Development of Lignin By-Products for Industrial Applications

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ABSTRACT

Small agro based paper mills of capacity less than 50 tpd discharge lignin rich effluents in the recipient stream which due to the bio-refractory nature of lignin results in heavy resource drainage in the form of energy through organic bio-mass and create severe pollution problems. This resource drainage of lignin accouns for about 1.0 million tonne equivalent of coal per annum at National level. Current strategies to decrease environmental impact from industrial activities emphasizes waste prevention and reutilization/ recycling. The increased concern over the discharge of effluents containing lignin rich black liquor have forced the field experts to give a serious thought to tackle the problem in a techno-economically viable and eco-friendly manner.

With sharp rise in petro-chemical products in the last 20 years, the interest in lignin utilization has been gaining much importance due to its phenolic aromatic based structure, which can replace some of the petro-chemical products to quite a degree of success. For last few years, Central Pulp and Paper Research Institute has been actively engaged in identification of effective and viable methods for utilization of black liquor lignin for development of industrially important lignin by-products. The studies incorporate utilization of precipitated lignin separated from the black liquor and also lignin present in the black liquor as dissolved colloidal molecules for its utilization in the adhesive to substitute urea-formaldehyde and phenol-formaldehyde type of resins and plasticizers in concrete making for the use in the road pavement construction. The cost economic calculations show larger benefits of lignin substitution with the commercially available resins and plasticizers, besides the other benefits that lignin based compounds have no adverse environmental impact as that of other compounds such as phenol and its derivatives, an essential feature in an increasingly restrictive market place.

INDIAN SCENARIO

In India, there are 515 paper & board mills with an aggregate capacity of approximately 5.0 million tonnes. Barring 63 mills closed with an installed capacity of 1.02 million tonnes, the demand for paper and board is projected from the present level of 4.2 million tonnes by end of 2000 A.D. further to 6.0 million tonnes by 2010. Out of 515 mills, approx. 180 are in medium and small agro based sector, ranging 10 to 80 TPD capacity and with exception of 8-9 number of mills, the others are without any chemical recovery plants and discharge their black liquor after secondary biological treatment system.

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ENVIRONMENTAL BURDEN

On the average, nearly 50% of the raw material and 80% of the chemicals entering pulp and paper mills become reject in the small agro based paper mills, mainly through raw material processing and black liquor discharge.

The agro based paper mills generate higher pollution load than large integrated paper mills. Single biggest technical problem remains with the small size of the agro based mills, which makes the installation of the soda recovery plant difficult. In case of these paper mills, the higher level of pollution load is mainly due to the non-utilization of spent pulping liquor. It is estimated that for every tonne of pulp produced, nearly 1.25 tonnes of black liquor solids are generated, which comprise mainly of 72-75% organics and 25-28% of inorganics. During the biological treatment process nearly 50% of the total organics in the form of carbohydrates and other lower mass organic molecules are degraded to simpler products, such as CO_2, CH_4 and H_2, etc., but lignin which contributes to the rest 50% of the organics remains as non-biodegradable entity. As already discussed under the article on Lignin Removal Process published in this issue, it has been shown that presence of lignin not only limits the treatment efficiency of the biological system to less than 50%, but also poses a major challenge of huge resource drainage.

UTILIZATION OF LIGNIN FOR MARKETABLE PRODUCTS

Concrete efforts have been made at CPPRI in the direction of lignin utilization either utilizing dissolved lignin present in the black liquor obtained after separation of lignin was subjected to biological treatment and the bioassay results indicated improved biodegradability of the resultant liquor after separation of lignin in the form of high molar fraction.

While, working on the utilization aspects of lignin, certain points were kept under consideration in use of either precipitated lignin or the black liquor lignin. The use of precipitated lignin was found suitable in case of mills, which are equipped with a full-fledged biological treatment system, but due to the presence of lignin in the black liquor are not able to meet the standard discharge limits. In such cases, it is essential for these mills to go for adoption of lignin Removal Process before biological treatment system, which has been identified and developed by CPPRI. Further, in order to make the process techno-economically viable, it is further envisaged to use the precipitated lignin for some of its commercially important by-products.

On the other hand, mills which have either expanded their pulping capacity or intend to directly use their weak black liquor as an alternate to conventional chemical recovery can go for black liquor utilization making use of the black liuor lignin for generation of value added by-products such as water resistant resin production.

USE OF PRECIPTIATED LIGNIN

Isolation of lignin from rice straw and wheat straw black liquor was carried out using suitable precipitating agents. The precipitated lignin was used after simple treatment of sun drying/filtration for various application purposes such as in making adhesive as replacement for urea-formaldehyde type of resin and as replacement for synthetic plasticizer in concrete making.

TABLE-1

CONDITIONS FOR PARTICLE BOARDS MAKING

Base: Rice Straw

Sl. No.	Particulars of Adhesive in the particle board	Temperature °C	Pressure in, the hydraulic press, kg/cm^2	Hours
1	No adhesive used	150	150	3
2	11% UF resin	150	150	1
3	9% straw lignin (pptd.)	150	150	1
4	14% straw lignin (pptd.)	150	150	1
5	10% PF Resin	150	150	1

REPLACEMENT OF PRECIPITATED LIGNIN AS BINDER IN PARTICLE BOARD MAKING

Medium density particle boards were prepared at CPPRI. The boards were made using rice straw and wheat straw dust as the raw material. The dust particles were of uniform size and contained nearly 8% water. In our experiments, varieties of particle boards using different binders such as precipitated lignin, commercial UF and PF resins in different proportions were used in the hydraulic press available at the institute to compare the characteristics of the particle boards. Particle boards of 1'x1' dimension and 1.0-1.5 cm thickness were prepared at a pressing temperature of 150^{0}C and under hydraulic pressure of 150 kg/cm^2 for 1-3 hours as shown in Table-1.

In our experiments no accelerator, hardening and sizing agents were used during making of particle boards as reported above.

The test results of density, water absorption are shown in Table-2.

Fig-1 depicts the swelling behavior of the different particle boards made using different binders. From the result, it is evident that addition of lignin causes bonding of fiberized-ligno-cellulosic materials with lignin during the hot pressing under optimized conditions of temperature and pressure.

These particle boards are comparable with those available in the market in terms of density, water absorption test. The results of swelling indicates that boards are suitable for use of the interior purposes, where not much of the weathering effect is required to be resisted. The results also show that in case of

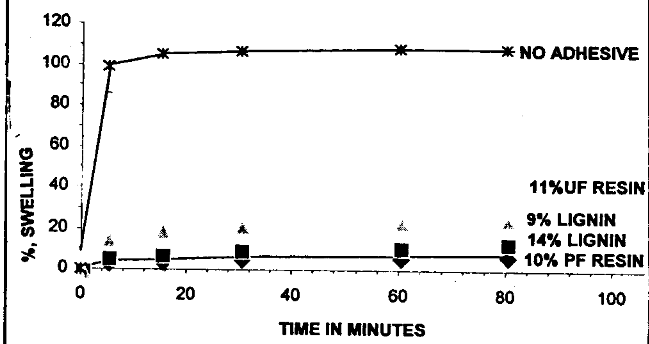

FIG. 1- Swelling Characteristics of Particle Boards using different binders

partcle boards made with PF resins, although the density and water absorption figures are slightly better, but the cost of these resins are three times higher than precipitated lignin.

USE OF LIGNIN AS PLASTICIZER IN CONCRETE MAKING FOR ROAD CONSTRUCTION

In recent years, plasticizers have come to play a central role in concrete technologies. When added to concrete, these chemical admixtures enable a substantial reduction of the amount of batching water, thereby reducing the porosity of the resulting materials.[1] This results in concrete with greatly enhanced properties, mainly compressive strength and durability. Precipitated lignin after drying was put to its use as admixture in concrete making. Table-3 gives the composition of the material and the results of comparessive strength with and without the use of

TABLE-2

CONDITIONS FOR PARTICLE BOARDS

Base: Rice Straw

Sl. No.	Particulars of binders in the particle board	Density, kg/m^3	Water absorption, %
1	No adhesive used	0.71	80
2	11% UF resin	0.81	55
3	9% straw lignin (pptd.)	0.83	45
4	14% straw lignin (pptd.)	0.98	32
5	10% PF Resin (Commercial)	1.0	30

TABLE-3

STRENGTH EVALUATION OF CONCRETE WITH AND WITHOUT PLASTICIZER

Particulars	With no admixture	With lignin as plasticizer
Cement	6.2 Kg	6.2
Sand	12.6 Kg	12.6
Coarse aggregate of 20 mm & 10 mm size	23.6	23.6
Admixture, %	Nil	1.0
Compressive Strength, Kg/cm²	**162**	**233**

lignin as admixture. From the results, it is quite evident that with 30% improvement in the compressive strength of the concrete, precipitated lignin can participate in the same type of reactions as that of other available plasticizers.

STRUCTURAL MODIFICATION OF LIGNIN

Lignin Based Phenol Formaldehyde Adhesives For Water Resistant Ply Board And Particle Boards

In the manufacture of the ply board and particle boards, phenol formaldehyde and urea-formaldehyde resins are most commonly used. The major advantage of UF resins are their low cost, lack of color and short curing time[2]. However, the glue line is not water proof and during recent years, a great deal of attention has been drawn to the emission of formaldehyde from the particle boards made from UF resins for a length period after production. The advantage of PF resin is the weather resistance of the manufactured product, their chief draw back lies in their high cost. In view of this, it was decided to substitute lignin with phenol which has a phenolic structure and due to its lower cost and environment friendly nature will be preferred over urea and phenolic components with respect to the end product quality and cost of the product respectively.

Co-Polymerization of the Phenol-Formaldehyde (PF) and Lignin substituted PF Resins (LPF)

PF Resins: PF resins of the resole type are made by condensing phenol with formaldehyde using alkaline catalysts. As phenol has three reactive sites, the first stage of the reaction with formaldehyde gives five hydroxymethyl phenols in varying proportions depending on the reaction conditions. The hydroxymethylol groups subsequently condense during the formation of methylene bridges.

LPF Resins: Lignin is the most important of the natural polyphenols. It is composed of phenyl propane

FIG-2 COPOLYMERISATION OF LIGNIN WITH PHENOL- FORMALDEHYDE

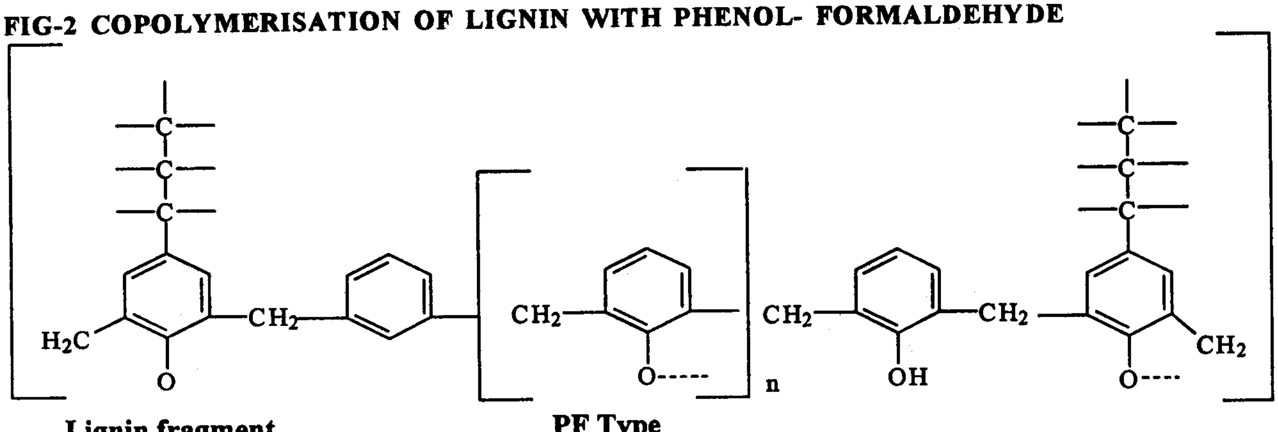

TABLE-4

SAVING IN COST WITH PARTIAL SUBSTITUTION OF PHENOL WITH LIGNIN

Lignin substitution with phenol %	Cost/tonne of resin Produced (Amount in Rs.)	Savings in cost with lignin substitution/tonne of product (Amount in Rs.)
0	17100	BASE
10	15550	1525
20	14000	3025
25	13280	3880
30	12500	4525
40	10926	6087
50	9700	7600

units, which are connected by carbon-carbon and ether bonds forming a polymertic product. In chemical pulping, part of the bonds between the phenyl-propane units are broken and lignin gets dissolved in the pulping liquor in the form of various sizes.

Fig.-2 illustrates a comparison between a structural detail of lignin and PF resin. It can be seen that similarities exist and therefore attempts were made to co-polymerize lignin with PF resin. Work carried out with softwood and hardwood black liquor lignin caused a deterioration in the properties of the PF type substituted resins which required longer press time, higher press temperature and poorer water resistance than pure phenolic resins.

On the other hand studies conducted at CPPRI showed that lignin from the agro residues showed much promising prospects for its use in phenol substitution, the prime reason being that unlike the wood kraft lignin, its ortho position are comparatively less blocked, which do not hinder the co-polymerization reactions. Studies carried out by other researchers have shown that soda lignin from agro based fibrous raw materials contain approximately 0.7 reactive sites per phenyl propane units. This value is about twice as high as that of wood kraft lignin. The lignin derived from the agro based raw materials is therefore expected to be a good substitute for phenol in LPF resin than wood kraft lignin.

Preparation of the LPF Resin

CPPRI has developed a lignin based resin derived from agricultural based black liquors and precipitated lignin. In this resin, 25-30% of the phenol is replaced with lignin, a natural non-poisonous polyphenol. The resin preparation method incorporates concentration of the black liquor/precipitated lignin followed by its reaction with phenol and formaldehyde. The co-polymerisation of the lignin with phenol-formaldehyde under alkaline catalytic conditions takes place and a structure similar to the one shown in Fig-2 is attained. The use of this resin makes it practical to make ply boards and particle boards for exterior use. The major advantages of production of lignin substituted phenol formaldehyde type of resin is that a substantial reduction in resin/adhesive cost can be attained as lignin is much cheaper than PF resin, a petrochemical product dependent upon the price and availability of phenol. Table-4 shows the economic evaluation of synthetic PF resin and the LPF type of resin obtained after substitution of lignin in different proportions.

Properties of Lignin-Phenol Formaldehyde (LPF) Resins:

The test boards were prepared by bonding together three veneers keeping grains of the core veneer at right angle to that of the two face veneer and with a dimension of 1'x1'. The veneer were assembled and loaded in the flat platen press for specified time.

Conditioning of Test Boards:

Immediately after the removal from the press, the boards were given a special treatment of dipping in water and then exposed at prevailing laboratory atmospheric conditions in a manner to ensure a free circulation of air around them for six to nine days.

Preparation of Test Pieces for finding the workability of the LPF Resins:

After conditioning of the test boards, test pieces were prepared by keeping of the test pieces along the direction of the grain of the outer plies.

Tests undertaken for Plywoods:

Some of the tests were undertaken to find the workability and performance of the plyboards prepared. A brief description of the test is as follows.

Test for Adhesion of Plies:IS : 1734 (Part5) -1983

This test was intended to estimate the tenacity with which the bonding material holds the adjacent plies together.

Determination of Water Resistance: IS: 1734 (Part 6)- 1983

This test is primarily intended to determine the acceptability or otherwise of plywood panel where it is subjected to alternate drying and wetting or high humidity. The results of the test and the conditions are shown in Table-5.

Determination of Nail and Screw Holding, Power: IS: 1734 (Part 19)-1983

This test is intended to assess the nail and screw holding capacity of the plywood. For this bright galvanised, diamond pointed screws were used.

Studies showed that ply boards prepared from resin using black liquor lignin and precipitated lignin confirm to the water resistant test, nail and screw holding capacity trials and test for adhesion of plies.

It is therefore clear that resins of the type of Lignin phenol formaldehyde can be produced from black liquor lignin or lingin isolated from the black liquor. However the advantage with the dissolved black liquor lignin is its lower base catalyst requirement in comparison to the resin prepared from precipitated lignin. The curing time of the LPF resins are comparatively longer than the PF resins. Studies are undergoing to use a suitable catalyst to reduce the curing time of the resin prepared.

CONCLUSIONS

Studies carried out at CPPRI have shown significant potential of lignin in development of various industrial products.

- Precipitated lignin acts as a good binder in the making of particle boards. The results obtained are found to be better than the

TABLE-5

CHARACTERISTICS OF LPF RESINS SYNTHESISED AT CPPRI

Test Conducted	Time of Immersion, hrs.	Temp. of water under normal atms. Press in which test pieces were immersed, ^{0}C	Status of applicability	Recommended use
Cold water resistance test	24	27 ± 2	Passed the test	Looking in to the results, adhesives of the LPF type are found suitable to make joints which are highly resistant to weather, micro-organisms, cold and boiling water, steam and dry heat.
Warm water resistance test	16	70 ± 2	do	
Boiling water resistance test	8	Boiling water	do	
Boiling water proof	72*	- do -	do	

commercially available Urea formaldehyde resin & quite at par with commercial PF resin which are atleast thrice as costly as precipitated lignin.

- Precipitated lignin act as good plasticizing agent, during concrete making for road pavement construction. A 30% improvement in compressive strength is achieved by the use of nearly 1% lignin.

- Black liquor lignin or the lignin isolated form the black liquor acts as a good source for partial replacement of phenols to the tune of 25-30%, without compromising the strength characteristics.

- The curing time is higher with LPF resins in comparison to the PF resins, for which certain catalysts are being examined to reduce the time.

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2. Finnish plywood, particle board and fibre board made with a lignin base adhesive. **K.G. Fross and Agneta Fuhrmann. Technical Report of Finnish Pulp and Paper Research Institute. Finland, 1979.**