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Estimation of Pulp Lignin Content in The High Yield Pulping of Prosopis

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Investigations carried out on the chlorination reaction of lignin with prosopis pulp by high yield pulping process indicated optimum reaction time to be 0.5 h for the estimation of chlorine number (CN). The chlorine number value determined with 0.5 h chlorination time is found to be correlated with the unbleached pulp lignin contents as % lignin 0.8992 chlorine number 0.4899 with 95 % confidence limit for the slope 0.8872 ± 0.052 I and for the intercept = -0.4688 ± 1.1300. 22 to 32 % of the total lignin content was observed to be acid soluble and therefore in the regression equation of lignin on the chlorine number value when total lignin value (soluble + insoluble) is fed to the equation the correlation ship gives more accurate data for pulp lignin content. This linear correlation ship between the total lignin content and the chlorine number is recommended for analytical simplification in the high yield range of pulping investigation.

Key Words: Prosopis, Lignin, Chlorine number, High yield pulp.

INTRODUCTION

Prosopis chinensis Linn belong to the family Leguminasae ;Mimosaceae: It is an unarmed tree or shrubs with drooping branches, found either in a wild of cultivated state in the drier parts of India. Bark grayish brown; leaves bipinnate with two to four pairs of pinnae; pinnules 10-46 pairs, 5-20 mm long, flowers small yellowish in dense spikes;pods yellow,10-25 cm × 8-15 mm, straight or falcate, flat or cylindrical, often with transverse depressions between the seeds; seeds 10-30 in a pod, ovoid, flattened 7 mm × 3 mm hard yellowish brown shiny.

The prosopis chinens is usually a small tree which may be attained a height up to 20 m under favourable condition, is often reduced to shrub in very dry situations. It grow branching and bushy form in the early stage together with its excellent coppicing power made it a very suitable soil. Now-a-days approximately there are 20-25 species of tropical hard wood which is being used in paper industries to some extant. The only limited use of various species is due to lack of availability of fundamental knowledge on the chemical composition of lignin and its relationship in technical process. Therefore in order to provide such data it is proposed to investigate the chemical composition and a relationship of lignin of the Prosopis[1-14].

The work present in this paper highlighted the experimental investigations carried out with the following objectives: (a) To study chlorination reaction of lignin for the estimation of optimum time to be used for the deduction of chlorine number. (b) To find the correlation ship of pulp lignin content (within the high yield range of pulping) with chlorine number evaluated on the basis of optimal level of chlorination time.

EXPERIMENTAL

Lignin in non-wood plant: The wood plant proposis were ground in a ball mill and the fraction -30 + 60 mesh were taken for lignin estimation which was done according to Tappi standard T-13 m 54 methods[15]. Extraction with 95 % alcohol was omitted. For acid soluble lignin UV spectra (200-350 mμ wavelength) of the property diluted (with 3 % H_2SO_4) filter after lignin estimation by the Klason method[16] was taken against 3 % H_2SO_4 in Shimadzu UV 160 1PC with the two cells for holding the sample of (1 cm internal distance) are use the result recorded in Table-1.

TABLE-1
TOTAL LIGUIN (SOLUBLE + INSOLUBLE) CONTENT OF WOOD

Sample	Secondary hydrolysis	P.C. of soluble liguin		P.C. of total liguin in unrestricted wood
		Based on total liguin	Based on unextracted wood	
1	With reflux	14.15	4.04	29.10
2	With reflux	16.20	4.25	29.14
3	With reflux	14.00	4.18	28.80
4	Without reflux	13.10	3.14	29.28
5	Without reflux	13.00	3.80	27.81
6	Without reflux	13.00	3.90	28.40

Lignin in wood (Prosopis) pulp: Tappi standard T222m-24 method was followed for estimating the acid insoluble lignin in higher yield wood pulp secondary hydrolysis was done without reflux and the liquid level was maintained by periodic addition of distilled water during the alcohol-benzene extraction step, was observed for samples, that good amount of lignin was dissolved. The residue which was left after evaporating alcohol and benzene was taken to its chlorine consumption. UV spectra of the filtrate with proper dilutions with 3 % H_2SO_4) against 3 % H_2SO_4 was taken in the above mentioned spectrometer. The results are reported in Table-2. For standard absorptivity of lignin and were treated with 5 % NaOH for 3 h at 160 ºC. After proper dilutions with distilled water UV spectra of the dissolved lignin in 0.01 % NaOH against 0.01 % NaOH in the blank was taken. Absorptions at 205 and 280 mμ were noted. To find out the interference of carbohydrate derived products during soluble lignin determination synthetic mixture of D Glucose and Dxylose in the ratio of 5:1 was taken and its acid hydrolysis was taken and its acid hydrolysis was done according to Kalson lignin determination method. UV absorption spectra of the resulting solution was taken against 3 % H_2SO_4.

Chlorine number: The pulp to be tested was completely disintegrated and a test specimen of 0.5 ± 0.0005 g off air dry pulp or powdered wood meal was weighted and at the same time duplicated sample were weighted for moisture content. The sample was put in 500 mL flask at room temperature, in which 250 mL of distilled water was added. The results are given in Table-2.

TABLE-2
TOTAL LIGUIN (SOLUBLE + INSOLUBLE) CONTENT AND
CHLORINE NUMBER OF UNBLEACHED HIGH YIELD PULP

Sample	Per cent of acid soluble liguin						Per cent of total liguin in unextracted pulp			Chlorine number gCl_2/100 OD pulp		
	Based on total liguin			Based on unextracted pulp								
	A	B	Avg.	A	B	Avg.	A	B	Avg.	A	B	Avg.
P(4)	26.40	26.34	26.37	6.54	6.45	6.49	23.40	23.81	23.60	27.52	27.00	27.27
P(5)	28.84	30.90	29.87	7.42	7.64	7.28	23.75	24.05	23.90	27.00	27.10	27.05
P(6)	31.45	31.35	31.40	7.54	7.50	7.52	23.15	23.05	23.10	26.40	25.89	26.14
P(7)	34.40	34.25	34.32	7.84	7.81	7.82	22.52	22.85	22.60	26.00	26.00	26.00
P(8)	28.50	28.00	28.25	6.90	7.05	6.97	25.10	25.40	25.25	28.84	28.52	28.78
P(18)	28.40	28.40	28.40	5.68	5.62	5.65	20.20	20.16	20.18	23.54	23.70	23.62
P(20)	26.00	27.10	26.55	3.84	4.04	3.94	16.42	16.02	16.22	17.54	17.54	17.54
P(21)	19.45	19.50	19.49	2.35	2.26	2.30	13.40	13.48	13.44	15.49	16.00	15.74
PM(1)	29.42	29.40	29.41	4.50	4.50	4.50	15.84	16.15	15.99	19.14	19.42	19.31
PM(2)	30.40	30.14	30.26	4.04	4.03	4.35	13.42	13.40	13.41	16.40	16.25	16.32
PM(17)	28.42	27.50	27.96	5.42	5.40	5.41	18.80	18.65	18.72	20.80	20.85	20.82
PE(1)	31.42	31.40	31.41	2.84	2.82	2.83	8.94	8.84	8.89	10.34	10.00	10.17
PE(2)	30.14	29.60	27.87	3.42	3.24	3.33	11.52	11.42	11.47	13.04	13.16	13.10

All % are on oven dry basis.

Preparation of high yield unbleached pulp: The pulp required study of correlation between lignin content and chlorine number of high yield unbleached pulp were obtained by pulping prosopis with NSSC Na_2SO_3 process pulp P4, P5, P6, P7, P8, P9,

Pulp Mixture PM1 PM2 experimental pulp PE1 and PE2 are obtained at pulping temperature between 160-170 and pulp P^{11} and P^{12} at 185 ºC. Pulping was carried out in stainless steel recovery digester-under the following condition.

(1) Na_2SO_3:Na_2CO_3::12:3 to 24:6
(2) L/M ratio-4
(3) Temperature range 160 to 185 ºC

Bleaching of pulp: Pulp with chlorine number 27.5 and pulp 2 26.5 gels per 100 g OD pulp were taken for bleaching experiments well known chlorination alkali extraction and sodium hydrochloride treatment sequence was followed. Pulp 1 was bleached with 25 and 5 % of its chlorine number and pulp 2 with 50 and 10 % of its chlorine number in chlorination and hypochlorite stage, respectively. The data required for bleaching to be carried out was taken from Kansal work[16]. The lignin and chlorine number of the resulting pulp are given in Table-3.

TABLE-3
TOTAL LIGUIN (SOLUBLE + INSOLUBLE) CONTENT AND
CHLORINE NUMBER OF HIGH YIELD PULP

Sample	Per cent of acid soluble liguin						Per cent of total liguin in unextracted pulp			Chlorine number gCl/110 g OD pulp		
	Based on total liguin			Based on unextracted pulp								
	A	B	Avg.	A	B	Avg.	A	B	Avg.	A	B	Avg.
BP (1)	30.60	30.70	30.65	5.84	5.86	5.85	18.42	18.40	18.41	18.46	18.50	18.48
BP (2)	38.94	38.90	38.92	4.14	4.11	4.13	10.54	10.62	10.58	10.64	10.62	10.63

RESULTS AND DISCUSSION

Experimental results relating to percent chlorine consumption against chlorination time for wood meal and pulp are presented in Fig. 1. It is clear that chlorination reaction of lignin consists of fast rate followed by asymptotic pattern when the equilibrium figure of chlorine consumption (for calculation purpose this may be taken as 35.30 and 30.15 for wood meal and unbleached pulp, respectively) is compared with the chlorine consumption at different time interval it is observed that there is significant variation between 15 and 30 min time interval. Incase of unbleached pulp, chorine consumption value (based on % OD pulp which is equivalent to chlorine number value) at 0.5 h chlorination is found to 7.25 % more as compared to 15 min chlorination time. After a chlorination time of 0.5 h, variation is found to be much lower. Similar trend is found in case of wood meals also.

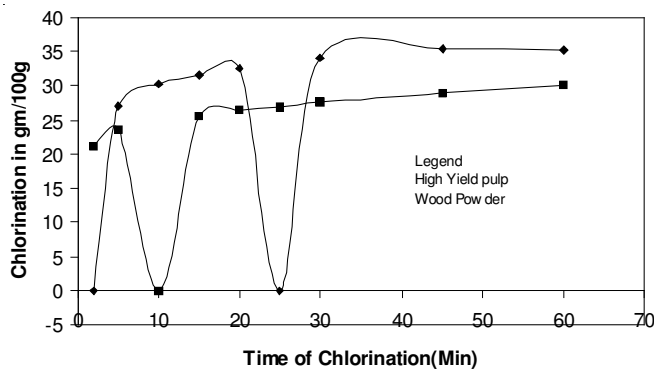

Fig. 1.

Quantitative determination of lignin in kalson lignin filtrate: Absorbivity of lignin were calculated as 106 and 21 L/g cm and of carbohydrate degradation products as 0.82 and 0.27 L/g at 206 and 280 μm, respectively. Knowing these value and the absorbance of the filtrate, after klason lignin estimation, at 205 and 208 μm *i.e.* a205 and a280, respectively the soluble lignin concentration (CL) was calculated for the following expression:

$$a_{205} = 0.27\ C_D + 106_{CL}$$
$$a_{208} = 0.28\ C_D + 21_{CL}$$

where C_D is the concentration of carbohydrates degradation products.

Disssolution of lignin in alcohol benzene extraction: During the alcohol-benzene extraction of pulp sample was observed that some amount of lignin was dissolved along with the extractives. The average extractive contents of those pulp were found to be 2.2 and 2.5 % (based on the pulp), respectively, which is more than a value (av. 06 %) obtained for other pulps. If we take extractive contents of the pulps as 0.6 % then amount of lignin dissolved during extraction is 1.6 and 1.9 %, respectively. These results were later on confirmed when the chlorine consumption values of the residue left after evaporating alcohol benzene mixture were put in linear regression of lignin content on chlorine number, which gave average amount of lignin dissolved as 1.70 and 2.05. From these observations, it was, postal that the higher temperature degradation of some fraction of lignin in pulp gives rise to low molecular weight lignin molecules, which are dissolved in alcohol-benzene mixture during the extraction step. The above mentioned statement is substantiated by the observation of lower acid soluble lignin. In other words, it may be stated that the acid soluble lignin value for the pulps are low because low molecular weight lignin fractions have already been moved in the extraction steps. During delignification of wood low molecular weight fractions of lignin are dissolved first decreasing values of acid soluble lignin gives the evidence of the above statement.

Condition of carbohydrates Degradation Products with lignin during refluxing step in lignin determination: From table it is clear that when secondary hydrolysis was done with reflux legnin value es are higher than the values obtained without reflux. It means that the compounds like furfural, hydroxymethyl furfural, which are result from the carbohydrates degradation during acid hydrolysis, if allowed to condense and refluxed back, combine with lignin and thus increase its weight. This condensation of carbohydrates degradation product occur both with acid insoluble and soluble lignin.

Correlation between Lignin content and chlorine number: A linear regression of % lignin content on chlorine number calculated from the average values of lignin content and chlorine no is shown in figure and the regression equation is:

$$\% \text{ Lignin content} = 0.8872$$
$$\text{Chlorine number} = 0.4688$$

And 95 % confidence limit for slope 0.8872 ± 0.0521 and for intercept = 0.4688 ± 1.1300 contents and chlorine number of bleached pulp were given in Fig. 2. It was found that the point give considerable scattering from the regression data for unbleached pulps. The reason for the low value of chlorine number. When lignin for the lignin content of bleached pulp, is thought to be due to partial oxidation of lignin during bleaching operation thus shows less amount of chlorine consumption during chlorine number determination. Therefore, the correlationship of pulp lignin content with chlorine number of unbleached pulp is not applicable and as such not recommended for bleached pulp.

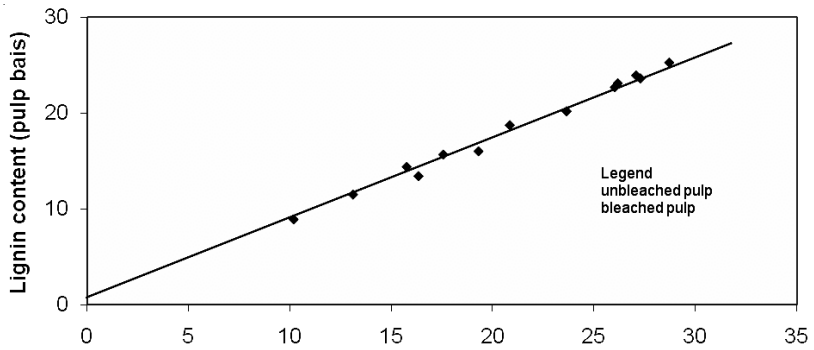

Fig. 2. Chlorine number g/100 g OD pulp->linear regiression of % liquin content (sol + insol) on chlorine number of higher yield pulp

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