IPPTA

Silver Jubilee International Seminar & Workshop
Appropriate Technologies For Pulp & Paper Manufacture
In Developing Countries.

New Delhi - 1989

UTILIZATION OF LIGNIN FROM AGRICULTURAL RESIDUES IN THE MANUFACTURE OF DISPERSANTS

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Abstract

Lignin sulphonates and sulphonated lignin products find use in diversified areas as oil well drilling, soil stabilizers, dyestuff dispersants, emulsifiers, additives etc. Lack of utilization of lignin from agricultural residues is due to their nature and not enough understanding of their structure. Preliminary studies were initiated to characterise and investigate potential utiliztion of lignin from three agricultural residues i.e. bagasse, rice straw and wheat straw for the manufacture of useful by-products. Concentrated lignin fractions obtained from ultrafitration of spent liquors of agricultural residues were subjectd to modifications by sulphonation. Studies involved optimization of temperature and mode of reaction (single or two step) for the preparations of lignosulphonates. Reaction temperature optimization was done varying the temperature from 70°C to 150°C and evaluating the products for their dispersion behaviour.

Based on the results of the preliminary investigations of chemical analysis, molecular sizes and dispersion behaviour of water soluble products suitability of lignin from agricultural reidues has been recommended for possible manufacture of dispersants.

Introduction

The lignin and Lignosulphonates find extensive use in diversified areas such as mud dispersant in oil well drilling, soil stabilizers, dyestuff dispersants, emulsifiers, additives, etc. These sulphonates can either be obtained from spent sulphite liquors or have to be manufactured from spent alkaline liquors by suitable chemical treatments. Number of patents have been issued concerning the potential use of such sulphonates in various areas primarily due to their collodial properties.

Almost all the work on lignosulphonates has been reported on their manufacture from either softwoods or hardwoods. Little is known about sulphonates from agricultural residues, it is due to insufficient understanding of their nature and struclure. Nevertheless technical lignins from agricultural residues can be a potential source of organic chemicals after suitable modification.

The work reported here was taken up as a part of the supporting activities of the project "Chemical recovery plant for small paper mills using non-woody raw materials".

Preliminary studies have been carried out on spent liquors from agricultural residues (rice straw, wheat straw and bagasse) with the following objectives :

-- Characterisation of spent soda liquors from agricultural residues for chemical constituents and molecular size distribution pattern.

-- Optimisation of reaction temperature for preparation of lignosulphonates and

-- Preparation of lignosulphonates from agricultiural residues lignin for use as dispersants.

Spent liquors from agricultural residues were analysed for, pH, total solids, lignin, sodium, silica, colour and molecular size (low and high molecular weight). The lignins from spent liquors were concentrated by ultrafiltration and subjected to chemical modification. Chemical modification had involved optimisation of reaction temperature of sulphonation, mode of sulphontion , single step or two step. After optimisation of reaction temperature and mode of sulphonation, the lignosulphonates were prepared from bagasse, wheat straw and rice straw. Reaction products were then evaluated for their dispersion behaviour on a standard slurry of clay suspension.

Result and Discussion

Characterisation of Soda Liquor from agricultural residues

For the preparation of lignosulphonates of desired properties, it is essential to hava an understanding of the chemical composition and molecular distribution pattern of the liquors from which they are to be manufactured. Spent sulphite liquors are approximately 10% solutions of a mixture of lignosulphonates and carbohydrates In softwoods, the lignosulphonates constitute about 55% and carbohydrates about 32% of the liquor solids. For hardwood liquors the proportions are about 42% lignosulphonates and about 45% carbohydrates. However for agricultural residues such figures vary widely and not enough data is available. Table I gives chemical composition of typical spent soda liquors from different agricultural residues.

In soda liquor of agricultural residues, in particular, the straws, lignin amounts are very low i.e. about 25-35% of total solids. Bagasse, however, has a slightly higher lignin content in the liquor. Any step towards, utilisation of technical lignins therefore should first aim at conventration of the lignin fractions by either precipitation or ultrafilteration. Presence of contaminants such as carbohydrates lent to inhibit chemical reations of lignins as also the desired properties of the end product.

Alkalii lignins from the three agricultural residues were purified by solvent-extraction procedure developed by Lundquist, which uses pyridine : acetic acid : water (9:1:4) solution to dissolve lignin followed by extraction in chloroform. The lignin is then recovered by pouring the concentrated organic extract into excess diethyl ether. These purified lignins were subjected to separation of low and high molecular weight fractions on sephadex G-25 column using water as an efluent, purified lignin products were studied using ultraviolet spectro-photometery to determine their extinction coefficients at 205 and 280 nm. Phenolic hydroxyl groups were determined quantitatively using the method by Goldshmid[3]. Results of analysis are given in Table II and figure 1. Spectroscopic data on further characterisation of the three lignins will be presented in a later study.

TABLE - 1

CHEMICAL CONSTITUANTS OF SODA LIQUORS
FROM AGRICULTURAL RESIDUES

Sample	pH	Total Solids%	Lignin (% on T.S.)	Colour PCU x 3/10	Na (g/1)	COD (g/1)	Silica (%on) T.S.
Rice Straw	7.7	6.8	32.3	38.4	12.4	40.0	1.75
Wheat Straw	9.6	4.4	25.8	50.0	6.3	19.2	1.23
Bagasse	9.8	5.7	43.2	46.4	9.3	-	0.83

From the absorptivity figures in Table II, it is evident that the three lignins have about the same values. Measurement of absorptivities of these lignins is of interest, because no authentic data is available for such lignins. These values can therefore be utilized for a rapid and accurate analysis of lignin content in any spent liquor by ultraviolet spectrophotometery. From Table II it is seen that, among the three lignins, rice straw lignin contains about one and a half times less free phenolic hydroxyl groups than that of wheat straw and bagasse. During alkaline pulping the lignin macromolecule apart from degradation, undergoes repolymerisation as well. These condensation reactions utilise the 3 and/or 5 positons of th aromatic ring. From the values of free phenolic hydroxyl the extent of condensation of the three lignins can be approximated. Bagasse and wheat straw lignins are therefore relatively lesser condensed then that of rice straw, because they have more of free phenolic groups at 3 and/or 5 position. However this statement has to be used with caution because the method of Goldshmid has its own limitations. The free positions at 3 and/or 5 which are reactive sites should be confirmed by other analytical methods also. The three lignins have about the same proportion of high and low molecular weight fractions. We had also determined free phenolic and molecular sizes of the technical lignins from soda liquors of the three agricultural residues. It is worthwhile to mention here that the technical lignins differed from the purified lignins both in free phenolics and molecular size distribution patterns.

Optimisation of Conditions for Preparation of lignin sulphonates

After characterisation of lignin the spent liquors were concentrated by ultrafiltration using a DDS RO laboratory unit 36-4.5. The membrance used were poly sulphone GR81PP, with MWCO value of 6000. The lignins from th concentrate fractions were subjected to chemical modification by single and two step sulphonation using formaldelyde and sodium sulphite as given in experimental. Experiments were conducted to optimise the reaction temperature and mode of reaction. For purpose of optimisation only, the rice straw lignin was used, as the optimised condition can also be used with other lignins. The reaction temperature was varied from 70°C to 150°C. Reaction products were evaluated for their dispersion behaviour using a slurry of standard clay suspension in IM Nacl electrolyte solution. Results of the optimisation experiments are given in Table III and figure 2.

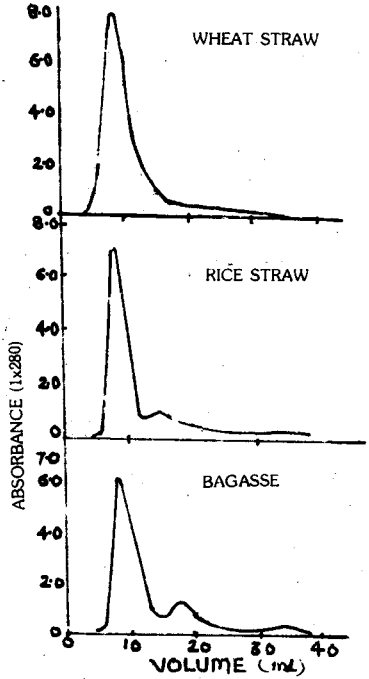

FIG. 1 : GEL FILTRATION CHROMATOGRAMS OF AGRICULTURAL RESIDUES LIGNIN

TABLE II

PERCENT PHENOLIC HYDROXYL AND MOLECULAR SIZE OF LIGNIN FROM AGRICULTURAL RESIDUES

Lignin	Absorptivity($1g^{-1}$ cm^{-1})		Phenolic-	Relative Mol. Wt.	
	205 nm	280 nm	OH(%)	Fraction % high mol. wt.	Low mol. wt.
Rice Straw	90.6	20.6	0.38	93.5	6.5
Wheat Straw	90.2	19.4	0.63	94.5	5.5
Bagasse	92.4	18.5	0.54	90.5	9.5

The results indicate that, modified lignins produced at temperature 140°C and 150°C have a good dispersion ability. The standard dispersion number which is defined as the ratio of the torque developed by blank to that by the sample increased from 1.7 for unmodified lignin to 14.0 for the modified product indicating better dispersion ability of the products. The modified ability of the products. The modified lignins treated at higher temperatures (140 & 150°C) results in much lower yields. The various modified products of the rice straw lignin were also subjected to separation of high and low molecular weight fractions on a sephodex G-25 column.

Preparation of Lignosulphonates

After the optimisation of reaction temperature and mode of preparation of lignosulphonates. These were also produced from wheat straw, bagasse. The procedure adopted for their isolation was precipitation from alkaline liquors by acid followed by thorough washing. It was observed that during washing a considerable amount of lignosulphonates were also removed because of their solubility in water and this could partly be responsible for the lower yields. In the case of lignosulphonates from wheat straw and bagasse a slightly different procedure was followed, which involved passing the solution through an exchange resin. The effluent was heated to 100°C and a stream of nitrogen was passed to remove sulphur oxide formed due to excess of sodium sulphite. The elimination of the inorganic acid was accomplished by passing the solution through an ion exchange resin[4]. The solution so obtained was dried at low temperature to obtain a completely water soluble product. These products were then analysed for their dispersion behaviour using the standard suspension of clay as before. Results obtained on reduction in viscosity of clay suspension are given in Table IV.

The lignosulphonates prepared from bagasse and wheat straw were evaluated for their dispersion behaviour. Results of dispersion as indicated by the drop in viscosity for a standard sample of clay slurry revealed that the bagasse lignin produce dispersants which are better than the lignosulphonates prepared from wheat straw. However, when we compare lignosulphonates from the three agricultural residues lignins, it is observed that rice straw lignin gives best dispersants among the three.

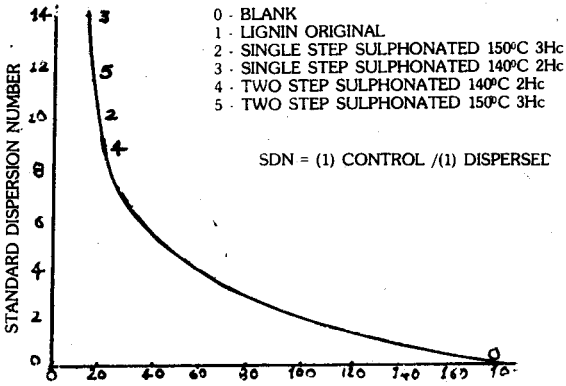

FIG. 2 : VISCOSITY (a) mPc sec.
STANDARD DISPERSION NUMBER N Vs INTRINSIC VISCOSITY
FOR AQUEOUS CLAY DISPERSED BY DIFFERENT LIGNIN SAMPLES.

TABLE III

OPTIMISATION CONDITION FOR PREPARATION OF LIGNOSULPHONATES

Sample	Yield	Std. Dispersion No.	Reduction in Viscosity (mPa sec.)
Original Lignin		1.7	70.0
One step sulphonated Lignin, 150°C	50	8.7	148
Two step sulphonated Lignin, 150°C	49	10.0	162
One step sulphonated Lignin, 140°C	48	14.0	155
Two step sulphonated Lignin, 140°C	56	11.7	160
One step sulphonated Lignin, 110°C	75	1.6	78
One step sulphonated Lignin, 90°C	--	1.1	36

Viscosity of blank for samples 1-5 = 175 mPa sec. and for samples 6 & 7 = 298 mPa sec.

EXPERIMENTAL

Purification of Alkali Lignins

Lignins were precipitated from spent liquors using hydrochloric acid and warmed to coagulate lignin. This lignin was allowed to stand overnight, filtered, washed to free from acid and dried at 55°C. The dried lignin (5g) was dissolved in pyridine; acetic acid : water solution (9:1:4) with stirring. After complete dissolution of lignin, the solution was extracted with chloroform (250 ml). The organic extract was reduced to about 100 ml under reduced pressure and poured slowly while stirring into 1.25 litres of anhydrous diethyl ether. The ether insoluble lignin was filtered, washed three times with 250 ml ether, separated from an aqueous suspension and dried.

Gel Fltration Chromatography

The samples of technical lignin, purified lignin and sulphonated lignin were subjected to gel filtration chromatography on sephadex G-25 gel using water as an eluant. Fraction collected at different time intervals were measured for their absorbance at 280 nm.

Free Phenolic Hydroxyl (Quantitative Estimation)

The free hydroxyl in lignins were determined by recording the spectra of a ph 12 solution vs pH 6 solution of lignin on a P.E. UV/visible spectrophotometer, Model 402, in the region 190-390 nm.

Sulphonation of Lignin

Technical lignins from agricultural residues were sulphonated using one and two step sulphonation methods as follows-

Two Step Sulphonation

i) Hydroxymethylation

It was accomplished by dissolving 2g of lignin in 0.5N NaOH solution (30 ml) and 37% formaldehyde (1.35g). The resulting solution (pH = 13.0) was heated to 55°C under mechanical stirring for five hours. The final reaction mixture was adjusted to pH 4 with dilute HCl to facilitate lignin precipitation. The heterogenous solution was centrifuged. Washed three to four times with water and dried at 55°C.

TABLE IV

DISPERSION BEHAVIOR OF LIGNIN AND ITS PRODUCTS

Sample	Reduction in Viscosity (mPa sec.)
Original wheat straw lignin	60
Two step sulphonated wheat straw lignin 150°C	77.5
Original Bagasse lignin	57.5
Two step sulphonated bagasse lignin	105
Commercial Lignosulphonate	65.0

Viscosity of blank slurry of clay = 230 mPa sec.

ii) Sulphonation

To a 50 ml stainless steel bomb was placed hydroxymethylted lignin (1.0g), 1N NaOH solution (15 ml) and sodium sulphite (0.75g). The bomb was heated to 150°C for three hours.

A homogenous solution (pH = 10) was obtained at the end of the reaction. This was passed through cation exchange resin (Amberlite H+). The effluent was treated at 100°C under nitrogen atmosphere in order to remove the sulphur dioxide formed from the excess of sodium sulphite. The elimination of inorganic acids eventually present was then accomplished by passing the solution through a column of the anion exchange resin. (Amberlite OH–). The product was then neutralized with aqueous base (NaOH) and dried at 55°C, to obtain finely divided water soluble powder.

One Step Sulphonation

To a 50 ml stainless steel bomb was placed ligning (2.Og) sodium sulphite (1.5g) and 37% formaldehyde solution (1.35g). The resulting solution (pH = 13.0) was heated in the bomb to and held at 150°C for three hours. The reaction mixture was purified as described previously. After neutralizing final affluent with aqueous base (NaOH). The solution was dried at 55°C, to obtain finely divided water soluble powder.

Standard dispersion No.

The standard dispersion Number of the samples was determined to evaluate the dispersion behaviour of the reaction products as follows.

A standard stable slurry of a 10 percent solution of clay was prepared, in 1M NaCl solution. The viscosity of this sample was measured with and without the addition of lignosulphonate (0.5% clay basis), on a Brookfiel'd viscometer.

Conclusions

- The amount of technical lignins in spent alkali liquors from agricultural residues is only 25–35% of total solids for straws and about 40 percent for bagasse.
- Rice straw lignin contains the least free phenolic hydroxyl groups.
- Ligno sulphonates from agricultural residues with good dispersion abilities can be prepared at 140° and 150°C by two step sulphonation procedure.
- Among the three agricultural residues lignins, best lignosulphonates for use as dispersants can be prepared from rice straw lignin.

Acknowledgements

We are thankful : to Dr. A. G. Kulkarni and Dr. R. M. Mathur for standardsing and determining dispersion behaviour of lignosulphonates.

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