Kinetics and Mechanism of Reactions of The Lignins of Wheat Straw, Rice Straw and Bagasse With Sulphite Ions

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ABSTRACT

Wheat straw, rice straw and bagasse were used as substrates to study the kinetics and mechanism of the reactions of lignins with sulphite ions. Native lignin characteristics were studied and C_9 formula of the lignins with methoxyl group for wheat straw, rice straw and bagasse were determined. The C_9 formula for wheat straw, rice straw and bagasse are $C_9H_{13.74}O_{2.30}(OCH_3)_{1.008}$, $C_9H_{12.71}O_{2.79}(OCH_3)_{0.89}$ and $C_9H_{11.49}O_{3.30}(OCH_3)_{0.99}$ respectively.

Variations of the ratio of syringyl to guaiacyl units was 1.014, 0.678 and 0.390 for bagasse, rice straw and wheat straw, respectively.

The process of delignification in case of all the three substrates i.e. wheat straw, rice straw and bagasse with sulphite ions buffered with sodium hydroxide followed second other kinetics in respect to lignin concentration. With wheat straw and rice straw the kinetics of delignification was governed by two rate laws. The value of second order rate constant K_2 for wheat straw was 6×10^{-4} 1 min^{-1} $mole^{-1}$ and for rice straw was 8×10^{-4} 1 min^{-1} $mole^{-1}$. In case of bagasse the value of second order rate constant increased linerarly with increasing concentration of sulphite ions and reaction temperature unlike with wheat straw and rice straw. It was 2×10^{-1} 1 min^{-1} $mole^{-1}$ at 150 °C, 3×10^{-4} 1 min^{-1} $mole^{-1}$ at 160 °C and 6×10^{-4} 1 min^{-1} $mole^{-1}$ at 170 °C. The kinetics of pentosans dissolution also exhibited two rate laws with wheat straw and rice straw. In case of bagasse the kinetics of pentosans dissolution was governed by only one rate law throughout.

The changes in lignin to carbohydrate ratio with pulp yield indicated that there are conditions when dissolution of carbohydrates took place for the most part and when both carbohydrates and lignin were removed in equal proportions. Such type of phases distinctly appeared in case of all the three substractes.

The reaction between isolated lignins of wheat straw, rice straw and bagasse with sulphite ions revealed that the rate of consumption of sulphite ions followed a second order kinetics with respect to sulphite concentration.

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The sulphonation of lignin model compounds namely vanillyl alcohol and veratryl alcohol and their methyl ethers with sodium sulphite in conjunction with sodium bicarbonate indicated that benzyl alcohol derivatives are readily sulphonated under neutral conditions when there is free hydroxyl group in the para position of the benzene ring, but are unreactive when methylated. Consequently it is unlikely that complete delignification would take place during neutral sulphite conditions. Demethoxylation and formation of methane sulphonic acid take place. However, dealkylation takes place very slowly.

INTRODUCTION

The realities about shortage of forest based cellulosic materials, viz. softwoods, hardwoods and bamboos, coupled with increasingly growing conciousness about environmental protection have led to identification of alternative resources of cellulose fibres for pulp and paper industry. Among various resources the non-wood lignocellulosic raw materials are gaining increasing importance in supplementing the requirment of renewable fibrous resources for production of paper a commodity which has rather become essential in every sphere of our every day life and is considered a vehicle on which our civilization today is moving. The agricultural fibrous resources available for papermaking mainly comprise of wheat straw, rice straw and bagasse. The efficiency of utilization of agricultural residues in small scale mill would depend on the availability of knowledge on process parameters and the details of the mechanism of delignification reactions in technical process. Elucidation of the mechanism of delignification reactions in turn is highly dependent on the fundamental knowledge on the chemical composition of the lignin and its origin. The reaction of lignin with sodium sulphite and sodium bisulphite combination can sulphonate the lignin selectively and retain more hemicelluloses and thus produce lignified cellulose fibres in much higher yields as compared to conventional alkali process of delignification. This is important for wider utilization of agricultural residues in papermaking furnishes and conservation of long fibre material bamboo for more retaional use. Therefore in order to provide such data, on chemical composition and reactions of lignin of wheat straw, rice straw and bagasse for seeking appropriate technology the kinetics of reactions of the lignins with sulphite ion is discussed in this paper.

EXPERIMENTAL

PROXIMATE CHEMICAL ANALYSIS

The methods employed for proximate chemical analysis were as described by TAPPI standard.

Isolation of lignin: In the present investigation the object of isolation of lignin has been to characterise the chemical and structural composition of lignin as it is found in the substrate ligno-cellulosic raw material. Therefore, organosolv lignins have been prepared for the investigations on chemical/structural composition of the lignins of the wheat straw, rice straw and bagasse, using the procedure described by Bland and Menshun (1). As lignin macromolecule is built up of phenyl propane units, empirically it is best represented by C_9 formula. Since all the lignins are principal carrier of methoxyl groups, the C_9 emperical formula generally incorporates representation of methoxyl groups. Therefore for chemical characterisation of lignins, C_9 formula with methoxyl per C_9 is usually calculated. A similar approach has been adopted in this investigation for the lignins of wheat straw, rice straw and bagasse.

Functional Group Analysis

For determination of methoxyl content the method described in TAPPI standard has been used (2). The carbonyl groups were determined by hydroxylaminehydrochloride method of Gierer and Sodenberg (3) the total hydroxyl conent (both aliphatic and aromatic) was determined by acelyation (4). Lignin oxidation products determination of lignin were determined by using Perkin Elmer Gas Chromatogram 3920 equipped with lame ionisation detector by using SE-30 column and injection temperature 250 ^{0}C. The peak area of various aldehydes detected on the chromatogram was determined by dividing the height of the peak with the width at half height.

Kinetics of reaction with sulphite ions

To study the reactions of wheat straw, rice straw and bagasse with sulphite ions powdered meal (5.0 g o.d.) was placed in a stainless steel bomb. To the stainless steel bomb cooking chemicals i.e. sodium sulphite and sodium hydroxide (Na_2SO_3, 8-12%, NaOH 2%) were added. The ratio of the material to liquor

Table-1

Proximate chemical analysis of wheat straw, rice straw and bagasse

Sl. No.	Particulars	Raw Material		
		Bagasse	Wheat straw	Rice straw
	Structural constituents			
1.	Holocellulose	75.07%	71.19%	69.00%
2.	Alpha cellulose	41.88%	43.21%	47.30%
3.	Pentosans	28.39%	26.83%	17.40%
4.	Klason lignin	21.32%	20.61%	17.40%
	Non-structural constituents			
5.	Hot water solubles	3.24%	10.59%	15.39%
6.	1% NaOH solubles	36.67%	41.39%	51.06%
7.	Ash	1.78%	9.41%	16.17%

ratio was maintained 1:6 by the addition of distilled water into the bombs. The bomb was tightly closed and placed inside a stationary pressure autoclave containing water. The autoclave was tightly closed and heated by gas to raise the reaction temperature to the desired level (i.e. 150-170 ^{0}C), which was maintained within the limits of $\pm$ 1^{0}C. After the completion of the cooking schedule the digester was blown and the bomb was taken out and cooled in a water trough. The cap of the bomb was opened, the contents filtered onto a pre-weighed sintered crucible (IGI) washed throughly with distilled water and then dried in an oven at 105 $\pm$ 3 ^{0}C. The overnight dried crucible was cooled in a desiccator and weighed to determine the yield of delignified pulp by difference in the weight of the sintered crucible. For determination of degree of delignification, delignified material was taken and the klason lignin content was determined according to the TAPPI standard (T-12m-59).

Pentosans degradation were determined by using TAPPI standard (T-19m-20).

RESULTS AND DISCUSSIONS

Wheat straw, rice straw and bagasse were used as substrates to study the kinetics and mechanism of the reactions of the lignins with sulphite ions. before carrying out studies on kinetics and mechanism of delignification with sulphite ions, all the three substrate materials were subjected to (1) Chemical characterisation in respect of their proximate chemical composition of structural and non structural constituents and (2) native lignin characteristics.

Structural constituents determinations comprised of alpha cellulose, pentosans, holocellulose and lignin. Determination of non-structural constituents included hot water solubles (polyphenols) 1% NaOH solubles and ash (mineral matter).

Studies on native lignin characteristics were composed of elemental analysis, C_9 formula, functional groups analysis (phenolic hydroxyl, methoxyl, carboxyl and total hydroxyl), identification of basic structural units of macromolecules and determination of syringyl to guaiacyl unit ratio.

The kinetics of delignification of wheat straw, rice straw and bagasse were carried out with sodium sulphite buffered with caustic soda at varying concentrations of sulphite ions and varying temperatures. The progress of the reaction was followed by estimating residual lignin in delignified fibres (pulp), pentosans, lignin to carbohydrate ratio etc. Rate of sulphite consumption with isolated lignins was also determined and the mechanism of sulphonation was elucidated with studies on model compounds.

Proximate Chemical Analysis

The results on proximate composition of structural and non structural constituents are recorded in Table-1.

A comparison of the values of holocellulose, pentosans, alpha cellulose, klason lignin with those of domestic hardwoods used for pulp and paper production indicated the suitability of all the three substrates for carrying out investigations on the chemical composition of their lignins and on the kinetics and mechanism of delignification, pentosans dissolution, changes in lignin to carbohydrate ratio, etc. as the percentage of all the structural constituents are within the range usually required in case of a

Table-2

Functional groups of the lignin of wheat straw, rice straw and bagasse

Lignin	Carbonyl per C_9	Total hydroxyl %	Phenolic hydroxyl per C_9
Wheat straw	0.198	8.68	0.25
Rice straw	0.147	7.42	0.21
Bagasse	0.172	8.22	0.24

ligno cellulosic material envisaged for assessment to manufacture pulp and paper.

Among non-structural constituents as well, the percentages are within acceptable limites. However, the lower is the percentage of the hot water solubles and 1% NaOH solubles, which corresponds to polyphenols, the better is the material, because polyphenols are regarded as non productive consumers of delignifying chemicals and are undesirable components, for they provide extra hydroxyl groups for condensation with spent liquor lignin making it more intricate for further processing. Similarly if ash, content which mainly corresponds to silica, is low, the material practically pose little problem in overall papermaking. Looking in these points of view it could be concluded that bagasse is better than both wheat straw and rice straw. But wheat straw in turn better than rice straw for papermaking.

CHEMICAL COMPOSITION OF LIGNINS

Elemental composition/C_9 formula

The C_9 formula of the lignins with methoxyl group for wheat straw, rice straw and bagasse are as under:

Wheat straw : $C_9 H_{13.74} O_{2.30} (OCH_3)_{1.008}$

Rice straw : $C_9 H_{12.71} O_{2.79} (OCH_3)_{0.89}$

Bagasse : $C_9 H_{11.49} O_{3.30} (OCH_3)_{0.99}$

The data on hydrogen per C_9 show that the lignin of wheat straw is in a more condensed state as compared to that of the other two materials. The lignin of bagasse is in least condensed state among the three. The methoxyl per C_9 varied in the following sequence: Wheat straw ($1.008/C_9$), bagasse ($0.99/C_9$), rice straw ($0.89/C_9$). The variation in C_9 formula weight, hydrogen per C_9 and methoxyl per C_9 indicated that emperically the lignins of wheat straw, rice straw and bagasse differ widely with each other.

REACTIVE GROUPS

Carbonyl groups: The data on carbonyl groups (Table-2) indicated that the lignin of wheat straw contains 13% higher carbonyl per C_9 than that of bagasse lignin and the value is 24% higher to what is found in rice straw lignin, bagasse lignin contains 19% higher carbonyl per C_9 unit in comparison to what is present in rice straw lignin.

Hydroxyl groups: The percentage of total hydroxyl groups varied from lignin to lignin but within a narrow range. Wheat straw lignin contained 8.68% total hydroxyl groups, rice straw, lignin contained 7.42% and bagasse lignin 8.22%. The phenolic hydroxyl content in the lignins of wheat straw, rice straw and bagasse revealed that there is very little variation in phenolic OH per C_9 unit of lignin. The values are between 0.21-0.25 per C_9.

STRUCTURAL CHARACTERISTICS

Molar ratio of Syringyul to Guaiacyl units: It was found that the molar ratio of syringyl to guaiacyl unit in the lignins of wheat straw, rice straw and bagasse varied widely from each other. The variations was in the following order: Bagasse (1.014); Rice straw (0.678), wheat straw (0.390). It has been reported by number of workers that the molar ratio of syringyl to guaiacyl unit vary from species to species, even in the same genus and exert its influence on rate of delignification. Higher the ratio, the better is

Table-3

Peak Area of aldehydes from Gas Chromatograms

Lignin	Peak area			S/V molar ratio
	Syringaldehyde	Vanillin	p-hydroxy benzaldehyde	
Wheat straw	1.52	3.25	2.04	0.390
Rice straw	1.95	2.40	1.26	0.678
Bagasse	2.55	2.10	2.64	1.014

the material from delignification and from processing lignin containing spent liquor points of view. Thus with this point of view bagasse could be considered superior to rice straw and wheat straw.

From the results presented above on the chemical composition C_9 formula, reactive groups, basic structural units and syringyl to guaiacyl units ratio it could be concluded that the chemical and structural composition of the lignins of wheat straw, rice straw and bagasse vary widely with each other, indicating thereby the face about the differences that may be encountered in the reactions of the lignin of different origin during modification reaction, degradation reactions and numerous other reactions in technical processes of pulping and bleaching.

REACTION OF LIGNIN/ CARBOHYDRATES WITH SULPHITE IONS

Kinetics of delignification with sulphite ions

The process of delignification in case of all the three substrates, i.e. wheat straw, rice straw and bagasse with sulphite ions buffered with sodium hydroxide followed second order kinetics in respect of lignin concentration. With wheat straw and rice straw the kinetics of delignfication was governed by two rate laws. nearly after 45 min of the reaction time, the second slower phase of kinetics appeared at all concentrations of sodium sulphite and reaction temperature. With bagasse the kinetics of delignification followed only one rate law throughout.

The value of second order rate constant (K_2) for the first phase of kinetics of delignification which lasted for about 45 min. in case of wheat straw and rice straw, was independent of suslphite ions concentration and reaction temperature. It was 6×10^4 1 min^{-1} $mole^{-1}$ and 8×10^{-4} 1 min^{-1} $mole^{-1}$ for wheat straw and rice straw, respectively. In case of bagasse the value of second order rate constant increased linearly with increasing concentration of sulphite ions and reaction temperature unlike with wheat straw and rice straw. It was 2×10^{-4} 1 min^{-1} $mole^{-1}$ at 150 ^{0}C, 3×10^4 1 min^{-1} $mole^{-1}$ at 160 ^{0}C and 6×10^4 1 min^{-1} $mole^{-1}$ at 170 ^{0}C. 80% sodium sulphite in conjunction with 2.0% sodium hydroxide were used as delignifying agent in all cases.

These results indicated that the value of second order rate constant for the kinetics of delignification varies with substrate.

Kinetics of Pentosans Dissolution

During the course of delignification of wheat straw, rice straw and bagasse with sulphite ions buffered with sodium hydroxide, the process of degradation/dissolution of pentosans, as determined by the amount of residual pentosans in delignified fibres, followed a zero order kinetics with respect of pentosans in case of all the three substrates.

Like the kinetics of delignification, the kinetics of pentosans dissolution also exhibited two rate laws with wheat straw and rice straw. In case of bagasse the kinetics of pentosans dissolution was governed by only one rate law throughout.

In case of wheat straw the value of zero order rate constant (Ko) was dependent of sulphite ions concentration and reaction temperature. Its value was 0.09×10^3 min^{-1}. In case of rice straw it was independent of sulphite ions concentration but changed with reaction temperature. The value being 0.04×10^{-3} min^{-1}, 0.12×10^{-3} min^{-1} and 0.06×10^{-3} min^{-1} at 150 ^{0}C, 160 ^{0}C and 170 ^{0}C, respectively. In case of bagasse the value of zero order rate constant was independent of the concentration of sulphite ions and reaction temperature. Its value was 0.05×10^{-3} min^{-1}.

These results indicate that although the process of pentosans dissolution followed zero order kinetics in respect of pentosans concentration, the value of zero order velocity constant was found to be substrate dependent.

Changes in lignin to carbohydrate ratio

The changes in lignin to carbohydrate ratio with pulp yield indicated that there are conditions when dissolution of carbohydrates took place for the most part and when dissolution of lignin took place for the most part and when both carbohydrates and lignin were removed in equal proportions. Such type of phases distinctly appeared in case of all the three substrates. Particularly these were influenced by reaction temperature. The data on pattern of changes in lignin to carbohydrate ratio with pulp yield could help in deciding upon the reation conditions to obtain desire composition of pulp at a particular yield. Such type of graphical representation works an analytical tool for controlling the process of delignification and dissolution of pentosans as per the requirement of pulp composition in view.

Kinetics of sulphite consumption

The reaction between isolated lignins of wheat straw, rice straw and bagasse with sulphite ions revealed that the rate of consumption of sulphite ions followed a second order kinetics with respect to sulphite concentration. The value of second order velocity constant (K_2) was 0.8 1 min^{-1} $mole^{-1}$, 1.0 1 min^{-1} $mole^{-1}$ and 2.5 1 min^{-1} $mole^{-1}$ for wheat straw, rice straw and bagasse respectively under the conditions studied.

Mechanism of sulphonation

Sulphonation of lignin model compounds namely vanillyl alcohol and varatryl alcohol and their methyl ethers with sodium sulphite in conjunction with sodium bicarbonate indicated that benzyl alcohol derivatives are readily sulphonated under neutral conditions when there is a free hydroxyl group in the paraposition of the benzene ring. But are unreactive when methylated. Consequently it is unlikely that complete delignification would take place during neutral sulphite conditions. Demethoxylation and formation of methane sulphonic acid takes place. However, dealkylation takes place very slowly.

CONCLUSIONS

Wheat Straw: In case the results reveals that changes in lignin to carbohydrate ratio with pulp yield at 8% sodium sulphite and 150 ^{0}C followed two distinctly different phases. When pulp yield falls from 74% to 73%, in early stage of reaction, it was lignin that got dissolved and practically little carbohydrate dissolution took place. In II phase when pulp yield dropped from 73% to 66%, both lignin and carbohydrate got dissolved. AT 160 ^{0}C in the first part where the pulp yield changed from 72% to 65% the dissolution of carbohydrate more pronounced as compared to lignin whereas in subsequent part when pulp yield changed from 65% to 63% dissolution of lignin was more pronounced in comparison to carbohydrate. At 170 ^{0}C results showed three distinct phase. In first phase yield changed from 68.5% to 67% lignin carbohydrate ratio changed uniformly. In II phase carbohydrate got dissolved to a greater extent than lignin from 67% to 61%. In II phase the yield dropped from 61% to 59% here lignin got dissolved to much greater extent than carbohydrate.

Rice Straw: For fice straw studies indicated that the change in lignin to carbohydrate ratio at 8% sodium sulphite and 150 ^{0}C with pulp yield followed two distinct phases. In first phase where the pulp yield dropped from 70% to 67% greater dissolution of lignin took place as compared to carbohydrates. On the other hand in the II phase where the pulp yield dropped from 67% to 64% there was only little change in lignin to carbohydrate ratio. AT 160 and 170 ^{0}C. It was observed that both lignin and carbohydrate were removed almost in same proportion.

Bagasse: In case of bagasse also change in lignin to carbohydrate ratio with pulp yield at 8% sodium sulphite at 150 ^{0}C took place in two phase. In first phase in the yield change from 79% to 76% dissolution of lignin was slightly more pronounced. In the II part when yield decreased from 76% to 72% lignin and carbohydrate got dissolved almost at same ratio. Similar trend was observed at 160 ^{0}C and 170 ^{0}C.

These results have direct application in deciding the chemical composition of pulp with respect to delignification and carbohydrate removal and consequently upon pulp yield and kappa number.

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