

# On the Chemistry of Lignin and Hemicelluloses and Kinetics of Pulping and Bleaching of Eucalyptus & Bamboo

By

S.V. Singh & S.R.D. Guha

Cellulose and Paper Branch, Forest Research Institute, Dehra Dun

## Introduction

Technological developments in pulp and paper industry are directly related to the availability of knowledge on various aspects of raw material properties such as composition of lignin and hemicelluloses and kinetics of pulping and bleaching processes.

In India, large scale plantations of *Eucalyptus* species mainly *E. grandis* and *E. tereticornis* have been raised to cater the growing needs of alternative raw materials for pulp and paper and conserve the present day long fibre raw material bamboo so as to sustain its supply in coming years.

It has been reported by Bland and Co-workers<sup>1</sup> that there is a considerable difference in ligning of different species of Eucalyptus and the chemical composition of lignins change under the influence of different climatic conditions. Sarkanen and Change<sup>2</sup> have shown that hardwoods having more syringyl building units to guaiacyl building units ratio have higher rate of delignification. This difference in lignin composition of various hardwood species is one of the important factors influencing the pulping and bleaching processes.

In plant tissues there exist in addition to lignin and cellulose, as a third main component,

various carbohydrates of low degree of polymerisation, called hemicelluloses, calling for primary consideration when an increase in the yield of pulp is in question. The presence of hemicelluloses is desirable for paper grade pulp, whereas they are regarded as undesirable for rayon grade pulps. Therefore an important consideration should be given to the composition and reactions of hemicelluloses of papermaking raw materials.

In order to provide basic data on the chemical composition of *Eucalyptus* species and *Bamboo* and on their pulping, bleaching and papermaking characteristics, a comprehensive course of investigation has been undertaken at the Cellulose and Paper Branch, Forest Research Institute, Dehra Dun. This paper presents studies on lignin, hemicelluloses and kinetics of pulping and bleaching of *Eucalyptus grandis* and - *tereticornis* and *Dendrocalamus strictus*, the most common species of bamboo being used at present.

## LIGNINS OF EUCALYPTUS AND BAMBOO

### Chemical Composition of *Eucalyptus grandis* and - *tereticornis* Lignin

The chemical composition of various lignins of *Eucalyptus*

*grandis* and - *tereticornis* has been investigated and the results are given in Table I. A perusal of data in Table I indicates that methoxyl content of organosolv lignins is in the range of 18—20; whereas soda and sulphuric acid lignins are of lower methoxyl content. Organosolv lignins therefore are considered better preparations for studying reactions of lignin in reaction to its structural examination, because methoxyl content is a direct measure of purity of lignin preparation.

It is also seen from these data that methoxyl values of organosolv lignins of both the species are comparable. The total hydroxyl content of *E. grandis* lignin is slightly more than that of *E. tereticornis*; whereas the phenolic hydroxyl portion of the former is double of the later one. Alkaline nitrobenzene oxidation of the lignins of both the species yielded syringaldehyde and vanillin but in different quantities. This suggests that the lignins of both these species are composed of syringyl propane and guaiacyl propane building units but their ratio differ in two cases. The data in Table II reveal that the ratio of syringyl to guaiacyl units in case of *E. grandis* lignin is more than that in *E. tereticornis*. This fact reflects the difference in pulping characteristics of the

two species, *E. grandis* should have higher rate of delignification than *E. tereticornis*.

Infrared spectroscopic studies of these lignins have revealed the presence of  $\alpha$ -keto and  $\beta$ -keto groups ( $1700-1600\text{ cm}^{-1}$ ). The band at  $1425\text{ cm}^{-1}$  indicated the presence of aromatic skeleton vibration. The bands at  $1270\text{ cm}^{-1}$  and  $1140-1080\text{ cm}^{-1}$  showed the presence of anylakyl ether groups and dialkyl ether groups respectively. The presence of hydroxyl and methoxy groups was confirmed in IR Spectra.

#### Chemical Composition of Bamboo Lignins (5'6'7')

The Chemical composition of various lignin preparations of *Dendrocalamus strictus* has been investigated and the results are given in Table III. A perusal of data in Table III also indicates that organosolv lignins have higher methoxyl content and are therefore purer to the lignins isolated by the chemicals which dissolve cellulose of the wood and leave lignin as residue and by the chemicals which dissolve lignin at elevated temperatures.

Bamboo lignin has been found to be composed of two fractions one carrying high methoxyl value (19%) and the other carrying low methoxyl value (12%). The former is easily extractable under mild conditions and the later requires drastic conditions for isolation.

Oxidation of bamboo lignin by nitrobenzene, cupric sulphate and potassium ferricyanide yield a number of products which are native of guaiacyl, syringyl and

TABLE I  
Chemical Composition of *Eucalyptus grandis* and *terecornis* lignins

Species	Lignin Preparation	Carbon %	Hydrogen %	Oxygen %	Methoxyl %	Total Hydroxyl %	Phenolic Hydroxyl
<i>E. grandis</i>	Ethanol	62.02	6.20	31.78	19.7	11.50	2.50
	Dioxane	60.50	6.38	33.12	19.4	—	—
	Acetic acid	59.94	6.30	33.76	18.1	—	—
	Isobutanol	61.54	5.95	32.61	19.0	—	—
	Soda	58.01	6.35	35.64	17.5	—	—
	Sulphuric acid	59.10	5.62	35.28	15.4	—	—
<i>E. tereticornis</i>	Ethanol	62.77	6.49	30.74	18.94	12.80	1.34
	Milled wood	60.60	5.80	34.32	19.8	—	—

TABLE II  
Oxidation Products of Lignins

Species	Lignin	Syringaldehyde, % (S)	Vanillin, % (V)	S/V R <sub>t</sub>
<i>E. grandis</i>	Dioxane	14.2	3.8	3.7
	Soda	11.7	3.7	3.1
<i>E. tereticornis</i>	Ethanol	278	13.5	2.1

TABLE III  
Chemical Composition of bamboo lignins

Lignin Preparation	Carbon	Hydrogen	Oxygen	Methoxyl
Ethanol	59.1	5.5	34.5	19.6
Dioxane	58.3	6.3	35.4	18.3
Milled Wood	59.6	6.1	34.3	18.1
(Extracted with 80% acetone)				
Periodate	54.0	5.3	40.7	12.6
Sulphuric acid	54.8	5.7	39.7	12.0
Soda	50.90	5.5	43.6	12.6

p-hydroxybenzyl units. Table IV gives the list of compounds isolated among oxidation products. The formation of these oxidation products suggests that bamboo lignin is composed of mainly guaiacyl, syringyl and p-hydroxybenzyl basic building units. The weight ratios of syringyl to guaiacyl compounds suggest that the order of these moieties is as follows: syringyl > guaiacyl > p-hydroxybenzyl. The formation of vanillil and syringyl suggests the presence of bivanillyl structure in bamboo lignin. Identification of acetoguaiacone as an oxidation product is due to the presence of 1-(4-hydroxy-3-methoxyphenyl)-3-hydroxypropane-1-one structure.

#### Reactions of Eucalyptus and Bamboo Lignins with Chlorine and hypochlorite

Chlorination of lignin is most widely studied. It has been reported that chlorination of lignin proceeds with initial rapid process, usually referred to as substitution, followed by a slow oxidation process. It has been found that chlorination even for a very short period (3-5 min.) brings about all the competing reactions, it is not entirely a substitution process.

Oxidation of lignin by hypochlorite was found to be highly dependent upon pH of the reaction and initial concentration of hypochlorite. It was found that the rate of oxidation decreased with increase in initial concentration of hypochlorite. The rate of reaction was found to be maximum at pH 7.0. The variation of rate of oxidation with pH and initial concentra-

TABLE IV  
Oxidation products of bamboo lignin

Oxidant	Lignin Preparation	Compounds obtained	Quantity, %
Cu (II) K <sub>3</sub> Fe (CN) <sub>6</sub> and C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	Dioxane and soda	Vanillin	10.42
		Syringaldehyde	11.93
		P-hydroxy benzaldehyde	1.56
		Acetoguaiacone	2.00
		Acetosyringone	4.06
		Vanillic acid	2.01
		Syringic acid	3.00
		P-Hydroxy benzoic acid	0.88
		Vanillil	—
		Syringil	—
		P-Coumaric acid	—
		Ferulic acid	—

tion of hypochlorite suggests that the concentration and composition of reaction species of Cl<sub>2</sub> water or hypochlorite system varies with initial concentration of hypochlorite and pH. The fact that the rate of oxidation has been found to be maximum at pH 7.0 suggests that the most probable reacting species is (HOCl)<sup>2</sup> (OCl)<sup>-1</sup> whose concentration is maximum at pH 7.0. These observations have been found in case of eucalyptus species as well as bamboo lignins.

#### HEMICELLULOSES OF EUCALYPTUS AND BAMBOO

The composition of hemicelluloses of *E. grandis*<sup>10</sup> and—*tereticornis*<sup>11</sup> and *Dendrocalamus strictus*<sup>12</sup> has been investigated and the results are given in Table V.

The results of Table V shows that the hemicelluloses of *E. grandis* and—*tereticornis* are composed of mainly xylose units

with small amounts of arabinose and glucuronic acid. In case of *E. grandis* every fourth xylopyranose unit carried a side chain unit of L-arabofuranose residue and on the average 4-O-Methyl-D-glucuronic acid is present on every seventh xylose units; whereas *E. tereticornis* hemicellulose is composed of (1→4) linked β-D-xylopyranose residues having approximately every tenth residue carrying a terminal 4-O methyl. D-glucuronic acid residue linked through position 2. In case of Bamboo (*D. strictus*) hemicellulose it was found that it is composed of (1→4) linked, β D-xylopyranose residues with an average every 8th xylose unit containing a side chain of D-glucuronic acid attached, glucosidically to the 2-position of xylose residue.

#### Reactions of Bamboo Hemicelluloses with Chlorine and Hypochlorite<sup>13</sup>

Oxidation of hemicellulose (glucuronoxylan) derived from

Bamboo (*D. strictus*) by hypochlorite in the pH range 2-12 has been investigated. In the pH range 6-12, the behaviour of oxidation has been rapid at the initial stage—a thing ascribed to the fact that freshly prepared reducing sugar solutions exhibit mutarotation. The rate of oxidation has been found to be maximum at pH 7.0. The main reacting species have been envisaged as HOCl and OCl in the form Cl<sub>2</sub>OH and the oxidation process was governed by free radical mechanism. In the pH range 2-4, the oxidation process was found to be governed by hydride transfer or proton transfer mechanism.

#### KINETICS OF KRAFT PULPING OF EUCALYPTUS AND BAMBOO<sup>14,15</sup>

Changes in pulp properties namely, yield, lignin to carbohydrate ratio and strength were followed throughout the cooking cycle consisting of a period of 90 min. to 170°C and a period of varying time (0-90 min) at maximum temperature. In case of Bamboo (*D. strictus*) three process control parameters were developed (1) H-factor meter to represent time and temperature as one variable (2) representation of changes in lignin to carbohydrate ratio on the Ross diagram—already analytical guide for pulp composition and (3) a mathematical model to predict kappa number or lignin content without prior knowledge of yield. The kinetics of removal of lignin to carbohydrate ratio revealed that down to 70% of yield the loss was carbohydrate for the most part and from 70% down to 43% carbohydrate and lignin were removed

TABLE V  
Composition of Hemicelluloses

Species	Xylose %	Arabinose %	Uronic acid %	Acetyl value %	Methoxyl value %	Ash %
<i>E. grandis</i>	77.2	5.2	17.2	—	2.65	9.99
<i>E. tereticornis</i>	76.1	0.71	21.6	—	2.03	2.3
<i>D. strictus</i>	78.0	9.4	12.5	—	—	—

in approximately same proportion. During the rise to temperature portion of the cooking cycle lignin was removed to a greater extent than pentosans—a characteristic of interest in the field of unbleached pulp for use as such.

The results of kinetics studies on Bamboo (*D. strictus*) when compared with *Eucalyptus tereticornis* and *Pinus patula* showed that upto 100° the drop in yield followed the order Bamboo > *E. tereticornis* > *P. patula*. The same order persisted at the end of rise to temperature period. At the end of cook both *P. patula* and *D. strictus* touched same level of yield and *E. tereticornis* gave 5.0% higher yield. Conditions of selective delignification were identified in case of all the three raw materials, when changes in lignin to carbohydrate ratio with yield were examined on the Ross diagram.

In case of *E. tereticornis* at early stages that is upto a yield of 82% both lignin and carbohydrates appeared to have been removed in same proportion. Thereafter also the removal characteristics were same upto 55% of yield but the amounts dissolved were less than that

gone into solution at the first stage. The decrease yield from 54% to 50% indicated the loss of all carbohydrates and practically no delignification occurred.

In case of *P. patula* down upto 78% yield the loss of carbohydrates was more than lignin, thereafter upto 68% of yield carbohydrates were removed in same proportion. Again this point down to 60% to yield, carbohydrates were dissolved more than lignin and carbohydrates were removed rapidly but in the same proportion. Beyond this point to the lowest yield (44%) for the most part the loss was carbohydrates and only little lignin was dissolved.

Under the conditions of cooking (A.A. 15% as Na 20; sulphidity 25%, material to liquor ratio (1:4) it was found, that on an average all the three raw materials gave best strength properties at about 50-52% yield. The decrease in strength properties in pulp of lower yield than this is attributed to degradation of carbohydrates on prolonged cooking. This optimum value of yield in relation to strength properties of pulp was obtained by terminating the cooking cycle after 35 min. at 170° in case of

*P. patula* and *E. tereticornis* both, whereas for *D. strictus* a period of 10 min at 170° was found sufficient.

The strength properties of *E. tereticornis* at 52% yield were breaking length (km.) 7.56; tear factor 115.6; burst factor 53.1. In case of *D. strictus* the strength properties at 50% yield were: breaking length (km.) 4.46, tear factor 151.0 and burst factor 30.2. In case *P. patula* the strength properties at 53% yield were breaking length (km.) 9.37, tear factor 171.2 and burst factor 40.0.

#### KINETICS OF OXYGEN-ALKALI PULPING OF HIGH YIELD EUCALYPTUS PULPS<sup>16</sup>

High yield pulps, namely hot soda (78.9% yield) cold soda (78.6% yield) and semi-chemical 70-6% yield were delignified with oxygen in alkaline medium. It was found that the process of delignification followed two pseudo first order kinetics in lignin concentration. The rate of delignification followed the order; hot soda < cold soda < soda semi-chemical. Hydrogen peroxide bleaching of oxygenated pulps gave good results of brightness improvement in case of hot soda and cold soda pulps; whereas soda semi-chemical pulp gave poor response to peroxide bleaching. This was due to presence of highly condensed form of lignin in soda semi-chemical pulps. On an overall assessment it was found that hot soda pulps of *E. tereticornis* could be easily pulped by oxygen in alkaline medium and bleached by hydrogen peroxide to a brightness of 60 at a yield of 71.5% the strength properties

being breaking length 4.4 km., tear factor 33.0 and burst factor 10.0.

#### KINETICS OF NSSC PULPING OF EUCALYPTUS SPECIES

A kinetic study of NSSC pulping of *E. tereticornis* showed that the rate of delignification followed a pseudo first order rate law with respect to both lignin and sulphite. The data on NSSC pulping of *E. obliqua* as reported by Higgins et al when analysed on kinetic basis gave similar results. The concept of H-factor meter for representing time and temperature as one variable was found satisfactorily applicable to NSSC pulping of both the above species. The fact that NSSC pulping of aspen wood and beech wood also exhibited excellent correlation between H-factor and yield, makes it adequately apparent that NSSC pulping of hardwoods like kraft process can be controlled by using H-factor meter as a device to represent time and temperature as one variable.

#### KINETICS OF BLEACHING STAGES FOR EUCALYPTUS AND BAMBOO KRAFT PULPS<sup>18,19</sup>

Kinetics of each stage of the bleaching sequence CEHD was examined with *E. tereticornis* kraft pulp of kappa number 25.0. In general term each stage was similar in that a rapid bleaching reaction took place immediately following the combination of pulp and chemical. The rapid bleaching reaction phase at chlorination, caustic extraction, hypochlorite oxida-

tion and chlorine dioxide reaction produced about 80%, 60%, 60% and 70% of the total bleaching effect of the stage, respectively. Following this was a slower bleaching reaction period at each stage which was studied in more detail. Bleaching at low consistency during caustic extraction and chlorine dioxide reaction stages improved the efficiency of bleaching effect.

The initial rapid reaction of chlorine followed first order kinetics in chlorine concentration whereas the slow reaction was found to follow a second order kinetics in chlorine concentration. In caustic soda extraction stage no satisfactory kinetic equation could be derived in terms of decrease in lignin concentration. However, the decrease in caustic soda concentration followed a zero order kinetics in caustic soda concentration upto 30 min. of reaction time, beyond that no consumption of caustic soda was observed. The disappearance of hypochlorite followed a first order kinetics in chlorine concentration after a lapse of five minutes reaction order at chlorine dioxide stage depended on reaction conditions. Orders of 4.5, 3.5, 2.8 and 1.3 were tentatively determined at the chosen reaction conditions.

In case of bleaching Bamboo (*D. strictus*) kraft pulp of kappa number 29.0 by CEH sequence, changes in pulp properties throughout bleaching sequence were investigated. It was observed that the strength properties increased during chlorination, remained almost constant during extraction stage but again improved at hypochlorite

stage to a maximum at 170 min. of hypochlorite treatment. Beyond this time, the value began to fall. The brightness improved gradually during chlorination, decreased slowly during caustic extraction stage and again improved sharply during the early stages of hypochlorite treatment which was followed by gradual improvement<sup>19</sup>.

#### References

1. Bland, D.E. and Kawamara, I., *Holz FORSCHUNG*, 3, 65 (1967).
2. Sarkanen, K.V. and Chang, Hou-min; *TAPPI*, 56 (3), 132 (1973).
3. Madan, R.N. and Karira B.G., Ph.D. Thesis, Agra University 1972-73.
4. Mehra P., Ph.D. Thesis, Meerut University, 1976.
5. Pant, R., Ph.D. Thesis, Agra University, 1971.
6. Singh, S.V., Unpublished work.
7. Bist, D.P.S., Singh, S.V., Singh, M.M. and Guha, S.R.D. *Indian Pulp & Paper*, 29, No. 6-7, 17 (1974-75).
8. Singh, S.V. Unpublished work.
9. Rawal, J.C., Ph.D. Thesis, Meerut University.
- 9A Anil Kumar, Ph.D. Thesis, Meerut University, 1972.
10. Shukla, C., Ph.D. Thesis, Meerut University, 1972.
11. Singh, S.P., Ph.D. Thesis, Agra University 1972
12. Negi, J.S., Ph.D. Thesis, Agra University 1969
13. Jain, D.K., Singh, S.V. and Guha, S.R.D., *Cellulose Chemistry and Technology*, 10, 703-72 (1976).
14. Singh, S.V. and Guha, S.R.D. *Indian Pulp & paper*, 30, No. 3, 15 (1975).
15. Singh, S.V., Pant R., and Sharma, Y.K. *Ippta, Souvenir* (1975-76)
16. Sharma, Y.K., Madan, R.N. and Singh, S.V., *Indian Pulp and Paper*, 29, No. 4-5 (1974).
17. Singh, S.V. Pant, R. and Guha, S.R.D., Presented at *Ippta Seminar 1977* (Under publication).
18. Singh, S.V., Goyal, R.P. and Guha, S.R.D., *Indian Pulp and Paper*, 29 No. 6-7, 25 (1974-75).
19. Jain, D.K., Singh, S.V. and Guha, S.R.D. *Ippta Souvenir* 1975-76