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UTILIZATION OF LIGNINS FOR PRODUCTION OF NUCLEAR SULPHONATED DERIVATIVES OF INDUSTRIAL VALUE.

S.V. Singh, A.K. Rai and S. P. Singh
Cellulose and Paper Branch,
Forest Research Institute,
Dehradun-248 006

Abstract

The present paper gives an account of the following chemical processes : (i) chlorination of isolated lignins followed by reaction of chlorolignins with sodium sulphite and (ii) nitration of isolated lignins with sodium nitrite in presence of hydrochloric acid followed by the reaction of nitrolignins with sodium sulphite, investigated for modification of milled wood lignin and kraft/soda lignins of Eucalyptus, Wheat straw and bamboo to prepare nuclear sulphonated derivatives. It was found that chlorination brings about all the three types of competing reactions-substitution (nuclear as well as side chain), oxidation and demethoxylation. Treatment of chlorolignins with sulphite results in consumption of sulphite mainly through adduct formation with chloroquinone. Chlorine is only partly removed by sulphite; the chloride ions are liberated mostly through hydrolysis. Nitration of lignin resulted in introduction of nitro group and formation of 4-oxime of 2-methoxy-p-benzoquinone type structure in lignin; which on reaction with sodium sulphite gave sulphonated derivatives, indicating reduction of nitro group into amino group and sulphonation of ring at another site. Both types of sulphonated derivatives of lignin thus produced possessed very high dissolving power for isolated lignins (a 10 g/1 solution in aqueous ethanol could dissolve over 300 g/1 of isolated lignins), good properties for use as dispersing agents, emulsifiers and surfactants.

Introduction

Of the three major components in wood-cellulose, lignin and hemicelluloses, the component most often used is cellulose. By contrast lignin with potentially high value polymer applications is underutilized. For example, in the predominant kraft pulping process producers burn it as an inhouse fuel. Lignins from agricultural residues based paper mills having no recovery unit are discharged with the effluent of the mill, which results in high pollution load. Utilization of lignin from different sources has been the subject of much research over the last few years. Numerous routes available for utilization of lignin could be summarised as follows :

(i) fragmentation to creosols, phenol, catechols, vanillin, organic-S-compounds, (ii) macromolecule in solution systems as dispersant, emulsion stabilizer, solvent for lignin, surfactant and (iii) macromolecule in material systems as thermosetting resins, polyblends, antioxidant, rubber reinforcement. Due to the presence of various types of ether linkage, hydroxyl groups (both phenolic and aliphatic), carbonyl and carboxylic groups, ester functions etc., lignin macromolecule is capable of under-going a variety of modification reactions. It is possible to change drastically its properties such as solubility, viscosity, hydrophilicity, polyelectrolytic behaviour, etc., through chemical modifications in the three dimensional structure of the macromolecule. With the significant lignin technological developments in hand, utilization of lignin is now entering a new phase where active commercialization of lignin products and fundamental research are being directed to the elucidation of property performance relationship of technical lignins and development of new chemical processes for lignin modifications and performance requirements of lignin chemicals for various industrial needs.

This paper gives an account of the chemical processes investigated to modify lignins with prime aim of preparing nuclear sulphonated lignin derivatives of industrial value. One possibility of nuclear sulphonation considered was to chlorinate lignin for a very short period to produce nuclear chloro substituted lignins and then treat those chlorolignins with sodium sulphite to replace chlorine with sulphonic acid group. The other possibility tried was to nitrate lignin with sodium nitrate lignin with sodium nitrite in presence of hydrochloric acid to produce nuclear substituted nitrolignin and then react the nitrated product with sodium sulphite to get nuclear sulphonated lignin derivatives. The sulphonated lignin derivatives prepared via above mentioned course of modification reactions were evaluated for their application as solvent for lignin, dispersing agents/emulisifiers and surfactants, these results are presented here.

Results and Discussion

Chlorination of lignin

Chlorination of lignins (milled wood lignin, kraft/soda lignins) with aqueous chlorine for 5 min. at 10-20 °C yielded highly chlorinated products. The chlorine content in chlorolignins varied from 15.6-16.9% and 1.07-1.16 per C9 unit. Chlorine substitution may be on the side chain of the lignin unit or on the aromatic nucleus. When elemental chlorine is the chief chlorinating agent at low temperature and low chlorine to lignin ratio, as under the conditions mentioned above, substitution of chlorine primarily occurs in the aromatic nucleus. Evidence of substitution of chlorine inside chain has been provided by a kinetic study of the reaction of chlorolignins with sodium sulphite[1]. Kratzl and Bleckman[2] obtained the alpha bromo derivative when either propioguaiacone or its methyl derivative was brominated. Substitution of beta and gamma positions of lignin side chain has also been postulated[3] chlorination of lignins was accompanied by considerable demethoxylation. A reduction from 18.90 to 11.76% in Eucalyptus kraft lignin, from 6.9 to 5.4% in wheat straw soda lignin and from 12.4 to 4.5% in bamboo kraft lignin was observed. Chlorolignins were found to contain greatly increased amount of carbonyl groups. The value rose from 0.09 to 0.39 per C9, 0.046 to 0.29 per C9 and 0.039 to 0.28 per C9 respectively, in case of the three types of lignin substrates mentioned above. Evidence for chloroquinone unit formation in lignin is afforded by a kinetic study of the reaction between chlorolignin and sodium sulphite[1]. These facts indicated that during chlorination even for 5 min. lignins underwent all the three types competing reactions, i.e. substitution, demethoxylation and oxidation.

Nitration of lignin

Treatment of lignins with sodium nitrite in presence of hydrochloric acid resulterd in introduction of nitrogen as follows : 1.64% in Eucalyptus kraft lignin, 0.81% in wheat straw soda lignin and 1.31% in bamboo kraft lignin. The infrared spectra of these nitrolignins did not show bands corresponding to aromatic nitration. Nitrogen in nitrous acid treated lignins is mainly oxime nitrogen. Bolker, kung and kee[4] found that the main product of nitrous acid treatment of guaiacol was 4-oxime of 2-methoxy-p-benzoquinone which was accompanied by small amount of aromatic nitrocompounds.

Sulphonation of chlorolignins

Sulphonation of chlorolignins with sodium sulphite resulted in introduction of sulphite groups in sulphonated products in the range of 1.76 to 2.25 per C9 unit of lignin, depending upon the type of chlorolignin substrate. Kinetics of the reaction between chlorolignins and sodium sulphite was marked by an initial rapid phase, lasting for about 5 min., followed by a slow process. The latter slow process of reaction followed second order kinetics with respect to sulphite concentration. The initial rapid consumption of sulphite is presumably due to the formation of quinone sulphite adduct; because chlorination of lignins produces some quinone structures including chloroquinones which are known to react with sulphite by fast reversible adduct formation[1]. Bishop at al.[5] have shown that the displacement of halides from substituted quinones with sulphite is preceded by rapid quinone-sulphite adduct formation. During rapid phase chlorine was liberated through hydrolysis. Braddon nd Dence[6] while studying the alkaline hydrolysis of chlorine substituted lignin model compounds have shown that approximately 50 percent of chlorine is liberated within first few minutes of the reaction between water and the model compound containing chlorine in side chain.

Consumption of sulphite could also be through reaction with vanillyl alcohol type groupings in lignin. Reactions of model compounds with sodium sulphite indicated that there was not much chance of displacement of aromatically bound chlorine by sulphite under the conditions used for preparing sulphonated lignins[1]. However, chlorine from chloroquinone units could have been displaced after quinone adduct formation; because aromatic nucleophilic replacement of halogens of halotrimethylbenzoquiononones by sulphite has been reported[5].

Sulphonation of nitrolignins

Treatment of nitrolignins with sodium sulphite brought about almost complete loss of nitrogen. Sulphur content in sulphonated products thus obtained indicated extensive sulphonation of nitrolignins. The sulphur content in nitrolignins prepared from Eucalyptus milled wood lignin, wheat straw soda lignin and bamboo kraft lignin was 13.4%, 13.9% and 14.80%, respectively. The infra red spectra of sulphite treated nitro lignins indicated that there was no displacement of nitrogen with sulphite and sulphonation of the ring took place at another site. The nitro groups present in small amounts were reduced to amino group by sulphite treatment.

Utilisation of Sulphonated Lignin Derivatives

A number of sulphonated derivatives were prepared using Eucalyptus kraft lignin, wheat straw soda lignin and bamboo kraft lignin substrates; using the following sequences of modification : (i) Chlorination of lignin with chlorine water followed by treatment of chlorolignin with sodium sulphite and (ii) nitration of lignin with sodium nitrite in presence of hydrochloric acid followed by reaction of nitrolignin with sodium sulphite. The sulphonated lignins thus prepared were designated as EKSCL, WSSCL and BKSCL when sequence (i) was used for modification and as EKSNL, WSSNL and BKSNL when sequence (ii) was applied. All these six samples of sulphonated lignin derivatives were tested as solvent for isolated soda/kraft lignins, dispersing agents, emulsifiers and surfactants. The results are recorded in Tables 1-3.

Solvent for isolated lignins

In contrast to chlorolignins and nitrolignins, their sulphonated lignin derivatives were freely soluble in water. A solution of over 40% could be easily prepared. Studies on application of these sulphonated lignin derivatives as solvent for isolated lignin were conducted with a view to improve upon organosolv pulping processes; particularly to overcome precipitation of lignin onto pulp fibers during washing. A perusal of data in Table-1 indicates that the solubility of lignin in 10g/l solution of both types of sulphonated lignin derivatives (i.e. prepared via chlorination or via nitration) in 50% aqueous ethanol was over 300 g/l as against 30.5 g/l in blank 50% aqueous ethanol.

TABLE - 1

SOLUBILITY OF ISOLATED KRAFT/SODA LIGNINS

SOLVENT/ SAMPLE CODE ★	SOLUBILITY OF ISOLATED LIGNIN g/L
BLANK AQUAEOUS	30.5
ETHANOL 50 %	
EKSCL	OVER 300
EKSNL	OVER 300
WSSCL	OVER 300
WSSNL	OVER 300
BKSCL	OVER 300
BKSNL	OVER 300

★ 10 G/L SAMPLE IN 50 % AQUEOUS ETHANOL WAS USED AS SOLVENT IN EACH CASE.

These results show that 50% aqueous ethanol containing small amounts of above types of sulphonated lignin derivatives could be used as a powerful solvent to dissolve lignin at ambient temperature. However, they did not possess the property to delignify soft-wood or hardwood to achieve fibre separation.

Dispersing agents and emulsifiers

Sulphoanted lignin derivatives find application as oil-well drilling mud additives, cement and concrete additives, dyestuff dispersants, tanning agents, rubber reinforcements etc. The effectiveness of the sulphonated lignin derivatives is generally attributed to their dispersing, binding, complexing and emulsion stabilizing properties.

The sulphonated lignin derivatives prepared by the methods described above were tested for their application as dispersing agents/emulsifiers. The data in Table-2 indicates that standard dispersion number of the sulphonated lignin derivatives prepared via chlorination or nitration was much less thant unity (0.02-0.04) at an addition level of 50 mg/12 ml. of colloidal solution of titanium dioxide (6.5 g in 0.01 m sodium chloride). This shows that they could possibly find application as gelling agents and emulsifiers.

TABLE - 2

STANDARD DISPERSION NUMBER OF SULPHONATED DERIVATIVES OF LIGNIN ★

SAMPLE CODE	TORQUE DYNES/CM	STANDARD DISPERSION NUMBER
BLANK ★★	36	---
EKSCL	984	0.0366
EKSNL	1520	0.0237
WSSCL	895	0.0402
WSSNL	976	0.0369
BKSCL	1246	0.0289
BKSNL	1682	0.0214

★ AMOUNT OF SULPHONATED DERIVATIVE OF LIGNIN ADDED 50 MG.

★★ TITANIUM DIOXIDE 6.5 G/12 ML. OF 0.01M SODIUM CHLORIDE.

Surface active agent

The efficacy of the sulphonated lignin derivatives as surfactants/additives in secondary oil recovery was examined by determining the interfacial tension of crude-oil-water emulsion without and with addition of these derivatives. A perusal of data in Table-3 indicates that addition of sulphonated lignin derivatives resulted in tremendous reduction in the value of interfacial tension of the crude-oil'water emulsion.

TABLE - 3

INTERFACIAL TENSION OF CRUDE OIL-WATER EMULSION AT 2.0 % ADDITION OF SULPHONATED DERIVATIVES OF LIGNIN.

SAMPLE CODE	INTERFACIAL TENSION DYNE/CM
BLANK	28.58
EKSCL	2.145
EKSNL	2.435
WSSCL	1.984
WSSNL	2.124
BKSCL	2.411
BKSNL	1.801
SSLLS ★ (10 %)	10.00

★ SPENT SULPHITE LIQUOR SULPHONATE.

The value of interfacial tension was reduced from 28.58 dynes/cm to about 2.5 dynes/cm by an addition of 2% of all the types of sulphonated derivatives examined. These data show that these sulphonated lignin derivatives could possibly be used as aids in secondary oil recovery and may replace partly if not fully, the expensive petroleum sulphonates being used at present.

Conclusion

The chemical sequences used for modification of isolated kraft/soda lignins yield highly water soluble sulphonated derivatives of lignins which were found to contain sulphonic acid groups in nucleus as well as in the side chain. Sulphite groups also got added up into the macromolecule through quinone-adduct sulphite formation. All the sulphonated derivatives of lignins prepared by employing the sequences: chlorination followed by reaction of chlorolignin with sodium sulphite and nitration by sodium nitrite in presence of hydrochloric acid followed by reactin of nitrolignin with sodium sulphite were found to possess (i) a very high power to dissolve lignin at a concentration of 10 g/l in 50% aqueous ethanol, and (ii) good properties for use as dispersants, emulsifiers and surfactants.

Experimental

Chlorination of lignin

Isolated kraft/soda lignins were chlorinated with chlorinewater for 5 min. at 10-20°C, under the following conditions: chlorine to lignin ratio 1:1, pH 2.0, and consistency 0.4 percent. The chlorinated product was recovered through filtration on a Buchner funnel, washed thoroughly and dried under vacuum at 42°C.

Nitration of lignin

Nitration was done by treating an aqueous suspension of lignin substrate (10.0 g) with sodium nitrite (10.0 g) dissolved in distilled water in presence of hydrochloric acid (100 ml, 1N) contained in a total reaction volume of 750 ml. The reaction was carried out in a fume cup-board for 1 hr at 70°C with constant stirring. The product was separated by filtration and washed thoroughly with water.

Sulphonation of chloro and nitrolignin

Sulphonated derivatives of lignins were prepared by refluxing the chlorolignin sample (10.0g) and sodium sulphite (10.0g) contained in 100 ml of distiled water for 1 hr. The soluble concentrated sulphonated product was precipitated by pouring into a vigorously stirred ethanol. The precipitated sulphonated derivative was washed with ethanol until free of sulphite and chloride ions and dried under vaccum at 42°C. Similarly, nitrolignin sample was refluxed with sodium sulphite in water. The sulphonated derivative was prepared in a similar manner as described above.

Standard dispersion number

Dispersion property is measured by the decrease in the viscosity of an aqueous suspension of titanium dioxide when known amount of sulphonated derivative of lignin is added in the medium. Standard dispersion is given by the formula:

SDN = torque (control)/ torque (dispersed with sulphonated derivative of lignin).

Surface active property

The interfacial tension was determined using infacial tensiometer. The system was crude-oil-water emulsion with and without sulphonated derivatives of lignin.

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