

PREPARATION AND UTILISATION OF LIGNIN BY-PRODUCTS AND LIGNOSULPHONATES OBTAINED FROM WOOD BLACK LIQUOR.

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ABSTRACT

Pulp and Paper industry is one of the major industry which produces huge quantity of high polymeric wastes. The discovery, in the latter part of the nineteenth century, that wood could serve as the principal raw material for cellulosic fibre, was the basis of modern pulp and paper industry.

Wood contains two of the most abundant naturally occurring organic polymers, Cellulose and lignin in the ratio 3:1 approximately. While Paper Industry utilises the cellulose fibre almost fully, hardly and serious attempt is made to convert lignin into its valuable by-products.

An attempt has been made, in this paper to review the potentiality of lignin by-products and their synthesis with an economic and practical approach. Lignin by-products are described in two categories viz. 1) Low molecular weight compounds and 2) Polymeric compounds e.g. lignocellulose and lignosulphonates.

Many paper mills in India discharge their lignin black liquor into rivers and lakes causing pollution problem and loss of valuable by-products.

However, it is not possible for these units to utilise the waste lignin for preparation of various chemicals e.g. lignin sulphonates and other industrial chemicals, since this involves expertise in Chemical Engineering and Fine Chemical manufacturer.

Hence in this paper an attempt has been made to highlight the possibility of utilizing lignin waste liquors, and possible alternatives have been suggested.

1. INTRODUCTION

Waste management is concerned with generation, onsite storage, collection, transfer and transport, processing, recovery and disposal

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of the waste from a technological society. Today waste management is a multidisciplinary activity that is based on engineering principles, but also involves economics, urban and regional planning. Technological advances have resulted in a change in emphasis in many important areas. While public health and economics remain primary considerations, great emphasis is now placed on environmental constraints. The relationship between resources depletion and the disposal of solid wastes is also coming under scrutiny.

Pulp and paper industry is one of the major industries which produces large quantities of polymeric wastes. Lignin is one of them. The only use of lignin until recent time was to burn it in Recovery boilers. Burning of lignin from spent liquor, at best, can give only marginal returns. But lignin on the other hand, can become a replenishable resource for a series of aromatic chemicals.

There is no denial that at present only a few simple chemicals are being produced from lignin. The difficulty lies in separation of pure lignin from spent liquor since the cost of separation of lignin from the large volume of water is uneconomical. It is further complicated by the fact that the isolated lignin is not pure but still contains ash, carbohydrates and extraneous materials. Thus an inexpensive method of separating pure lignin from spent liquor is the need of the hour. If this can be achieved lignin can become a competitive resource for fine chemicals.

2. STRUCTURE OF NATIVE LIGNIN

Wood contains approx. 20-35 % lignin. Although lignin is one of the most abundant natural macromolecule and is available at exceedingly low cost; it has received very little attention as a polymer. Lignin may be regarded as a family of three dimensional polymers, spherical in solution containing a variety of functional groups.

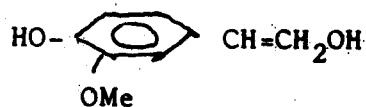
Elementary composition of lignin reveals that carbon content is between 63-67 %, hydrogen 5-6 % and oxygen 29-54 % of total lignin.

Further evidences from chemical analysis of functional group determination, the aromatic nature of lignin in site can be convincingly demonstrated as consisting of three or more phenyl propane units linked by different functional groups..

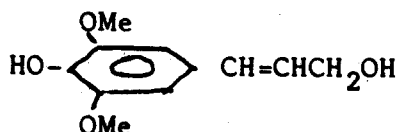


In simpler terms lignins are considered to be polymeric natural products arising from an enzyme initiated dehydrogenerative polymerisation of three primary precursors, viz.

1. Trans coniferyl



2. Trans sinapyl



3. Trans-P-coumaryl alcohols



In brief these three structures constitute so called 'Lignin core' and 'model compounds to represent a lignin monomer.

3. BY-PRODUCTS FROM LIGNIN

Generally by-products from lignin can be catagorised as follows:

1. Low molecular weight compounds
2. Polymeric products.

Table No.1 gives a detailed picture of by-products (both commercial and non-commercial) obtained from kraft cooking of wood using different methods of isolation, It can be seen from the table that the main by-products of kfta cook are the degradation products of carbohydrates and lignin. The most consistent efforts on dry distillation of the alkaline black liquor powdered together with excess lime or alkali, were made to obtain methanol,

acetone, methylethylketone, higher ketones and other components of light and heavy oils in appreciable quantity (60-70 Kg/ton of pulp each of the low molecular and high molecular compounds).

4. LOW MOLECULAR WEIGHT COMPOUNDS

The most practical approach to synthesis low molecular weight compounds from lignin is to heat the black liquor for 10-20 mins at 250-290°C together with small amount of alkali and sodium sulphide. Table No.2 covers the chemicals obtained during this process with their corresponding yield in Kg/PTP. Under optimum conditions (291°C, 20.4 % of organic substance, 3.2 % Na₂S and 1.6 % of the NaOH based on total liquor) a maximum yield of 33 % of the organic products can be obtained as ether soluble phenols.

Of all chemicals listed in Table No.2 the following chemicals are most important,

1. Vanillin
2. Organosulphur compound
 - a) Dimethyl sulphide (DMS)
 - b) Methyl mercaptans (MM)
 - c) Dimethyl sulphoxide (DMSO)
 - d) Dimethyl sulphone (DMSO₂)
3. Phenolic compounds.

4.1. VANILLIN

Vanillin is the most widely used flavouring agent, commonly known as vanilla, due to its pleasant aroma and its property of enhancing other flavours. Generally vanillin is synthesised from Guaiacol or eugenol. It can be produced from lignin through oxidation of spent liquor with suitable oxidising agent.

Commercial process based on alkaline oxidation of lignin with oxidising agent as cupric oxide, various nitrobenzene compounds, mercuric oxide etc. have reported a better yield of vanillin

from lignosulphonates. For example cupric hydroxide oxidation of lignin gives 22 % of vanillin at 160°C and 12.5 % at 102°C. In comparison a maximum yield of 23 % is obtained from nitrobenzene oxidation under optimum conditions of 1 hr at 180°C. Table No. 3 gives the product obtained by alkaline oxidation of lignin. While vanillin is the most commonly reported simple compound obtained by alkaline oxidation of lignin, there are a number of other products that are formed which may eventually prove to be of commercial interest.

Purification of vanillin is an essential step when synthesised from lignin. Most practical way to purify it is to distillate under reduced pressure or co-distillation with saturated hydrocarbon.

Vanillin has a wide range of industrial application. It is universally used as flavouring agent with a property to mask other odours. Vanillin also finds use as a reductant and as material absorbing ultraviolet light. It can be incorporated into various plastics such as regenerated cellulose, polyvinyl ethers and polyamides to protect them against ultraviolet radiation. Ointments for protection against sunburn on the skin can be prepared with vanillin as active agent. Polymeric materials prepared from vanillin and vanillic acid have potential as fibres and films.

4.2. ORGANO SULPHUR COMPOUNDS FROM LIGNIN

Depending upon the source of lignin whether softwood or hardwood, the methoxyl contents of kraft lignin varies from 14-20 %. Since methyl group represents about half of the weight of the methoxyl group, it is theoretically possible to recover 7-10 % of lignin calculated as methyl radicals.

The four major organosulphur compounds obtained from lignin are as follows:

1. Dimethyl sulphide (DMS)
2. Dimethyl sulphoxide (DMSO)
3. Dimethyl sulphones (DMSO₂)
4. Methyl mercaptans (MM)

The most important products are DMS and DMSO.

4.2.1. Synthesis of DMS

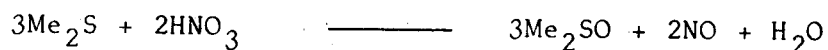
Method of production of DMS and MM is by heating kraft spent liquor with sodium sulphide at 200°C and to purify the product obtained. The yields of DMS are about 3 % and MM 0.2-3 per cent on lignin solids.

Commercial process consist of heating concentrated spent liquor with elemental sulphur to a temperature of 200-250°C. The DMS formed is flashed from the reactor along with some water, MM and H₂S and collected by means of a condensor. The crude DMS is scrubbed by passing it through Sodium hydroxide and distilled.

DMS itself does not find any application but is a precursor for its heloginated and oxidised derivatives.

4.2.2. Synthesis of DMSO

This is a compound obtained from lignin with a variety of applications in chemical and pharmaceutical industries. This can be commercially obtained by oxidising DMS by nitrogen-dioxide under optimum conditions. The reaction can be summerised as



The application of DMSO have extended in many fields. It has been used as a outstanding medium for promoting organic reactions and as a reactant solvent itself. The following points outline some of the most potential application of DMSO.

- 4.2.2.1. As catalyst: It is used as a catalyst and organic solvent for dyes and other chemical reactions.
- 4.2.2.2. Solubilizing reaction solvent: Since DMSO is an excellent solvent for many carbohydrate materials, it has found application in preparation of sugar derivatives.
- 4.2.2.3. Biological applications: DMSO also has found utility as a material to protect cellulose tissue from freeze damage. In

this case, it has been shown to penetrate the cell walls better than glycerine and thus prevents excessive concentration of electrolytes in the cell during freezing. It has also been used successfully to protect red blood corpuscles against freezing. Widespread interest in DMCO as a solvent for carrying drugs across cell membrane and as a drug itself have been developed.

5. POLYMERIC COMPOUNDS FROM LIGNIN

In many ways kraft lignin is a versatile raw material. It can be easily isolated by acidification, preferably carried out with carbon dioxide (stack gas), where by phenolic groups are liberated and lignin precipitates. The precipitated lignin can be removed by filtration at elevated temperature and purified further by redissolution in water and reprecipitation by sulphuric acid.

Chemical modification of kraft lignin drastically changes its properties and product obtained are of commercial value.

Common modifications can be summarised as follows:

1. Formation of ethers by reaction with alkyl/aryl halides.
2. Formation of esters by reaction with carboxylic acid.
3. Formation of polymeric condensation product with phenols, aldehydes and amines.
4. Conversion to sparingly soluble phenol derivatives in reaction with various salts of heavy metals.
5. Sulphonation to kraft lignosulphonates.
6. Nitration carried out with nitric acid.
7. Chlorination with aqueous chlorine.
8. Oxidation, with air or oxygen produces derivatives with changed solubilities and melting points.
9. Demethylation of lignin can be accomplished by acidic and alkaline treatment and results in the formation of catechol group increasing the reactivity in condensate e.g. with formaldehyde.

5.1. LIGNOSULPHONATES

This class of lignin polymers have attracted a great deal of interest because of their diversified uses. They can also be utilised as the base for industrial detergents such as washing powders and liquid soaps.

5.2.1. SYNTHESIS OF LIGNOSULPHONATES

Lignosulphonates can be easily prepared from purified kraft lignin by sulphonation with solutions of alkali sulphites at elevated temperature and pressure. Sulphite spent liquor contains lignosulphonates which are formed during pulping reactions. Practical approach to isolate and purify this compound is to remove most sulphite and sulphate by lime addition upto pH of 10.5, more lime is added to the filtrate to give basic calcium lignosulphonate which precipitates in the pH interval of 10.5 - 12.2. More than half the lignosulphonate is thereby removed and separated by filtration. By the addition of sulphuric acid and magnesium and sodium lignosulphonates can be obtained.

5.2.2. UTILISATION OF LIGNOSULPHONATES

Fundamental studies on the colloidal properties of purified lignosulphonates demonstrated their specific value for emulsification, deflocculation, chelation and adsorption uses. In addition to the use per se of lignosulphonates, they have been employed to some extent for the production of chemicals. Other major industrial application can be summarised as follows:

- 5.2.2.1. Oil well drilling muds: In the drilling of oil wells, water and dispersants are continuously fed into the hole, to form, together with suspended fine clay, called as 'drilling mud'. Oil in water emulsions in a drilling fluid have been in use since the 1940's. Lignin sulphonates are valuable for stabilizing these emulsions which give the mud improved properties in control of water loss, reduction of torque on the drill stem, increase of bit life and general improvement of bore hole condition.

5.2.2.2. Cement and concrete additives: Lignosulphonates are used grinding aids in cement and concrete. Their function is to reduce the agglomeration of the ground particles, to reduce surface tension at the solid-air interference of the particles and to keep the surface of the grinding media clean & free. These can also be used as air entraining agents in concretes. The entrained air gives increased resistance to spalling and cracking of the finished concrete. The dispersive action of lignosulphonates is useful in mixing and placing concrete. Incorporation of 0.07 - 0.15 kg of lignosulphonates-concrete admixture per sack of cement will allow water reduction upto 20 %. This results in better compressive strength and durable concrete.

5.2.2.3. Dispersants: Lignin sulphonate dispersants usually have a molecular weight in the range of 10,000 - 40,000. The colloidal lignin coat the surface imparting a negative charge to the particle. The similarly charged particles now repel one another and a good dispersion is obtained.

5.2.2.4. Emulsifiers and stabilizers: Lignin emulsifiers are quite competitive with other commercial emulsifiers stabilizing oil-in-water emulsions. The stabilization of fire fighting foams that results from the interaction of sodium bicarbonate solution and alum is achieved by an addition of sodium salt of kraft lignin. Better results can be obtained by using lignosulphonates.

5.2.2.5. Electrolytic Refining: Lignosulphonates have been successfully used as 'Brightening' agent for the plated surface preventing pitting and deposition of rough surface in electroplating.

5.2.2.6. Binders and adhesives: Large tonnage of spent liquor solids are used as binders for pellets and briquetts. 2% calcium lignin sulphonate in iron ore gives a pellet ten times as hard as that made with bentonite binder. The most familiar adhesive product is linoleum cement containing principally lignin sulphonates and clay. These cements are

also used as adhesive for ceiling tiles.

5.2.2.7. Resin ingredients: Combination of lignin sulphonates with low molecular weight urea and phenol formaldehyde resins have received attention as adhesive for plywood, particle and chip board. Many good quality glues can be produced by incorporating lignin sulphonates with polyvinyl acetate or alcohol.

5.2.2.8. Rubber additives: Many types of latices such as neutral nitrile and neoprene are compatible with lignin either in the acid or sodium salt form. Mixture of rubber with kraft lignin are also suitable for use as rubber to glass adhesives.

Other uses of lignosulphonates are as tanning agent sequencing agent (about pH 7), lime plastering medium and many more.

CONCLUSIONS

Although lignin and its chemical by-products are valuable, and can be used in a wide range of applications, no serious attempts have been made by the Indian Paper Industry to utilize lignins for various reasons.

Important amongst them are:

1. The Paper Industry is totally dependent upon the lignin black liquors as a source of energy fuel in Recovery Boilers.
2. In large integrated paper mills, efficient recovery of Caustic soda from Black liquors is crucial in order to operate the mills economically.
3. In medium and small paper mills, where recovery of Caustic Soda, from Black liquor is un-economical, further investment in establishing plants and machinery for extraction of fine chemicals such as Vanillin or DMSO, become highly capital intensive and also call for expertise in Chemical Engineering Organic synthesis.
4. Since paper mills are very often located in remote areas, easy and cheap access to lignin Black liquors is not possible for other units manufacturing fine chemicals.

5. Lignin sulphonates, the most popular and versatile by-product from lignin is produced in Sulphite/bisulphite pulping, which is not at all done in India except in one or two mills.

Sodium lignate readily available in kraft pulping(alkaline)in India, is difficult to convert into Lignin sulphonate.

6. Fine chemical manufacturers today prefer to synthesize vanillin and other chemicals through organic synthesis of easily available chemicals such as Guaicol or Eugenol, and not depend upon Lignin Black liquors.
7. Unlike a Sugar Mill - Bagasse Paper Mill Complex, which is considered feasible today, a sulphite/kraft pulp mill - Chemical manufacturing unit is not considered viable due to various socio economic constraints.

Thus in summing up, although lignin Black Liquors have excellent potential for reuse in Fine Chemical Manufacture. The Indian Paper Industry is not yet ready for such a drastic transformation, since it will jeopardize the Chemical Recovery Processes.

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TABLE - 1

BY-PRODUCTS(BOTH COMMERCIAL & NON-COMMERCIAL) OF THE KRAFT COOK

Compound	Origin	Quantity Kg per ton of pulp
Methanol	Methoxyl groups of lignin & possibly glucuronoxylan	5
Acetate	Acetyl groups of the xylan as well as degraded carbohydrates	100-200
Formiate	Degradation of carbohydrates	40
Lactate	Degradation of carbohydrates	100
Saccharinic acids & lactones	Degradation of carbohydrates	250
Aliphatic sulfur compounds(methyl mercaptan, sulfide, disulfide)	Methoxyl groups of lignin and possibly glucuronoxylan	1
Turpentine	Terpenes	8-10
Tall oil(fatty & resin acid salts, phytosterols, etc.)	Wood resin components	20-100
Alkali lignin	Lignin	400-600

TABLE - 2

BY-PRODUCTS OF THE KRAFT COOK AND FROM SUBSEQUENT PRESSURE HEATING OF THE BLACK LIQUOR WITH ALKALI AND SULFIDE AT 250-285°C (48a)

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Before Pressure Heating		After Pressure Heating	
.....		
	Kg ptp		Kg ptp
Tall Oil	50	Acetic acid	60
Turpentine	17	Formic acid	60
Acetic acid	40	Methyl sulfide	40
Formic acid	40	Methyl mercaptan	8
Methanol	5	Pyrocatechol	30
Vanillin	2	Methyl catechol	11
Acetoguaiacone	2	Ethyl catechol	9
Guaiacol	2	Other ether-soluble phenols	150
Pyrocatechol	1	Homoprotocatechuic, protocatechuic and other phenol carboxylic acids, perhaps	150
Other phenols	42		
Phenol carbonic acids	45	Ether soluble acids of carbohydrate origin	150
Non-volatiles and lactic acids	145	Demethylated lignin of novalac properties	100
		Butanol-soluble lactones	35
TOTAL	<u>391</u>	TOTAL	<u>803</u>
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