starting material for production of vanillin. In this process the filter cake is mixed with caustic soda, which solubilizes it, and the resulting solution is subjected to a pressure cook with simultaneous introduction of air to produce a controlled oxidation. The cooked liquor is subjected to a liquid extraction with butanol. The vanillin which enters into the butanol phase is recovered from the solvent and purified to give a U.S.P. grade vanillin. The extracted cooked liquor contains partially desulfonated lignosulfonate from which a purified fraction is isolated and marketed under the trade name "Marasperse CB" as a dispersing agent, particularly effective for aqueous carbon black dispersions. Efficient boiler water treating agents are also produced by processing the extracted vanillin liquor.

English Abstracts

MOISTURE CONTENT MEASUREMENT BY ELECTRICAL METHOD. Mitsuo Ishida, Minoru Kometani & Hiroshi Kasai—A new instrument for moisture content of pulp or paper by electrical method has been designed. Variation in the amount of moisture in the pulp or paper changes dielectric properties. The electrostatic properties of the condenser is read from the meter, and by use of curve or table the moisture content is determined.

Test pieces of unbleached sulphite pulp and tissue paper of various moisture contents were tested with this instrument.

Then the moisture was determined by oven drying. This instrument is suited for quick test.

STUDIES ON THE LARCH WOOD PULPING. By Koichi Takamatsu—In Japan, the larch woods have many different properties according to their location, species and rate of growth.

The rate of growth is larger than the pine wood, so the larch wood can use for pulping about 15—20 years after plantation.

Chemical composition of larch wood are as following.

	splint wood	heart wood
Ash	0.43	0.52
Ether soluble	0.34	0.78
Alcohol soluble	0.72	1.69
Cold water soluble	1.80	5.90
Hot water soluble	2.06	6.50
1 % NaOH soluble	12.37	17.26