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EFFECT OF OXYGEN TREATMENT ON OXIDATIVE DEGRADATION PRODUCTS OF *ANTHOCEPHALUS INDICUS* PULPS LIGNIN

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Abstract

In present investigation pulping of *Anthocephalus indicus* (kadam) were carried out using 12 and 14, % active alkali and pulps produced corresponding to kappa number 36.49 and 24.76 were treated with oxygen at 8 kg/cm^2 oxygen pressure. At pressure, treatment was given 100^{o}C and 110oC temperature for 60 minutes using 1.00 and 2.00 % alkali charge. Unbleached and pulps subjected to delignification by oxygen under alkaline conditions under pressure the residual and removed lignins were treated with nitrobenzene oxidation and the products was analysed by high performance liquid chromatography (HPLC). Compound like P-hydroxy benzoic acid, Vanillic acid, Syringic acid, p-hydroxybenzaldehyde, vanillin, Syringaldehyde, Acetovanillone, Acetosyringone was identified. The effect of oxygen treatment with different temperature and alkali charge on compound like vanillin, Syringaldehyde and Vanillic acid was analysed in adequate length of paper.

Key words: *Anthocephalus indicus*, lignin, Nitrobenzene, vanillin, Syringaldehyde, Oxygen treatment.

Introduction

Lignocellulose biomass is comprised mainly of three macro molecular species cellulose, hemicelluloses and lignin . Lignin is a generic name of a complex high molecular weight, three dimensional aromatic biopolymer arising from an enzyme initiated dehydrogenative polymerization of trans- p- coniferyl, trans- p- sinapyl and trans – p- coumaryl alcohols in nature (Kirk et al 1987, Vanholme et al 2010) .

Oxidation of residual lignin in nitrobenzene in alkaline media leading to the formation of carboxylic acid and aromatic carbonyl compounds. Which may be important in the production of valuble aromatic compounds commercially from by-product of pulp and paper industry(Korányi, et al 2020, Mathias et al 1995).

Isolation and identifications of low molecular weight lignin oxidation products has been a tedious job. Brauns (1952) estimated vanillin and syringaldehyde classical methods of analysis based upon differential solubility and / or derivative preparation. several individual compounds were isolated and characterised by paper chromatography (Toppel 1961) Column chromatography (Simpson and Sandhmir 1960) , thin layer chromatography (Kratzl and Puschmann 1960) and ion-exchange chromatography (Jayne 1953) Gas chromatography (Simionescus and Anton 1965) was used for rapid analysis and with more qualitative and quantitative informations. But, the gas chromatography of phenols, phenolic aldehydes and phenolic acids arising from oxidation lignin was hampered by their polarity as they have a tendency to form strong hydrogen bond with polar liquod phase and in some instances by their thermal instability (Ottenstein 1963) . In brief, the Gas chromatography of lignin oxidation products proved to be difficult and less informative. High performance liquid chromatography (HPLC) has several advantages over other methods for qualitative and quantitative analysis of oxidation products (Chawala and Puri 1981, Scalbert and Monties 1986, Nandanwar et al 2016) . the technique is sensitive, rapid and does not require preparation of derivatives before analysis.

In the present investigation unbleached and oxygen treated pulp lignins of *Anthocephalus indicus* (kadam) were subjected to alkaline nitrobenzene oxidation. High performance liquid chromatography (HPLC) was adopted for the separation and analysis of lignin oxidation products, acetic acid and acetonitrile is used as eluting media at different scanning wavelength of aromatic regions.

Lignin is one of the most abundant biopolymers on earth accounting for 10- 40 % by weight (Sun et al 2002, Kirk et al 1987, Awungacha et al 2015). Lignin may have a huge source of commercial value-added aromatic compounds. But more than 98 % of the lignin produced by the pulp and paper industry is used as a fuel while only 2 % is used in the production of commercially value-added aromatic compounds (Busch et al 2006, Rodrigues et al 2018, Silva et al 2009, Pinto et al 2013) the large-scale exploration of lignin as a source of value-added aromatic compounds may be possible by the understanding the oxidative products. (Beckham etal 2016, Behling et al 2016, Gillet et al 2017).

A number of articles have also appeared in the literature on nitrobenzene oxidation. Nitro benzene oxidation probably proceeds through two steps (i) the alkaline hydrolysis of the alkyl aryl ether linkages coupled with side chain modification. (ii) the oxidation of the side chain with the generation of an aromatic carbonyl or carboxylic compound. Schultz, and Templeton (1986) suggested that the initial reaction involves the absorption of one electron from the benzylic hydroxyl. The radical cation then losses a free radical to form a benzylic alkyloxy radical, which forms a benzaldehyde and an alkyl radical. The Cα- Cβ bond is probably a cleaved phenyl compound (Alder 1964, Anderson 2016). The homolytic oxidative reactions of alcohols particularly, benzylic alcohol derivatives (Walling and El- taliawi, 1983, Araújo 2010) indicate that the free p-hydroxy group is not necessary for the generation of carbonyl compounds. Thus, the formation of quinine methide and ketone is fairly stable. Once the aldehyde group is formed, base-catalyzed hydrolysis of ether bonds can occur, assisted by the newly formed electron-withdrawing substituents. Thus, alkaline hydrolysis of inter-unit ether bond may initially be important to depolymerize and solubilize the lignin. But may also be important after the oxidation reaction has occurred to protect the survivability of aldehyde already formed. (Anna Kalliola et al 2011)

Experimental

Raw Material: Anthocephalus indicus belongs to the family Rubiaceae. It is a large deciduous tree commonly known as Kadam.

Pulping: Anthocephalus indicus logs were debarked, chipped and chips were screened. Screened chips (15-30 x 10-20 x 2-3 mm) were taken for pulping experiments. Pulping experiments were carried out in an air pulping bath unit consisting of six bombs of 2.5-liter capacity using 12 and 14, % active alkali as Na2O at 23.0 % sulphidity level. The bath ratio 1: 4 maximum temperature, 170oC was kept constant in all the cases. Room temperature to 100oC temperature was raised in 90 minutes followed by a 10oC rise in 15 minutes to 170oC and kept at maximum temperature for 60 minutes. Pulping schedule corresponds to H-factor, 1110. Cooked material was washed with hot water, fiberized in a laboratory disintegrator, and screened over a flat laboratory screen having 0.25 mm slots.

Oxygen Treatment of Kraft Pulps: Unbleached kraft pulps using 12 % and 14 % active alkali in pulping corresponding to kappa numbers 36.49 and 24.76 were treated with oxygen at

8 kg/cm2 oxygen pressure. At pressure, treatment was given 100oC and 110oC temperatures for 60 minutes using 1.00 and 2.00 % alkali charge, in each case 1:12 bath ratio was maintained. 0.25 % magnesium sulphate was added in the oxygen treatment stage.

Alkaline nitrobenzene oxidation: wood dust and unbleached pulps obtained under optimum conditions of pulping were subjected to alkaline nitrobenzene oxidation adopting the procedure of Gee et al (1968). Test specimens were unbleached and oxygen-treated pulp lignins 0.10 g were treated with 0.8ml of nitrobenzene in presence of 2 N 6.0ml of NaOH in a sealed hard glass test tube for 90 minutes at 170oC, room temperature to 170oC was raised in 60 minutes.

Purification of nitrobenzene oxidation products: Nitrobenzene Oxidation products were extracted with diethyl ether The solvent fraction was washed with sodium hydroxide solution and added to the fraction obtained after removing nitrobenzene and its reduction products. Combined sodium hydroxide solution and original solution were mixed and acidified to pH about 2 with hydrochloric acid followed by extraction with dichloromethane and diethyl ether both the solvent fractions were mixed together. The combined solvent fraction was dried over anhydrous sodium sulphate, reduced to a small volume in a rotary evaporator under reduced pressure, then transferred to a dry vial and reduced to near dryness under a nitrogen atmosphere.

Alkaline nitrobenzene oxidation products were characterized using high-performance liquid chromatography. Analysis was performed on Perkin Elmer (USA) model -235 High-Performance liquid Chromatograph equipped with the programmable LC binary pump and Perkin- Elmer UV diode array programmable detector model-235.

Elution Media: 0.5 N acetic acid and acetonitrile were used for the separation of oxidation products. The separation was achieved at 0.5ml/min elution rate and 85:15v/v ratio of 0.5 N acetic acid and acetonitrile. Reverse phase ecosphere sphere C18 column of 30mm followed by 150 mm, in series having 12% loading of bonded monomer, particle size 5µm of spherical shape is used. The guard column was fitted in series prior to the C18 column. The average pore size of the column was 80 Ao units corresponding to a plate number of 100,150/m2. Oxidation products were scanned at 225,280 and 290 nm. On the basis of results obtained for the resolution pattern, scanning wavelength 280nm was considered to be optimum for the resolution of phenolic carbonyl and carboxylic compounds under investigation.

Quantitative estimation of oxidation products:

An equal amount of authentic sample (~0.01 g) of all the identified compounds was taken and dissolved in 100 ml of the elution media, 0.5 N acetic acid: acetonitrile (35: 15 v/v). From the prepared stock solution, 5, 10, 15, and 20 ml solution was taken in the volumetric flask (25 ml) and further diluted to 25 ml to have solutions of different concentrations of an authentic sample. 20 microlitres of each diluted solution were injected into the chromatograph and the peak area in each case was calculated. The peak area for an equal amount of a single compound in different diluted solutions was computed from the values. (Table 1)Table 1 High Performance liquid Chromatography of authentic samples at different concentration

Particulars	P-hydroxy benzoic acid	Vanillic acid	Syringic acid	p-hydroxybenzaldehyde	vanillin	syringaldehyde	Acetovanillone	Acetosyringone
Relative retention time ,min	0.65	0.72	0.75	0.84	1.00	1.12	1.18	1.30
Absorption maximum, nm	225	260	275	285	280	305	276	299
Peak area of 20ug, nm^2	57.05	72.25	79.62	204.73	114.85	54.55	63.27	66.16
Peak area of 40ug, nm^2	114.10	144.51	159.25	409.45	229.70	109.11	126.54	132.32
Peak area of 60ug, nm^2	171.15	216.76	238.87	614.18	344.55	163.66	189.81	198.47
Peak area of 80ug, nm^2	228.20	289.02	318.49	818.91	459.40	218.22	253.08	264.63
Peak area of 100ug, nm^2	285.25	361.27	398.12	1023.64	574.25	272.78	316.35	330.79
Constant	0.3506	0.2768	0.2512	0.19769	0.1741	0.3666	0.3161	0.3023

Results and discussion

Unbleached and oxygen-treated pulp lignins were subjected to alkaline nitrobenzene oxidation studies. The identity of eight compounds was established by taking advantage of their higher polarity / better partition coefficient in the polar solvent like of acetic acid and acetonitrile (Higuchi et al 1967, Chang et al 1971). The order of elution was P-hydroxy benzoic acid, Vanillic acid, Syringic acid, p-hydroxybenzaldehyde, vanillin, Syringaldehyde, Acetovanillone, Acetosyringone. From the elution pattern, it is clear that the comparatively more or less the same, the low molecular weight compound was eluted first as expected in reverse phase chromatography using polar elution media.

Alkaline nitrobenzene oxidation products of *Anthocephalus indicus* unbleached (12%) and Oxygen treated pulps

Data recorded in tables 2 and 3, nitro benzene oxidation products of unbleached pulps produced using 12 % alkali during pulping and 2 % alkali during oxygen treatment at 100°C and 110 °C. In general, the relative percentage of acids was higher except for syringic acid. The ratio of p-hydroxyl benzoic acid and vanillic acid was 34.420: 14.484 and 37.811: 14.126 in oxygen-treated pulp lignins at 100°C and 110 °C as compared to unbleached pulp lignin, where it was 18.426:10.349. The relative percentage of p-hydroxyl benzaldehyde: Vanillin: syringaldehyde was 3.847: 6.379:19.237 and 3.881: 5.585:16.375 for oxygen-treated pulp lignins at 100°C and 110 °C and lower than the unbleached pulp lignin 6.694:11.641:24.558. The decrease of aldehyde unit in the oxidation mixture may be due to the easy cleavage of P-hydroxyl phenyl moieties during the course of delignification i.e., prior to oxidation (Higuchi et al 1990, Tai et al 1989).

Table 2 Relative retention time, peak area, weight and relative percentage of alkaline nitrobenzene oxidation products of unbleached (12 %) and oxygen treated pulps of *Anthocephalus indicus*

Particulars	P-hydroxy benzoic acid	Vanillic acid	Syringic acid	p-hydroxybenzaldehyde	vanillin	Syringaldehyde	Acetovanillone	Acetosyringone
Relative retention time ,min	0.65	0.72	0.75	0.845	1.00	1.12	1.18	1.30
Unbleached pulp produced using 12 % alkali during pulping								
Peak area nm^2	20.13	14.32	18.81	26.25	25.61	25.66	11.21	8.550
Weight, micro grams	7.058	3.964	4.725	2.564	4.425	9.407	3.543	2.585
Relative %	18.456	10.349	12.335	6.694	11.640	24.558	9.250	6.748
Pulp produced using 12 % alkali during pulping and 2.0 % alkali at 100°C during oxygen treatment								
Peak area nm^2	75.42	45.20	27.20	30.25	28.15	40.13	18.72	12.80
Weight, micro grams	26.442	11.127	6.833	2.955	4.901	14.778	5.917	3.869
Relative %	34.420	14.484	3.895	3.847	6.379	19.237	7.702	5.036
Pulp produced using 12 % alkali during pulping and 2.0 % alkali at 110°C during oxygen treatment								
Peak area nm^2	86.12	40.75	35.00	31.72	25.62	35.67	16.12	10.500
Weight, micro grams	30.194	11.280	8.792	3.099	4.460	13.076	5.096	3.174
Relative %	37.811	14.126	11.001	3.881	5.585	16.375	6.382	3.975

Table 3 Relative percentage, moles and molar ratio of nitrobenzene oxidation products of unbleached (12%) and oxygen treated pulps of *Anthocephalus indicus*

Particulars	Pulp produced using 12 % alkali during pulping								
	Unbleached pulp			Oxygen treatment using 2.0 % alkali at 100°C			Oxygen treatment using 2.0 % alkali at 110°C		
	Relative %	Relative moles	Relative molar ratio	Relative %	Relative moles	Relative molar ratio	Relative %	Relative moles	Relative molar ratio
Vanillin	11.64	0.077	12.520	6.379	0.042	6.646	5.585	0.037	5.864
Vanillic acid	10.349	0.062	10.081	14.484	0.086	13.608	14.126	0.084	13.312
Aceto vanillone	9.250	0.056	9.106	7.702	0.046	7.278	6.382	0.038	6.022
Total of guaiacyl units	--	0.195	31.707	--	0.174	27.532	--	0.159	25.198
Syringaldehyde	24.558	0.135	21.951	19.237	0.106	16.772	16.375	0.090	14.263
Acetosyringone	6.748	0.034	5.528	5.036	0.026	4.114	3.975	0.020	3.170
Syringic acid	12.335	0.062	10.081	8.895	0.045	7.120	11.001	0.056	8.875
Total of Syringyl units	--	0.231	37.560	--	0.177	28.006	--	0.166	26.308
p-hydroxybenzaldehyde	6.694	0.055	8.943	3.847	0.032	5.063	3.881	0.032	5.071
P-hydroxy benzoic acid	18.426	0.134	21.789	34.420	0.249	39.399	37.811	0.274	39.144
Total of P-hydroxyl units	--	0.189	30.732	--	0.281	44.462	--	0.306	48.494

The relative mole of oxygen-treated pulp lignins at 100°C and 110° C were 12.520: 21.951: 8.943: 10.081: : 10.081: 21.789 for unbleached pulp lignin producing using 12 % alkali during pulping and 6.649: 16.772: 5.063:13.608:7.278:39.399 and 5.864: 14.263: 5.071:13.312:8.875:39.144 for oxygen treated pulp lignins at 100°C and 110 °C, respectively. Relative moles of actovanillone and acetosyringone for oxygen-treated pulp lignins at 100°C and 110 °C were 7.278:4.114; 6.022: 3.170 respectively increased in unbleached pulp lignin 9.106: 5.528 mole respectively.

Table 4 Ratio of various units of nitrobenzene oxidation products of unbleached (12%) and oxygen treated pulps of *Anthocephalus indicus*

Particulars	Pulp produced using 12 % alkali during pulping		
	Unbleached pulp	Oxygen treatment using 2.0 % alkali at 100°C	Oxygen treatment using 2.0 % alkali at 110°C
Total Syringyl/ Total guaiacyl units	1.184	1.017	1.044
Total Syringyl/ Total p-hydroxyphenyl units	1.222	0.630	0.542
Total guaiacyl/ Total p-hydroxyphenyl units	1.032	0.619	0.520
Total Syringaldehyde/ Total vanillin units	1.752	2.524	2.432
Total Syringaldehyde/ Total p-hydroxy benzaldehyde units	2.255	3.313	2.812
Total vanillin / Total p-hydroxy benzaldehyde units	1.4005	1.313	1.560

The molar ratio of syringaldehyde: vanillin for unbleached pulp lignin was 1.752: 1.000 and increased to 2.524:1.000 and 2.432:1.000 for oxygen-treated pulp lignins at 100°C and 110 °C respectively. The malar ratio of total syringyl units to total guaiacyl units was 1.184:1.000 for unbleached pulp lignin 1.017: 1.000 and 1.044:1.000 for oxygen-treated pulp lignins at 100°C and 110 °C.

Table 5: Molar ratio of various units of nitrobenzene oxidation products of unbleached (12 %) and oxygen treated pulps of *Anthocephalus indicus*

Particulars	Guaiacyl : Syringyl : p-hydroxyphenyl	Vanillin: Syringaldehyde: p-hydroxy benzaldehyde
Unbleached pulp produced using 12 % alkali during pulping	0.884 : 1.000 : 0.818	0.570 : 1.000 : 0.407
Pulp produced using 12 % alkali during pulping and 2.0 % alkali at 100ºC during oxygen treatment	0.983 : 1.000 : 1.588	0.396 : 1.000 : 0.301
Pulp produced using 12 % alkali during pulping and 2.0 % alkali at 110ºC during oxygen treatment	0.958 : 1.000 : 1.843	0.441 : 1.000 : 0.356

The syringaldehyde: P-hydroxy benzaldehyde ratio in unbleached pulp lignin was 2.455: 1.000 and 3.313: 1.000; 2.812:1.000 for oxygen-treated pulp lignins at 100ºC and 110 ºC. The ratio of total syringyl : total hydroxyl phenyl units for unbleached pulp lignin was 1.223:1.000 and 0.632: 1.000; 0.542: 1.000 for oxygen-treated pulp lignins at 100ºC and 110 ºC. These observations indicated that the syringaldehyde-generating moieties in unbleached pulp lignin were lower that of oxygen-treated pulp lignins than that of vanillin-generating moieties but lower than that of P-hydroxy benzaldehyde generating moieties. However, a comparison of the molar ratio of the total of each class of moieties suggested that the frequency of syringyl unit-generating moieties was lower in oxidation product than that of guaiacyl and p-hydroxyl phenyl unit-generation moieties (Table 5)

The molar ratio of vanillin: P-hydroxy benzaldehyde was 1.400: 1.000 and 1.313: 1.000; 1.156;1.000 in unbleached and oxygen-treated pulp lignins at 100ºC and 110 ºC respectively. The same trend for the molar ratio of the total of guaiacyl : a total of p-hydroxyphenyl units 1.032:1.000 and 0.619:01.000; 0.520: 1.000 for unbleached and oxygen-treated pulp lignins at 100ºC and 110 ºC respectively. These results indicated that although both yielded higher amounts of p-hydroxyl phenyl unit but p-hydroxyl phenyl was much higher in oxygen-treated pulp lignins as compared to unbleached pulp lignin.

The relative molar ratio of vanillin: syringaldehyde: P-hydroxy benzaldehyde for unbleached pulp lignin and oxygen-treated pulp lignins at 100ºC and 110 º C was 0.570:1.000:0.407; 0.396 :1.000: 0.301 and 0.441:1.000: 0.356 respectively. Similarly the molar ratio of the total of guaiacyl : syringyl : p-hydroxyl phenyl unit was 0.844:1.000:0.818; 0.983:1.000:1.588 and 0958:1.000:1.843 for unbleached pulp lignin and oxygen treated pulp lignins at 100ºC and 110 ºC.

Alkaline nitrobenzene oxidation products of *Anthocephalus indicus* unbleached (14%) and Oxygen treated pulps

Data recorded for nitro benzene oxidation products of unbleached pulps produced using 14 % alkali during pulping and 1 % alkali during oxygen treatment at 100ºC and 110 ºC revealed that relative percentage (Table -6) p-hydroxy benzoic acid and vanillic acid increased while the percentage of syringic acid was decreased with the increase in oxygen treatment temperature. The relative percentage was 11.769 for unbleached pulp lignin and decreased to 7.603 and 9.275 for oxygen-treated pulp lignins at 100ºC and 110 ºC.

Table 6 Relative retention time, peak area, weight and relative percentage of alkaline nitrobenzene oxidation products of unbleached (14 %) and oxygen treated pulps of *Anthocephalus indicus*

Particulars	P-hydroxy benzoic acid	Vanillic acid	Syringic acid	p-hydroxybenzaldehyde	vanillin	Syringaldehyde	Acetovanillone	Acetosyringone
Relative retention time ,min	0.65	0.72	0.75	0.845	1.00	1.12	1.18	1.30
Unbleached pulp produced using 14 % alkali during pulping								
Peak area nm^2	16.45	11.50	17.17	25.18	22.63	30.62	11.03	7.520
Weight, micro grams	5.767	3.183	4.313	2.429	3.940	11.225	3.487	2.273
Relative %	15.737	8.686	11.769	6.710	10.751	30.630	9.515	6.202
Pulp produced using 14 % alkali during pulping and 1.0 % alkali at 100ºC during oxygen treatment								
Peak area nm^2	60.00	26.62	20.55	40.27	33.68	45.18	15.81	10.730
Weight, micro grams	21.036	7.092	5.162	3.933	5.864	16.563	4.998	3.244
Relative %	30.985	10.446	7.603	5.793	8.637	24.396	7.362	4.778
Pulp produced using 14 % alkali during pulping and 1.0 % alkali at 110ºC during oxygen treatment								
Peak area nm^2	70.32	30.43	25.92	41.720	25.81	42.82	12.10	8.320

Weight, micro grams	24.654	8.423	6.511	4.076	4.494	15.698	3.825	2.515
Relative %	35.122	11.999	9.275	5.807	6.402	22.363	5.449	3.583

The syringaldehyde: vanillin molar ratio in unbleached pulp lignin was 2.366:1.000 and increased to 2.351:1.000; 2.928: 1.000 in oxygen-treated pulp lignins at 100ºC and 110º C. While the total syringyl : total guaiacyl unit ratio was decreased. The ratio of syriangaldehyde : P-hydroxy benzaldehyde was 3.055:1.000 for oxygen-treated pulps. The ratio of total syringyl : total hydroxyl phenyl units was decreased from 1.640: 1.000 in unbleached pulp lignin to 0.721: 1.000 and 0.620: 1.000 for oxygen-treated pulp lignin at 100ºC and 110º C. vanillin: P-hydroxy phenyl ratio was 1.291: 1.000 for unbleached pulp lignin and almost same to 1.213: 1.000 ; 0875: 1.000 for oxygen treated pulp lignins at 100ºC and 110º C, while the ratio of the total of guaiacyl : a total of p-hydroxyphenyl units for unbleached pulp lignin was 1.065: 1.000 and decreased to 0.599: 1.000 and 0.482: 1.000 for oxygen treated pulp lignins at 100ºC and 110º C (Table -7)

Table 7 Relative percentage, moles and molar ratio of nitrobenzene oxidation products of unbleached (14 %)and oxygen treated pulps of *Anthocephalus indicus*

Particulars	Pulp produced using 14 % alkali during pulping								
	Unbleached pulp			Oxygen treatment using 1.0 % Alkali at 100ºC			Oxygen treatment using 1.0 % Alkali at 110ºC		
	Relative %	Relative moles	Relative molar ratio	Relative %	Relative moles	Relative molar ratio	Relative %	Relative moles	Relative molar ratio
Vanillin	10.751	0.071	11.678	8.637	0.057	9.033	6.402	0.042	6.593
Vanillic acid	8.686	0.052	8.553	10.446	0.062	9.826	11.999	0.71	11.146
Aceto vanillone	9.515	0.057	9.375	7.362	0.440	6.973	5.449	0.033	5.181
Total of guaiacyl units	--	0.180	29.605	-	0.163	25.832	-	1.146	22.920
Syringaldehyde	30.630	0.168	27.632	24.396	0.134	21.236	22.236	0.123	19.309
Acetosyringone	6.202	0.032	5.263	4.778	0.024	3.803	3.583	0.018	2.826
Syringic acid	11.769	0.059	9.704	7.603	0.038	6.022	9.275	0.047	7.378
Total of Syringyl units	--	0.259	45.599	-	0.196	31.062	-	0.188	29.513
p-hydroxybenzaldehyde	6.710	0.055	9.046	5.793	0.047	7.448	5.807	0.048	7.535
P-hydroxy benzoic acid	15.737	0.114	18.750	30.985	0.225	35.658	35.122	0.255	40.031
Total of P-hydroxyl units	--	0.169	27.796	-	0.272	43.106	-	0.303	47.567

Table 8 Ratio of various units of nitrobenzene oxidation products of unbleached (14 %) and oxygen treated pulps of *Anthocephalus indicus*

Particulars	Pulp produced using 14 % alkali during pulping		
	Unbleached pulp	Oxygen treatment using 1.0 % alkali at 100°C	Oxygen treatment using 1.0 % alkali at 110°C
Total Syringyl/ Total guaiacyl units	1.540	1.202	1.287
Total Syringyl/ Total p-hydroxyphenyl units	1.640	0.721	0.620
Total guaiacyl/ Total p-hydroxyphenyl units	1.065	0.599	0.482
Total Syringaldehyde/ Total vanillin units	2.366	2.351	2.928
Total Syringaldehyde/ Total p-hydroxy benzaldehyde units	3.055	2.851	2.563
Total vanillin / Total p-hydroxy benzaldehyde units	1.291	1.213	0.875

Table 9: Molar ratio of various units of nitrobenzene oxidation products of unbleached (14 %) and oxygen treated pulps of *Anthocephalus indicus*

Particulars	Guaiacyl : Syringyl : p-hydroxyphenyl	Vanillin: Syringaldehyde: p-hydroxy benzaldehyde
Unbleached pulp produced using 14 % alkali during pulping	0.649 : 1.000 : 0.610	0.4230 : 1.000 : 0.327
Pulp produced using 12 % alkali during pulping and 1.0 % alkali at 100°C during oxygen treatment	0.832 : 1.000 : 1.388	0.425 : 1.000 : 0.351
Pulp produced using 12 % alkali during pulping and 1.0 % alkali at 110°C during oxygen treatment	0.777 : 1.000 : 1.612	0.341 : 1.000 : 0.390

The molar ratio of the aldehyde was 0.423:1.000: 0.327 for vanillin: syringaldehyde: p-hydroxy benzaldehyde in unbleached pulp lignin and 0.425 :1.000: 0.351 and 0.341: 1.000: 0.390 for oxygen treated pulp lignins at 100°C and 110° C the ratio of Guaiacyl : Syringyl : p-hydroxyphenyl units was 0.649: 1.000:0.610 for unbleached pulp lignin as against 0.832:1.000: 1.388; 0.377: 1.000: 1.612 for oxygen treated pulp lignins at 100°C and 110° C. These observations revealed that with respect to syringaldehyde and syringyl there was a drastic drop in the vanillin (Table – 9)

Conclusion

On oxygen treatment of pulps, it yielded a lower amount of aldehyde and a higher amount of acids as compared to their respective unbleached pulps the relative molar ratio of Guaiacyl: Syringyl: p-hydroxyphenyl units reveals that during the course of oxygen treatment perhaps the Syringyl unit suffered more degradation or demethoxylation leading yielding lower Syringyl units in oxidation products.

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