Kinetics and Mechanism of Hypochlorite Oxidation of Lignins from Eucalyptus Hybrid in the pH Range 2-10

By

J.C. Rawal, Man Mohan Singh and S.R.D. Guha Cellulose and Paper Branch, F.R.I., Dehra Dun

In the present study, kinetics and mechanism of sodium hypochlorite oxidation of soda and thio lignin isolated from Eucalyptus hybrid (mainly E. teretieornis) in the pH range 2-10 has been reported. All the reactions studied have been found to fit in the second order rate law equation :

$$1/C_t = 1/C_0 + k_s t$$

The behaviour of oxidation reaction has been rapid at the initial stage—a thing ascribed to the presence of some hemicellulose carbohydrate fraction linked to the lignin molecule, getting oxidized at a much faster rate.

The maximum rate of oxidation has been found at pH 7, in the case of both lignins. The probable rate law equation is given as

$$-\frac{dc}{dt} = k[R][L]$$

The reaction in this pH range was explained on the basis of free radical mechanism, the main reacting species are HOCl and OCl in the form of Cl₂OOH.

The energy parameters for both the lignins have been reported. C₉ formulae for both the lignins have been calculated, which are respectively :

 $C_9H_{7.38}O_{4.8}$ (OCH₃) 0.95 for soda and $C_9H_{5.31}O_{4.92}S_{0.32}$ (OCH₃)1.13 for thio lignin.

The thio lignin is oxidized at a faster rate than soda lignin — a

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fact attributed to the differences in composition with respect to reactive groups and the degree of condensation.

Introduction

The plant tissues are comprised of polymers like cellulose, lignin, hemicelluloses and extractive matter. During the course of chemical pulping processes like soda and sulphate, of the plant fibres, most of lignin is removed besides the romoval of extraneous matter and part of the carbohydrate fraction (low molecular weight). Residual lignin imparts brown colour to the pulp. The bleaching is usually done by compounds native in chlorine e.g. chlorine, chlorine dioxide and hypochlorite. This reaction is mainly oxidation.

To elucidate the reactions mechanism involved it is necessary to study the kinetics of reaction of hypochlorite on the lignin.

Composition of lignin

Lignin is an amorphous, highly branched, three-dimensional polymer whose complex chemical structure has come into sharp focus only recently after many years of research. The structure is complicated and cannot be described in detail here, but it is possible to point out the main structural features. The lignin polymer is comprised of oxiphenylprone units derived from three substituted cinnamyl alcohols: p-coumaryl coniferyl and sipapyl alcohols (Fig. 1), their proportions differ greatly between conifers and hardwoods and among the various species of hardwoods. In a polymerization process that involves primarily radical coupling, these monomeric starting materials are combined to produce the lignin polymer. The nature of the polymerization process is such that the bonds linking the individual phenylpropane units together are of several different types. This, as well as the fact that three cinnamyl alcohols are involved, and that secondary reactions occur, leads to the complexity of lignin structure.

About 70 per cent of the lignin in woody plant cells is located in the secondary wall layers. The rest of the lignin is located in very thin middle lamella regions where it is the main constituent.

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Fig. 1—Substituted cinnamyl alcohols which are oxidatively polymerized to give legnin.

Oxidation of lignin

Being phenolic in nature the lignin macromolecule is prone to oxidation by either homo or heterocyclic pathway¹, depending on the oxidant and the reaction conditions used.

Since the lignin macromolecule is susceptible to a wide variety of oxidants, the oxidation reactions have been arbitrarily classified in three categories according to the degree of lignin degradation achieved. These comprise oxidations (a) degrading lignin to aromatic carbonyl compounds and carboxylic acids (b) degrading aromatic rings and (c) limited to specific groups.

• The second category is of technical importance and cover the action of strong oxidants including peracetic and nitric acids, chlorine, chlorine dioxide and the oxidizing anions of hypochlorous and chlorous acids.

Chemical reaction of lignin with sodium hypochlorite

The problem of analysing the chemical reactions of lignin with sodium hypochlorite is not a simple one. The complexity arises due to the unknown structure of lignin and the possibility of numerous reactions taking place simultaneously since each of elemental chlorine, hypochlorous acid, and hypochlorite ion may react in more than one way; and also due to the formation of unknown products. A complete description of the mechanism of a complex reaction such as the one under study is known to be very difficult. Some conclusions may, however, be drawn based on published literature.

Reaction with elemental chlorine

Studies carried out by Hibbert and co-workers² and by Dence and Sarkanen^a revealed that four types of reactions of chlorine with lignin occur. These are (i) addition of chlorine to double bond, (ii) a rapid substitution of chlorine into aromatic portion of the guaiacyl-propane unit, (iii) the degradation of lignin polymer chain into water and alkali soluble fragments, and (iv) oxidation of both lignin and chlorolignin formed. This concept of chlorination of lignin was further supported by the kinetics of studies of Carmody and Mears⁴ and Schmidt-Nielsen⁵.

Reaction with hypochlorous acid

The reaction of hypochlorous acid in halogenide-free systems, acidified with sulphuric or perchloric acid have been the subject of numerous kinetic studies⁶⁻¹⁰. From the work on chlorination of lignin² it is known that hypochlorous acid oxidizes lignin, or at least chlorolignin the reaction is characterised by a rapid consumption of chlorine during the first few minutes as found with phenols^{11'12}, and thereafter the chlorine content decreases roughly in proportion to the log of the elapsed time. The reaction was found to be second order one in chlorine concentration.

Reaction with hypochlorite ions

The hypochlorite treatment of various lignin preparations show an initial rapid hypochlorite consumption followed by a slower reaction. The slow reaction was found to be second order in chlorine concentration³. The main result of the reaction is oxidative destruction, chlorination of lignin and its concomitant demethylation are relatively unimportant⁴. Hypochlorite oxidations of lignin preparations and lignin model compounds have shown that only those nuclei having free phenolic hydroxyl groups are oxidized. The side-chain of both type of nuclei are oxidized, if unsaturated groups are present or if oxygen containing substituents are located in the alpha position. Kinetic studies have shown that nucleic oxidation is a rapid reaction whereas the rapidity of the sidechain oxidation varies somewhat with the constitution of these catenae. Model compound

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studies have also revealed that the nucleic oxidation is preceded by chlorination. It may be presumed that the reactive species in the chlorination reaction is hypochlorous acid. As hypochlorous acid is a weak electrophile, it can only chlorinate phenolate anions at their orthoand para-positions.

The oxidation products formed during the action of hypochlorite with lignin are unstable and difficult to be characterise^{13,14}.

EXPERIMENTAL

1. Isolation and purification of lignin

Soda and thio lignins are isolated from alkaline pulping spent black liquor obtained after digestion of the wood by soda or sulphate process.

Eucalyptus hybrid was obtained from Haldwani (U.P.). It was debarked, chipped and screened on the pilot plant equipment. The screened chips were digested in the laboratory electrically heated rotary autoclave of 25 litres capacity under the following conditions.

	Soda Process	Sulphate Process
Total Chemi-		
cals	20%	20%
Sulphidity	0%	25%
Cooking	• -	
Temp.	162°C	162°C
Cooking		
period	4 hours*	4 hours*
Bath ratio	1:4	1:4

*(including 1½ hrs. to raise to the max. temp.).

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The cooked pulp was washed thoroughly with fresh water to remove the black liquor. The black liquor obtained was filtered and acidified with dilute hypochloric acid till the precipitation was completed. The precipitate thus obtained was allowed to settle down and the supernatent liquor was decanted off. The precipitate was washed till free of chloride ions and dried yielding crude soda lignin and thio lignin.

Purification of the crude lignin was carried out according to the Ahlm's method¹⁵.

2. Analysis of lignin

Both the lignins (soda lignin and thio lignin) were analysed for their carbon, hydrogen and sulphur contents. Oxygen was determined by difference to each case. Methoxyl contents were also determined. The mol-weight of these lignins was also determined by vapour pressure osmometer by the method of Martin and Martin¹⁶.

Based on the studies, C_9 formula were derived. Klason lignin was also determined by the tappi standards methods.

The results are recorded in Table 1.

The infrared absorption spectra of soda lignin and thio lignin samples were determined using Perkin Elmer Infrared Spectraphotometer. Isolated lignin samples were examined in clear discs containing 4 mg. of lignin in 100 mg. of potassium bromide (Fig. 2 and Fig. 3).

3. Preparation of hypochlorite

The solution of sodium hypochlorite was prepared by passing a slow stream of chlorine gas into a well cooled solution of 2 N sodium hydroxide (S. Merk Grade Pellets) until the increase in weight indicated that about 50 g. per litre of chlorine was absorbed. The solution was stored in a dark bottle at 3°C. Solutions for oxidation were prepared from it by suitable dilutions.

4. Oxidation of lignin

The reaction was studied in 500 ml., five necked pyrex glass round bottom flask, Fig. 4. A thermostatic bath with a of variation temperature $\pm 0.1^{\circ}$ C was used for maintaining the temperature. To prepare the reaction mixture sodium hypochlorite solution and 0.5 N sodium hydroxide solution or 0.5 N hydrochloric acid gas were mixed in such a proportion so that a solutions of required [NaOCl]₀ concentration and pH was obtained.

Known weighed amount of lignin was transferred to the reaction vessel and calculated quantities of distilled water were added so that the total volume of this lignin suspension after the addition of hypochlorite reaction mixture becomes equal to 300 ml. pH during the reaction was kept constant by addition of 0.5 N sodium hydroxide solution from burette fixed "b" (Fig. 4). Two electrodes of the pH meter were inserted through E_1 and E_2 two of the necks of the reaction vessel and were sealed. Central neck of the reaction vessel holds a glass

stirrer (operated electrically), which is sealed by means of mercury seal. Neck 'A' which is rubber stoppered was used for the addition of the hypochlorite solution and for the removal of aliquotes for the estimation of residual chlorine.

The residual chlorine was estimated iodometrically, 5 ml. of aliquotes of the liquid were removed periodically from the reaction vessel and introduced into a mixture of 10 ml. of 10 per cent potassium iodide and



Analysis of Ligh	1105	15
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		· · · ·		
		Soda lignin	Thio Lignin	
Carbon	%	53.84	53.46	
Hydrogen	%	4.66	3.86	
Oxygen	ő	41.50	42.23	
Sulphur	%		0.445	
Methoxyl	%	13.40	15.50	
Klason lignin	%	69.00	74.01	
Molecular weight		2100	1400	

C₉ formula C₉H₇38°4.8 (CH₃) 0.95 C₉H_{5 81}O_{4 92}S_{0.32}(OCH₃)_{1.13}



FIG. 2 SODALIGNIN (4% IN KBr)



FIG. 3. THIOLIGNIN (4% IN KBr)

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10 ml. of 2 N sulphuric acid. The liberated iodine was titrated with standard N_{40} sodium this sulphate.

RESULTS AND DISCUSSION

1. Analysis of lignin

Data recorded in Table 1 indicate that the thio lignin contains higher methoxyl content, lower molecular weight and some amount of sulphur, otherwise there are very minor differences in the elemental composition of soda and thio lignins. C₉ formulae of both the lignins also reflect the above stated facts.

The infrared spectra of soda and thio lignins (Figs. 2 and 3) reveals that band at 3400cm⁻¹ is assignable to methoxyl groups. In this lignin the band at 1700 cm⁻¹ and 1660 cm⁻¹ are absent. these bands represents carbonyl groups (\beta-keto structure) and keto carbonyl (∝-to an aromatic ring) respectively. Two peaks at 1600 cm⁻¹ and 1500 cm⁻¹ are characteristic of aromatic compounds and are due to C=Cvibrations of benzene ring. The band at 1270 cm⁻¹ has been assigned to aryl-alkyl ether groups and the band at 1200 cm⁻¹ has been assigned to phenolic groups.

Rest of the bands are not very clear. Carbon sulphur vibrations occur at 600-700 cm⁻¹ region which are not recorded in the graph.

A comparison of infrared spectra of soda and thio lignins shows that apart from few dissimilarities regarding the intensity of various bands, the spectra are very similar. This signifies that sulphidity does not affect the chemical constitution of thio lignin to any appreciable extent. This is also confirmed by analytical results.



FIG 4. REACTION APPARATUS

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2. Oxidation of lignin

It was established in preliminary experiments, that under the conditions employed in our investigation, sodium hypochlorite solution was quite stable and that the substrate was always present in sufficient excess so that the rate of reaction with respect to hypochlorite concentration, expressed as available chlorine, could be legitimately established by studying the change occurred in the chlorine concentration with time alone. In some representative cases chlorate formation was also studied. It was found that no chlorate is formed during the reaction.

The oxidation of both soda and thio lignins with hypochlorite was marked by an initial rapid reaction for few minutes, followed by a low reaction (Figs. 5,6). Generally speaking the plots obtained in this series, by comparing residual available chlo-



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rine against time are best fitted in with the linear relationship :

$$1/C_t = \frac{1}{C_0} + k_s t$$

Where C_t is the concentration of available chlorine at time 't' and C_0 the initial concentration of available chlorine, k_1 being the rate constant.

With a view to comparing the oxidation rate, manifested under

different conditions, the values k_2 were calculated from the slope of the first straight-line at all pH values (Figs. 7-10) represent these data.

The behaviour of oxidation reaction being rapid at initial stage may be attributed to the presence of some hemicellulose carbohydrate fraction, linked to the lignin molecule, and this carbohydrate as impurity getting oxidized at a much faster rate. Lignin preparations like soda and this invariably contain some hemicellulose attached to them. This has been the case in the present study also, since the analysis of these lignins for klason lignin content gave the value 69.00 and 74.01 respectively for soda and this lignins, the remainder by difference, being hemicellulose carbohydrate impurities. The subsequent slow rate of oxidation corresponds to the oxidation of lignin.



FIG 7. EFFECT OF PH

Bependence of the providation rate on initial concentration of hypothiorite that is stellable and all a statements

The oxidation rate of both the ligning was found to decrease with the increase in the initial concentration of bypochlorite. The effect was found more pronounced in the lower concentration range (Figs. 11, 12) show the variation of oxidation rate with initial hypochlorite concentration expressed in terms of available chlorine. The decrease in the rate of oxidation has been ascrided to the concentration of reaching species of hypochlorite--water--alkali system varied with initial concentration of hypochiorite.

The experimental data indicated that the oxidation rate was directly proportional to the concentration of lignin shown in (Figs. 13-16).

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FIG. 8 EFFECT OF PH

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Dependence of the rate of oxidation on temperature and energy parameters of the reaction

The effect of temperature, on

the oxidation rate and the values of energy parameters of the reaction are recorded in Tables 2 & 3 for the soda and thio lignins respectively. A perusal of the data recorded in the adove (Tables 2 & 3) indicate that the rate of reaction increases nearly three times for every 10° rise of temperature.



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[NaOCI]	pH	Temp.	Rate Con	nst.	Temp.	ΔE	A last	x 70-18	∧ F %	λS
x 10 ⁻⁵ M		°C	LM ⁻¹ M	in-1	Coeff.	Kcal. Mole	5-1	Sec-1	Kcals Mole ⁻¹	<i>E.U.</i>
100	8	20	0.68					7.33	20.35	- 1 52
100	8	30	2.00		2.94	18.	96	7.59	20.37	- 1.69
	•	+0	0.00	· · ·	3.00			7.84	20.38	- 1.64
and a second					2.97	19.	88	7.55	20.39	- 1.61
		-				(graphi	cally)	•		
200	8	20	0.80	······	_	,		0.90	21 50	- 5 73
200	8	30	0.24		3.00	19.3	33	0.93	21.65	- 5.81
	0	40	2.71		2.96	20.4	47	0.97	21.71	- 5.83
•					2.98	19.9	0	0.93	22.67	- 5.79
-						(graphi	o cally)			
200	10	30	0.05			(8 F	;)	2.04	22.62	4.15
200	10	40	0.15		3.00	20.7	78	2.04	22.03	- 4.15
200	10	50	0.45		3.00	21.8	32	2.17	22.71	- 4.27
	•				3.00	21.3	5	2.11	22.64	- 4.23
, ,						21.2	2			
 		·	· · · · · · · · · · · · · · · · · · ·		·	(graph)	cally)	;		
				ТА	BLE 3					X.
Thio li	gnin=0.1g		•				Total	volum	e=300 ml pH	=8
NaOCI]₀	Temp.	Rate (Const.	Temp.	· · ·	$\triangle E$	A x 10	18	$\Delta F\%$	∆ <i>S</i> %
x 10 ⁻⁴ M	°C	<i>LM</i> -۱	M_{in}^{-1}	Coeff.		Kcais Mole ⁻¹	Mole-1		Kcals Mole ⁻¹	E.U.
75	20	5.0	0	• • • •			2.05		19.42	5.80
75	40	45.0)	3.00	- 1	19.32	2 10		10.11	
	F O ¹			2.94	22.43	22.43	2.19		19.11	5.55
. 13	50	133.3	3	·			2.26		19.05	5.59
				2.97		20.875	2.16		19.19	5.65
					(010	21.09	•			
100	20	1 1	0		(510	(pincany)	1.07		<u> </u>	
100		4.1	~	3.00		12.32	1.87		20.07	0.031
100	30	3.3	0	2.02			1.90		20.07	0.020
100	40	10.0	0	3.03	· · ·	20.97	1 02		20.69	0.000
×				3.01		20 145	1.75		20.09	0.022
				2.01	2	20.145	1.90		20.07	0.024
······································				· · · ·	(gra	phically)	5		· . · ·	
200	20	0.0	7				1.26		21.66	5.97
200	30	0.2	1	3,00		19.32	1 30		01.00	
		0.2		2.95		20.47	1.30		21.72	6.10
200	40	0.6	2				1.34		21.78	6.12
				2.97		19.895	1.30	•	21.72	6.03

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The values of free activation energy showed that indices were practigally the same no matter to what concentration of available chlorine the substrate lignin is subjected. This was an identification of tendency for heat and entropies to compensate one another leading to only a slight change in the free actiyation energy. Guha and coworkers reported the same effect in their studies on hypochlorite oxidation of bamboo hemicelluloses.

When the logrithams of rate constants were plotted against

reciprocals of respective temperatures in absolute (°K) straight lines were obtained (Figs. 17-19) showing thereby that the Arrhenius equation :

 $\log k = \frac{2.303}{RT} + \text{Constant}$ is followed.



FIG 10 EFFECT OF PH

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Dependence of the rate of oxidation on pH Constant. Alteration . 1.5.84

When the rate constant were plotted against pH (Figs. 20-21) the curves thus obtained have maximum at pH 7. Showing thereby that the rate of oxidation for both the lignins is maximum at pH 7. Similar variations of the oxidation rate with pH have been obtained by Clibbens and Ridge and Epstein and Lewin during their studies of the oxidation of cotton by hypochlorite. dt n.s.H

The variation being noticed in

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the posidation rate compotobe attributed to the self decompose tion of hypochlorite to chlorate since no chlorate has been found to be formed during the oxidation process. terbata in aph.

Consequently, it must be assumod that the variation in the



FIG 11 RATE CONSTANT VS [Naod] .

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oxidation sate with pH, is due to the chaoges occurring in the composition of hypochlorite and reacting species at varying pH values. [DOH] = 10 (DOH] = 10 3. Rate law

Before writing the rate law for

exidation process of soda lignin and this lignin in the pH range 2-10 it, is necessary to first visualise the system of chlorine alkali and water which gives hypochlorite of different compositions according to the pH values of the system. The equilibrium of chlorine-water system is represented as :

 $Cl_2+H_sO \Rightarrow Hocl+H^++Cl_5$ Thus hypochlorous acid and

hydrochloric acid are formed to an extent depending on the total chlorine concentration and equilibrium constant, the later of



FIG. 12. RATE CONSTANT VS [NAOCE] .

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which is changing slightly with temperature. The hydrochloric acid is completely ionized whereas hypochlorous acids, being fairly weak, is mainly undissociated at the pH of the chlorine

water system. On the addition of alkali to the system increasing amounts of hypochlorite ions are formed, the points of half neutralization being reached at around pH 7.5. The concentra-1.04

tion of hypochlorous acid is governed by equilibrium, a trat

Kh	=	[H ⁺]	[Cl-] [HOCI	/ [Cl ₂]
Ka	=	[H+]	[ClO-]	/ [HC	CI]
Cl-	=	[HÔC	CI] +	[CIO ⁻]	The Property
0x		[C1]	+ [C]	0-] +	[HOCI]



FIG. 13 RATE CONSTANT VS LIGNIN CONCENTRATION OF SODA-LIGNIN

where O_x is the total oxidizing capacity of hypochlorite system as experimentally determined.

Then solving these equations simultaneously for $[Cl_2]$, $[ClO^-]$ and [HOCl], the concentration of each species can be calculated for any given values of $[Cl^-]$ and

[H⁺]. The values of K_h and K_a at 25°C are 4.5×10^{-4} and $3.2+10^{-8}$ respectively.

Any rate law which will account for the kinetics of oxidation by hypochlorite as an oxidant consider the relative concentrations of both HOCl and ClO⁻. Therefore, it is now adequate to discuss the composition of hypochlorite species in pH range 2-10 studied in this investigation.

The assumption that only HOCI is an oxidizing species may work well in alkaline pH range where the variations in the con-



FIG. 14. RATE CONSTANT VS LIGNIN CONCENTRATION OF SODA-LIGNIN

centration of ClO⁻ are small as compared with the total concentration of this species¹⁸. This assumption breaks, down however, at pH values lower than 7.5. The composition of hypochlorite system in the range of pH 5-10 is represented in Fig. 22. If HOCl was the only oxidizing species then the maximum rate of oxidation with hypochlorite should occur at pH 4.7 where this species has the maximum value [Fig. 22]. But experimental results recorded in this investigation did not exhibit such type of behaviour (the rate of oxidation of both soda lignin and thio lignin was maximum at pH 7). Kaufmann¹⁹ suggested that oxidizing species is a complex [HOCl] [ClO⁻]. In that case rate of oxidation should be given by the equation,


FIG. 15. RATE CONSTANT VS LIGNIN CONCENTRATION OF SODA-LIGNIN

-dc/dt = k [HOCl] [OCl⁻]

r .

which has a maximum value at pH 7.5, Fig. 49, where the concentration of HOCl and OCl⁻ are equal. This possibility also does not hold good for our experimental results. As worked out by Epstein and Lewin²⁰, it is seen that the following function have a maximum value in the neighbourhood of pH 7.

[HOCI]³[OCI⁻] maximum at pH 7

[HOCl]² [OCl⁻]¹ maximum at pH 6.9 Therefore it is appropriate to postulate that either of the two above mentioned functions are the reacting species combination of hypochlorite system in oxidation of soda lignin and thio lignin too.

On the basis of these evidences

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16 1.5 [Naocl] = 200x10 1-4 [Naoch]. 1.3 = 10 ÞH [Naoce]. = 200 ×10 1.1 Min-1.1 [Naocl]o -- W 1.0 5 0.9 4 0 è o 0.4 0-3 0.2 0.1 9.819 1.092 0-273 0-546 LIGNIN CONCENTRATION (GRAMS LIGNIN PER LITRE)



and our experimental results now it is possible to write that the kinetics of the oxidation of soda lignin and thio lignin by hypochlorite in the pH range 2-10 was governed by the rate law equations (i) and (ii),

 $-dc/dt = k_1 [HOC1]^{\frac{1}{2}} [OC1^{-\frac{1}{2}}]^{\frac{1}{2}} [L]$... (i)

$$-dc/dt \Rightarrow k_{2} [HOC1]^{2} [OC1^{-}] [L]$$
... (ii)

or in a more appropriate manner by the equation,

$$-dc/dt = k [R] [L] ... (iii)$$

where [R] is the concentration of the reacting species combination and [L] is the concentration of lignin, while [C] is the concentration of available chlorine.

Epstein and Lewin²⁰ have shown in their study that when these two functions were plotted against rate of oxidation, the second function fits the results better than the first. A general shape of this function is shown in Fig. 23.



FIG. 17 ARRHENIUS PLOT FOR THE OXIDATION OF SODO LIGNIN

4. Reaction machanism

The self-decomposition of hypochlorite has been described to be of a free radical nature. The general resemblance of the oxidation reaction of soda lignin and this lignin to the selfdecomposition of hypochlorite indicated the possibility of free radical mechanism for this pH range.

It is assumed that the reaction proceeds by a free radical mechanism, the main reacting species being HOCl and OCl⁻ possibly in the form of Cl₂OOH. This hydroperoxide of Cl₂O may react with lignin by a chain mechanism in ways similar to those suggested by Epstein and Lewin²⁰ and Entwistle and coworkers²¹ for oxidation of cotton



FIG.18 . ARRHENIUS PLOT FOR THE OXIDATION OF THIOLIGNIN

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and alkali cellulose. The reactions may proceed as :

where

$$K$$
HOCl + HOCl Cl_2O
+ H_2O
K'
Cl_2O + OH \rightleftharpoons Cl_2OOH
rapid
Cl_2OOH + L \rightarrow Products

The rate is given by

 $- dc/dt = k[HOCl]^{3}$ [OH] [L] ... (iv)

 $\mathbf{k} = \mathbf{K}\mathbf{K}^{\mathbf{i}}$

The radical OH may form according to the equations

> k₁ HOCl**≓OH** + Cl

 k_2 Cl + HOCl \rightleftharpoons OH + Cl₂

 k_3 Cl₂ + H₂O \rightleftharpoons HOCl+ H⁺ + Cl⁻ Now

as postulated by Lewin and Epstein.

Further

k₀ HOCl⇔H⁺ + OCl⁻







FIG 20 RATE CONSTANT VS AH OF SODA LIGNIN

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This expression is identical to expression (iii) except that for the appearance of $[Cl^{-}]^{\frac{1}{2}}$ in the denominator which would suggest that the reaction is retarded by addition of chloride ions. This has been actually found correct experimentally also³⁰.

This expression further makes it

selective that $[HOCI]^3$ $[CIO^-]^{\frac{1}{2}}$ is the reacting species combination for the oxidation as soda lignin and thio lignin.

5. Comparative behaviour of soda and this ligning during hypochlorite oxidation

The main possibilities of reac-

tions between lignin and chlorine water are addition to chlorine to double bonds, substitution of a hydrogen atom of the benzene nucleis with chlorine and oxidation of both lignins and the chlorolignin formed. As the double bonds are only likely to occur at two phenylpropane monomers out of a hundred,



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the discussion can be limited to oxidation and substitution.

Studies on the halogenation of lignin have shown, chlorine replaces the hydrogen atom at the 5-and 6- position of the benzene nucleis.

Chlorine substitution may be

more likely at 5-position if the phenolic hydroxyl in 4-position is unetherified. Substitution of the phenylpropane units etherified in the 4-position probably occurs in the 6-position and will cause cleavage of alkylaryl ether bond. The methoxyl group at 3-position is hydrolysed, yielding a pyrocatehol which is oxidized to orthoquinone. The cleavage of alkylaryl ether bond is dependent upon previous condensation in the lignin molecule which makes the ring less reactive towards chlorine oxidation.

In protolignin 3 monomers out of ten contain unetherified phenolic hydroxyl group at

FIG.22 COMPOSITION OF HYPOCHLOROUS ACID AT VARIOUS PH AT 25C



FIG 23 BEHAVIOUR OF THE FUNCTION R = [HOC] 2 [OC] 2 IN THE PH RANGE 5-10



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4-position, whereas this lignin contains considerably more.

Soda lignin and thio lignin differ considerably in structural composition and reactivity because of difference in condensation reaction during cooking which is more pronounced in former case. The difference in rate of oxidation of soda lignin and thio lignin may be well attributed to their difference in composition with respect to reactive groups. The thio lignin being in loss condensed state is oxidized faster than soda lignin, since the condensation makes the ring less reactive. So is the case with hydrolysis methoxyl group and cleavage of alkylaryl ether bond.

Conclusion

The thio lignin is more reactive and can easily be oxidized with less consumption of chemicals than the soda lignin. It can be concluded that the sulphidity during cooking is essential as it makes lignin more reactive and thus its rate of removal can be increased.

References

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