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

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In the present study the kineties and mechanism of sodium hypochlorite oxidation of soda and sulphate pulps prepared from eucalyptus hybrid are reported. In the pH range studies all the reactions have been found to fit the second order rate equation :

$$\frac{1}{c_t} = \frac{1}{c_0} + k_i t$$

The behaviour of oxidation has been rapid at initial stage—a thing ascribed to the presence of residual lignin as impurity, the subsequent slow rate of oxidation corresponds to the oxidation of carbohydrate fraction of the pulp.

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

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

The reaction in this pH range was explained on the basis of free radical mechanism the main reacting species are HOCI and OCI in the form of Cl₂ OOH.

Soda pulp reacts faster during the slow process—a fact attributed to the difference in the klason lignin content of the pulps and the degree of degradation of the carbohydrate fraction during pulping process.

Introduction

In chemical pulping process, the lignin is not removed completely and residual lignin imparts

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brown colour to the pulp. So when chemical pulps are used for making white papers they are further processed i.e. bleached to yield a white product. The bleaching is usually done by compounds native in chlorine, e.g. chlorine, chlorine dioxide and hypochlorite. Oxidation is one of the important process involved in pulp bleaching.

In hypochlorite bleaching of pulp, two main competing reactions occur: the oxidation of lignin and other colouring matter and the oxidation of cellulose and hemicelluloses. Except for dissolving pulps, where low D.P. is some times desired, the bulk of the literature on hypochlorite bleaching deals with efforts to obtain maximum lignin oxidation with minimum cellulose oxidation. This seemingly simple subject is complicated by the existence of a large number of interrelated variables.

The first detailed study of the effect of progressive hypochlorite bleaching on pulp properties was performed by Forni¹, who found that lignin reacted relatively quickly, while cellulose reacted more slowly. Later Work^{2,3,4} on the competition of the pulp com-

ponents for hypochlorite showed that the amount of bleach consumed in the faster first stage increases with increasing lignin content, while in the slower second stage, the efficiency of bond breaking (i.e. the decrease in the fluidity per unit of bleach consumed) increases with decreasing initial lignin and hemicellulose content and decreasing accessibility of the pulp. Delignification predominates in pulps of high lignin content⁵. It is necessary therefore to study the kinetics of the reaction of the oxidative bleaching agent with pulp, because the kinetic investigation could provide valuable information about mechanism of the reactions and may be helpful in fixing the optimum parameters for bleaching of the pulps of various grades.

To meet the growing needs of the industry large scale plantations of Eucalyptus hybrid are being raised in various states of the country. Investigations have been undertaken to compare the bleachability of soda and sulphate pulps with sodium hypochlorite at pH from 2 to 10, temperature 20 to 50°C and at varying concentration of hypochlorite. Kinetic data as well as mechanism of reaction of the

two pulps is presented in this paper.

EXPERIMENTAL

Preparation of pulps :

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 by both soda and sulphate processes under the following conditions:

Kappa number and cupriethylene

diamine disperse viscosity ac-

cording to Tappi Standards and

results are presented in Table 1.

Preparation of sodium hypo-

The solution of sodium hypo-

chlorite 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

	Soda Process	Sulphate Process		
Total Chemical	20%	20-90		
Sulphidity	0%	25		
Cooking temperature	162°C	162°C		
Cooking period	4 hrs. (including 1½ hrs. to raise the max. temperature)	4 hrs. (including $1\frac{1}{2}$ hrs. to raise the max. temperature)		
Bath ratio	1:4	1:4		

The cooked pulps were washed thoroughly with fresh water to remove the black liquor. After washing, the pulp was screened on laboratory Lambert Screen of 35/100 mm. slot width to remove the uncooked material. The sheets of this pulp were then prepared, dried and stored for studies.

Analysis of pulps

Soda and sulphate pulps were analysed for their klason lignin,

ТΛ	DI	P	1
IA	BL	.E	1

chlorite

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Soda Pulp	4.3	30.48	11.76
Sulphate pulp	1.9	21.06	15.32

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.

Oxidation of pulps

The reaction was studied in 500 ml., five necked pyrex glass round bottom flask, Fig. 1. A thermostatic bath with a temperature variation of $\pm 0.1^{\circ}C$ was used for maintaining the temperature. To prepare the reaction mixture sodium hypochlorite solution and 0.5 N hydrochloric acid or 0.5 N sodium hydroxide solution were mixed in such a proportion so that a solution of desired [NaOCL]_o concentration and pH was obtained.

In a typical experiment, 9 g. of pulp (oven dry basis) was weighed out from the lot, transferred into a 1-litre beaker containing about 400 ml. of distilled water and disintegrated for 45 minutes into individual fibres with a disintegrator. The contents of the beaker were transferred on a wire sieve (150 mesh) and the filtrate was again poured over the pulp on the sieve. The pulp was then squeezed and transferred to the reaction vessel and calculated quantities of distilled water were added so that the total volume of the substrate 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 at 'b' (Fig. 1). Two electrodes of the pH meter were inserted through E_1 and E_2 , two of the necks of the reaction

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vessel and were sealed. Central neck of the reaction vessel holds a glass stirrer (operated electrically) is sealed by means of mercurry seal. Neck 'A' which is rubber stoppered was used for the addition of the hypochlorite solution and substrate and for the removal of aliquotes for the estimation of residual chlorine.

The progress of reaction was followed by estimating residual available chlorine iodemetrically at different intervals of time.

RESULTS AND DISCUS-SIONS

1. Analysis of Pulp

Data recorded in Table 1 indicate that Kappa number and klason lignin are higher in the case of soda pulp than the sulphate pulp, indicating thereby that the degree of delignification is more in the case of sulphate pulp in comparison to soda pulp. On the other hand cupriethylenediamine disperse viscosity of sulphate pulp is higher than the



FIG. 1. REACTION APPARATUS

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soda pulp, which shows that the degree of degradation of carbohydrate fraction is more in soda pulp than in the sulphate pulp.

2. Oxidation of Pulp

It was established in preliminary experiments, that under the conditions employed in this investisodium hypochlorite gation. 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 changes 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 sulphate pulps with hypochlorite was marked by an initial rapid reaction, lasting for a few minutes, followed by a slow reaction (Figs. 2 & 3). The slow reaction followed a second order kinetics with respect to oxidant concentration, when expressed as available chlorine. In general of all pH values the plots obtained with this series of hypochlorite oxidation could be best fitted by a linear relationship:

$$1/C_t = 1/C_0 + k_2 t$$

where

- C_o=Initial available chlorine concentration
- $C_t = Available chlorine con$ centration at time t

 K_2 =Specific rate constant.

For comparing the effect of variables on rate of oxidation the values of K_2 were calculated from the slope of the straight lines (Figs. 4 to 8).

Unbleached pulp, the substrate under oxidation, contains mainly carbohydrates (cellulose plus hemicellulose) alongwith little residual lignin as impurity. The behaviour of oxidation being rapid at initial stages can be ascribed to the oxidation of this residual lignin impurity. The subsequent slower rate of oxidation corresponds to the oxidation of carbohydrates of pulp.

Dependence of the Oxidation rate on initial concentration of hypochlorite

The oxidation rate of both the pulps was found to decrease with the increase in the initial concentration of hypochlorite (as available chlorine). The





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effect was found more pronounced in the lower concentration range (Figs. 9 & 10). This variation in oxidation rate has been ascribed to the fact that the concentration of the reacting species of hypochlorite-wateralkali system varies with initial concentration of hypochlorite.

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

The effect of temperature, on the oxidation rate and the values of the energy parameters of the reactions are recorded in Tables 2 and 3 for soda and sulphate pulps respectively.

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TABLE 2

Soda pulp	=	9 g (O.D. basis)	Consistency		3%
Total volumes	=	300 ml.	pH	=	8
NaOClo		3131×10 ⁻⁵ M	- ·		

Temperature	Rate Const. LM ⁻¹ Min ⁻¹	Temp. coeff.	$ \Delta F \\ K cals \\ Mole^{-1} $	A × 10 ⁻⁸ Sec ⁻¹	∆F Kcals Mole⁻	ΔS E.U.
20	3.6			7.60	19.41	- 19.67
30	7.3	2.03	12.45		~	
		·		7.87	10.61	<u> — 19.87</u>
40	14.7	2.01	13.21			
				8.13	19.81	— 19 .9 7
		2.14	15.11			
50	31.5			8.37	20.00	- 19.89
		2,06	13.56	7.99	19.71	- 19.89
			13.65			
(Graphically)						



OF SULPHATE PULP

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[NaOCI].

Sulphate to pulp = 9 g. (O.D. basis)

Consistency

pН

= 3%

= 8

Temp.	Rate Constant	Temp.	$\triangle F$.	A × 10-8 Sec-1	$\Delta F\%$	∆ <i>S</i> % <i>E U</i>
	LM ⁻¹ Min ⁻¹	coejj.	Mole ⁻¹	Det	Mole ⁻¹	<i>L</i> .0.
20	0.3	-		3.13	20.81	- 20.67
		2.26	14.32			
30	0.68			3.24	20 07	- 26.06
		1.91	12.24	-		
40	1.30			3.34	21.33	- 26.26
		1.91	12.85			
50	2.50			3.45	21.60	- 26.22
		0.02	13.14	3.29	21.20	- 26.18
			12.95			
	·	((Graphica	lly)		

A perusal of the data recorded in Tables 2 and 3 indicate that the rate of reaction increases nearly two times for every 10° rise of temperature.

The values of free activation energy showed that indices were practically the same at different reaction temperatures. This shows the tendancy for heat and entropies to compensate each other leading to only a slight change in the free activation energy.

When the logrithams of rate constants were plotted against reciprocals of respective temperatures in absolute (°K) straight lines were obtained (Figs. 11 &



Total Volume = 300 ml.

 $= 3535 \times 10^{-5} M$

FIG 4 EFFECT OF PH OF SODA PULP

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12). Showing thereby that the Arrhenius equation :

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

Dependence of the rate of oxidation on pH

Perusal of the kinetic data recorded in table indicate that when the rate constants were plotted against pH (Figs. 13&14). The curves thus obtained have maxima 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 on the oxidation of cotton by hypochlorite.

The variation in oxidation rate cannot be attributed to the self

decomposition of hypochlorite to chlorate, since no chlorate has been found to be formed during the oxidation process.

Consequently, it must be assumed that the variation in oxidation rate with pH is due to the changes occuring in the composition of hypochlorite and reacting species at varying pH values.



FIG 5 EFFECT OF DH OF SODA PULP

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Rate law

For deciding the rate law the equilibrium of chlorine, alkali and water was visualized as under :

 $Cl_{2}+H_{2}O \rightleftharpoons HOCl+H^{+}+Cl^{-}$ HOCl $\rightleftharpoons H^{+}+OCl^{-}$

Thus the relative concentrations of both HOCl and OCl⁻ will decide any rate law. Since the maximum rate of oxidation was found at pH 7 and not at pH 4.7 at which the concentration of HOCl is maximum. It was suggested by Kaufman⁶ that the oxidizing species is not only the hypochlorous acid but a complex [HOCl] OCl⁻. It was shown by Epstein and Lewin⁷ that either of the following two functions are having a maximum value in the neighbourhood of pH 7. [HOCl]^a [OCl⁻] Maximum at pH 7 ... (i) [HOCl]^a [OCl⁻]¹ Maximum at pH 6.9 ... (ii)

On the basis of these evidences and our experimental findings the probable rate law equation has been proposed as,

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

Where [R] is the concentration



FIG. 6 EFFECT OF \$H OF SODA PULP

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of the reacting species combination and [P] is the concentration of pulp. Epstein and Lewin⁷ have also reported in their studies on the oxidation of cotton cellulose with hypochlorite that the second function fits the results better. chlorite has been described to be a free radical nature. The general resemblance of the oxidation reaction of soda and sulphate pulps to the self-decomposition of hypochlorite indicate the possibility of free radical mechanism for this pH range.

Reaction Mechanism

The self-decomposition of hypo-

It is assumed that the reaction

proceeds by a free radical mechanism, the main reacting species being HOCl and OCl⁻ possibly in the form Cl₂OOH. This hydroperoxide of Cl₂O may react with pulp by a chain mechanism in ways similar to those suggested by Epstein and Lewin⁷ and Entwistle and co-workers⁸ for oxidation of cotton and alkali cellulose. The reactions may proceed as :



FIG.7 EFFECT OF PH OF SULPHATE PULP





FIG.8 EFFECT OF AN OF SULPHATE PULP

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1/RESIDUAL

as postulated by Lewin and Epstein. Further

HOCI
$$\xrightarrow{k_0}$$
 H⁺ + OCl⁻

Giving

$$k_{c} = \frac{[H^+][OCl^-]}{[HOCl]} \dots (viii)$$

or .,

$$\frac{[OCI^{-}]}{k_0} = \frac{[HOCI]}{H^+} \quad \dots \text{ (ix)}$$

from equations (v), (vi) and (vii)

$$k_1 k_2 k_2 = \frac{[OH]^3 [H^+] [Cl^-]}{[HOCl] [H_2O]} \dots (x)$$

Therefore solving (ix) and (x) and value of OH was determined to the,

$$OH = \frac{\left[k_1 \ k_2 \ k_3 \ / \ k_c\right]^{\frac{1}{2}} \left[OC\right]^{\frac{1}{2}}}{\left[C\right]^{\frac{1}{2}} \ \dots \ (xi)}$$

Thus equation (iv) becomes.

$$-\frac{dc}{dt} = \frac{k'' [HOC]]^{\frac{1}{2}} [CLO^{-}]^{\frac{1}{2}} [P]}{[Cl^{-}]^{\frac{1}{2}} \dots (xii)}$$
$$= \frac{k'' [R] [P]}{[Cl^{-}]^{\frac{1}{2}}} \dots (xiii)$$

This expression is identical, to) express (iii), except that for the

appearance of [CI][‡] in the denominator which would suggest that the reaction is retarded by addition of chloride ions. This has been actually found correct experimentally also.

This expression further makes it selective that $[HOCI]^2$ $[CIO^{-1}]^2$ is the reacting species combination for the oxidation of soda pulp and sulphate pulp.



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Comparative Behaviour of soda and sulphate pulps during Hypochlorite Oxidation

It is clear that the behaviour of both soda and sulphate pulps is similar towards the hypochlorite under different reaction conditions that is why same rate law and same reaction mechanism is suggested for both, but the significant difference noted is that the pulp differs in the rate of oxidation with hypochlorite, soda pulp reacts faster than sulphate pulp during the slow process. The causes for the same are as under :

(a) Klason lignin content of soda pulp (4.3%) is more than sulphate pulp (1.9%).

(b) The main difference in soda

and sulphate processes is in the sulphidity of liquor, which makes lignin more readily soluble. Hence the effect of presence of sulphur is selective degradation of the lignin without attack on the cellulose polymer chain, which is also supported by the data given in Table 1, that the viscosity (showing average D.P.) of the unbleached





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sulphate pulp is higher than the soda pulp. As the carbohydrate fraction which is the main reacting species during slow part of the pulp's reaction with hypochlorite and is less degraded in sulphate pulp than soda pulp, it is found that soda pulp has a higher rate of oxidation than sulphate pulp.

Conclusions

The present study has shown that presence of sulphidity during cooking is most essential, as in its presence selective degradation of lignin takes place without much attack on the carbohydrate fraction. Hence in the sulphate process lignin is removed to a greater extent than the soda process.

Present study also show that the oxidation reaction with hypochlorite in the case of sulphate pulp is slower than the soda pulp, confirming thereby that the attack on carbohydrate fraction during hypocylorite



FIG.11 ARRHENIUS PLOT FOR THE OXIDATION OF SODA PULA

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 All productive structures of the second se Second seco

 $\begin{array}{c} \left\{ \begin{array}{c} \left\{ x_{1}, x_{2}, x_{3}, x_{3}$





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FIG. 14. RATE CONSTANT VS BH OF SULPHATE PULP

treatment is less in the former case than in the latter case. Hence the sulphate process is to be preferred to soda process for the commercial pulping of Eucalyptus hybrid as the pulp will be of better quality and yield.

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